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THE DPPH INHIBITED THERMAL POLYMERIZATION OF STYRENE - KINETICS, MECHANISM AND PRODUCTS

BY

© MICHAEL CHRISTOPHER HALL

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR

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DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

SPRING, 1972

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled THE DPPH INHIBITED THERMAL POLYMERIZATION OF STYRENE - KINETICS, MECHANISM AND PRODUCTS submitted by Michael Christopher Hall, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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Date Spring 1972

TO MY MOTHER AND FATHER

ABSTRACT

The kinetics of the DPPH inhibited thermal polymerization of styrene and styrene-*o*-*o*'-d_2 (11) were measured at 75° by following the rate of disappearance of DPPH. The rate of disappearance of DPPH was found to be zero order with respect to DPPH above a concentration of 5×10^{-5} M for styrene and 2.3×10^{-4} M for styrene-*o*-*o*'-d_2. The analysis of the kinetic data showed that there was a deuterium isotope effect of $k_{1H}/k_{1D} = 0.75 \pm 0.07$. It was concluded that this was an inverse secondary isotope effect and was a measure of the kinetic deuterium isotope effect in the formation of the Diels-Alder adduct, 1-phenyl-1,2,3,9-tetrahydronaphthalene(1), from two molecules of styrene-*o*-*o*'-d_2 in the initiation step of the thermal polymerization. A value for the kinetic deuterium isotope effect in the hydrogen abstraction by DPPH from 1 was concluded to be $k_{2H}/k_{2D} = 1.96 \pm 0.49$. This was interpreted as a primary isotope effect, and was consistent with the mechanism proposed for the inhibition of the thermal polymerization of styrene by DPPH.

An analysis of the dimer fractions, formed in the presence and absence of DPPH, revealed that the formation of *cis*- and *trans*-1,2-diphenylcyclobutanes, (3) and (4), are occurring by a separate mechanism, in agreement with previous work.

1,1-Diphenylazoethane(32) and 4,4'-diphenylazo-1- tetralin(35) were prepared as sources for the 1-phenylethyl

ralin(35) were prepared as sources for the 1-phenylethyl and 4-phenyl-1-tetralyl radicals, respectively. The decomposition of 32 and 35 in the presence of DPPH yielded 1,1-diphenyl-2(2,6-dinitro-4(1-phenylethyl)phenyl)-hydrazine(43) and 1,1-diphenyl-2-(2,6-dinitro-4(4-phenyl-1-tetralyl)-phenyl)-hydrazine(50)as the radical-DPPH adducts. A mechanism of radical capture by DPPH has been proposed, involving initial attack of the radical at the para-position of the picryl ring of DPPH, at a carbon bearing a nitro group. Subsequent loss of nitrogen dioxide, followed by hydrogen abstraction yielded the isolated hydrazines 43 and 50. Previously reported radical-DPPH reactions are interpreted in the light of this mechanism.

The isolation of 50 from the DPPH inhibited thermal polymerization of styrene is taken as evidence for the production of the 4-phenyl-1-tetralyl radical in the inhibition process and for the formation of (1) in the thermal initiation sequence of styrene polymerization. The formation of (30) is also consistent with the proposed inhibition mechanism.

The isolation of 1,4-phenanthraquinone(71 and dibenz-[a,h]-anthra-9,10-quinone(73) among the products from the thermal polymerization of styrene in the presence of p-benzoquinone is taken as evidence for a Diels-Alder reaction between styrene and p-benzoquinone. 73 has been isolated, but not identified, by other workers from similar thermal polymerizations of styrene in the presence of p-

benzoquinone. A tentative mechanism for the inhibiting action of p-benzoquinone in the thermal polymerization of styrene is proposed.

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The author is grateful to the University of Alberta and the National Research Council for the financial assistance throughout this research work.

Finally, the author wishes to thank his wife, Susan, for the typing of this thesis, and for her infinite patience, understanding and encouragement during this research work.

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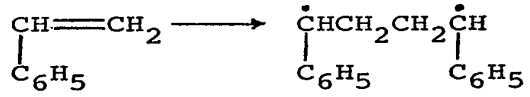
CHAPTER I

Kinetic Deuterium Isotope Effects in the Inhibited Thermal Polymerization of Styrene

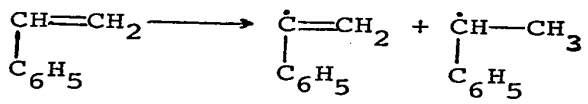
INTRODUCTION

It has been known for a long time that pure styrene undergoes spontaneous polymerization under thermal conditions. The reproducibility of the thermal polymerization rates of styrene by several workers (1) is convincing evidence that the polymerization reaction is not initiated by adventitious impurities, but involves initiation by styrene molecules only. The thermal polymerization can be inhibited by radical scavengers (2,3) showing that a radical initiation process is occurring. Early kinetic investigations suggested that the radical forming reaction in solution in various solvents was second order in styrene (1,4). A mechanism involving formation of the 1,4-diphenyl-1,4-butadiyl radical, eq. [1], (5),

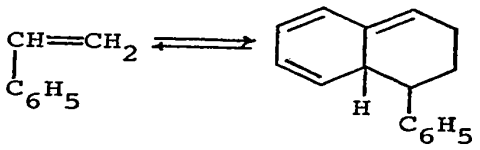
[1] 

which would add further molecules of styrene at the radical carbons in a propagation step, was shown to be inadequate by kinetic arguments (6). Other diradical

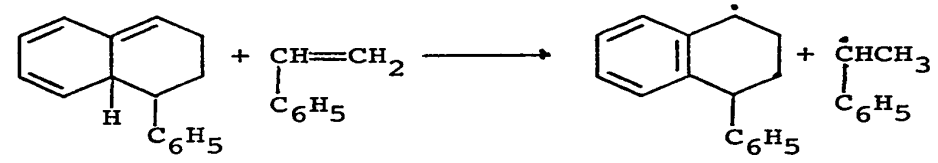
sources, such as 3,6-diphenyl-3,4,5,6-tetrahydropyridazine, which decomposes to give the 1,4-diphenyl-1,4-butadiyl radical (7,8), and cyclic disulphides which yield diradicals photochemically (9), do not initiate styrene polymerization appreciably. This evidence led to the conclusion that the initiation step must involve only monoradicals. Several routes to the formation of monoradicals have been proposed. Still assuming a bimolecular process, a proposal was made for monoradical production (10) involving hydrogen atom transfer between two molecules of styrene, eq. [2].

[2] 

More rigorous kinetic investigations (11,12), however, showed that the radical forming reaction is third order in styrene, discounting the bimolecular process in eq. [2]. The isolation of 1-phenyltetralin from the thermal polymerization of styrene in the presence of inhibitors (11, 13), led to the suggestion that the polymerization is initiated by monoradicals which are produced as in eqs. [3] and [4].

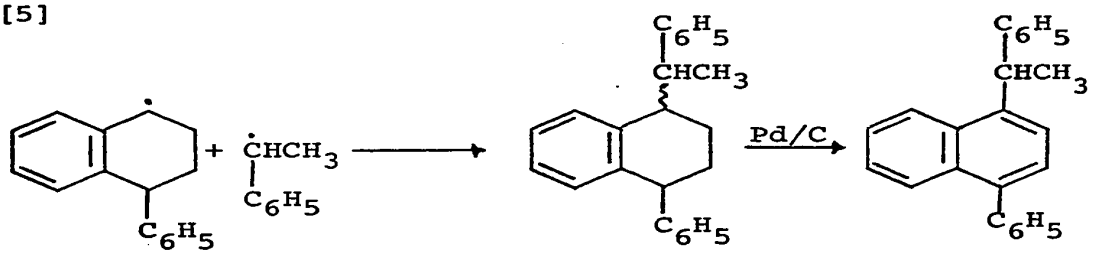
[3] 

(1)

[4] 

(1) (2)

1-Phenyltetralin and 1-phenyl-1,2-dihydronaphthalene have also been identified from their retention times by gas chromatography of the dimeric fraction from the uninhibited thermal polymerization of styrene (14,15,16,17). The isolation of the isomeric radical recombination products of eq. [4], (14), and their subsequent dehydrogenation to 1-phenyl-4-(1-phenylethyl)-naphthalene, eq. [5],

[5] 

(2)

is convincing evidence for cage recombination of the monoradicals produced in eq. [4]. The dehydrogenation product was identical in all respects to an authentic sample prepared by an independant route. An alternative route to the formation of monoradicals which appears to

be energetically feasible and consistent with the observed third order kinetics, is given by eq. [1] followed by eq. [6] (12).

[6] 

The lack of an isotope effect in the thermal polymerization of β,β-dideuteriostyrene (18,19) was taken as evidence against this mechanism.

Assuming a third order initiation step for the thermal polymerization of styrene, the overall rate of polymerization, R_p, is given by eq. [7] (3), in which [M] is the monomer concentration

$$[7] \qquad R_p = k_p[M]^{5/2}(k_i/k_t)^{1/2}$$

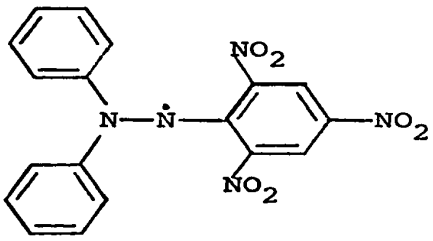
and k_p, k_i and k_t are the specific rate constants for the propagation, initiation and termination reactions, respectively. The kinetic deuterium isotope effect for the thermal initiation reaction, k_{iH}/k_{iD}, is then given by eq. [8].

$$[8] \qquad k_{iH}/k_{iD} = \left(\frac{R_{PH}}{R_{PD}}\right)^2 \left(\frac{k_{pD}k_{tH}^{1/2}}{k_{pH}k_{tD}^{1/2}}\right)^2 \frac{[M_D]^5}{[M_H]^5}$$

The kinetic parameters for normal and deuterated styrenes are denoted by H and D, respectively. Kopecky and Evani (18) have shown that for styrene-o-o'-d_2, a value of k_{iH}/k_{iD} = 1.80 was obtained, indicating a primary isotope effect in the rate determining step. Other deuterated styrenes, with the deuterium atoms located in the side chain, gave values that were interpreted as secondary isotope effects. Their findings are consistent with the thermal initiation mechanism shown in eqs. [3] and [4].

It is generally accepted that the initiation step in the thermal polymerization of styrene can be represented as a fast, reversible formation of a Diels-Alder adduct (1), followed by hydrogen atom transfer between 1 and a third molecule of styrene in a slow step, to give two monoradicals, eqs. [3] and [4].

2,2-Diphenyl-1-picrylhydrazyl (22, hereinafter abbreviated as DPPH),



(22)

a stable free radical, has been used for measurement of the rates of initiation of monoradical initiated polymerizations (20,21,22). In the presence of this substance there is an induction period during which inhibitor is consumed. The induction period may be determined either by dilatometry (21), or more conveniently, by spectrophotometric methods (3), as DPPH absorbs very strongly in the ultraviolet and visible spectrum. The rate of consumption of inhibitor, R_{DPPH}, is taken to be equal to the rate of initiation, R_i, which would prevail with the inhibitor absent. It is assumed that one molecule of inhibitor stops one radical chain. This assumption has been proved where the initiation occurs via a fragment from an active monoradical producing catalyst by comparison of R_{DPPH} with R_i determined by two independant methods (20,24). The relationship (3), eq. [9],

$$[9] \qquad R_P^2 - R_{P,th}^2 = \frac{k_P^2 [M]^2}{2 k_t} R_i$$

holds for the bulk polymerization of styrene initiated by monoradical-producing catalysts, e.g., azobisisobutyronitrile (AIBN). In eq. [9], R_p is the total rate of polymerization, $R_{P,th}$ is the rate of thermal polymerization, and R_i is the rate of initiation of the polymer chains which started from catalyst fragments. The

quantities k_p and k_t are the specific rate constants for propagation and termination respectively, and [M] is the monomer concentration. For moderate concentrations of active monoradical-producing initiators, $R_{P,th}$ can be neglected and eq. [9] reduces to eq. [10].

[10] $$R_p^2 = \frac{k_p^2 [M]^2 R_i}{2 k_t}$$

Values for [M], k_p, k_t and R_p can be measured independantly and a value for R_i can be calculated from substitution in eq. [10].

In the absence of added initiators, DPPH still inhibits the thermal polymerization of styrene (3,25). Russell and Tobolsky (3) have shown that the rate of disappearance of DPPH is zero order, with respect to DPPH between concentrations of 3.6×10^{-4} and 1.2×10^{-4} mole/litre, during the inhibited thermal polymerization of styrene. However, the rate of initiation of radicals at 60° in pure styrene, as measured by R_{DPPH}, was some 85 times greater than a calculated thermal rate of initiation, $R_{i,th}$. $R_{i,th}$ was derived from eq. [10]. If thermal polymerization proceeds with the same mechanisms of propagation and termination as does polymerization initiated by monoradical-producing catalysts then eq. [11] should follow:

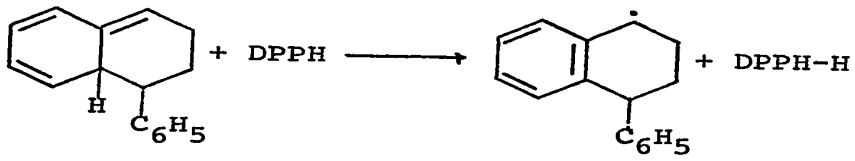
[11] $$R_{P,th}^{2} = \frac{k_P^{2}[M]^{2}}{2\,k_t} R_{i,th}$$

where $R_{i,th}$ represents the rate of initiation of growing polymer radicals. Using literature values for $R_{P,th}$, k_p and k_t, they calculated $R_{i,th}$ to be 1.3×10^{-10} mole/litre/sec at 60°. A value for R_{DPPH} at this temperature was measured to be 1.1×10^{-8} mole/litre/sec. These authors could offer no explanation for this increased rate of consumption of inhibitor. Since the values of R_i and R_{DPPH} are equal for monoradical initiated polymerization, further reaction of the product from DPPH and a radical cannot be the cause of this anomalous behaviour. From two experiments with styrene in benzene solution, it was shown that the inhibition by DPPH was second order with respect to styrene. In contrast to the work of Russell and Tobolsky, Tudos and Furst (24) found that the inhibition period for pure styrene, which was measured by visual estimation of the time for loss of the violet color of DPPH, was not a linear function of the DPPH concentration. They concluded that the DPPH, in addition to inhibiting, also simultaneously initiates the polymerization of styrene. Russell and Tobolsky measured the rate of loss of absorbance for a solution of DPPH in benzene at 75°, and found it to be very slow compared

to the inhibiting action of DPPH in styrene. However, at 120°, the temperature at which Tudos carried out his measurements, this independant disappearance of DPPH could be significant. No consideration of this source of error appears to have been made in his conclusions. No further references could be found concerning this apparently complex inhibiting action of DPPH.

The purpose of this work was to investigate further the DPPH inhibited thermal polymerization of styrene. If the termolecular initiation sequence given in eqs. [3] and [4] is operative for styrene then it might be expected that a DPPH molecule would take the place of a third styrene molecule and abstract a hydrogen from the Diels-Alder adduct 1, replacing eq. [4] by eq. [12].

[12]

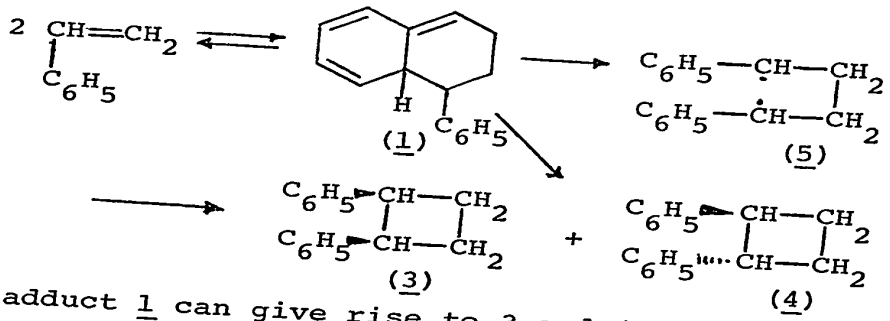


(1) (2)

Use of styrene-o-o'-d_2 would allow a determination of the kinetic deuterium isotope effect in the inhibition step. The values of the kinetic isotope effect for both the reversible adduct formation and hydrogen (deuterium)

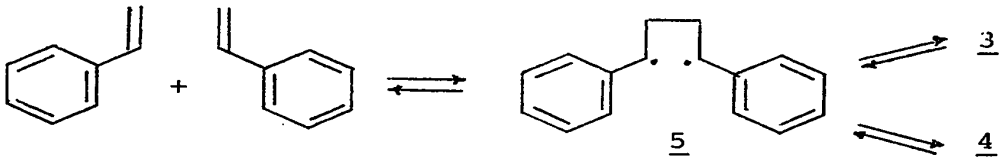
abstraction by DPPH are determined.

The dimeric fractions isolated from the thermal polymerization of styrene have been found to contain appreciable amounts of cis- and trans-1,2-diphenylcyclobutanes, 3 and 4, (14,15,16,17). Brown (17) has suggested that the cyclobutanes are formed by way of the Diels-Alder adduct 1, (Scheme 1).



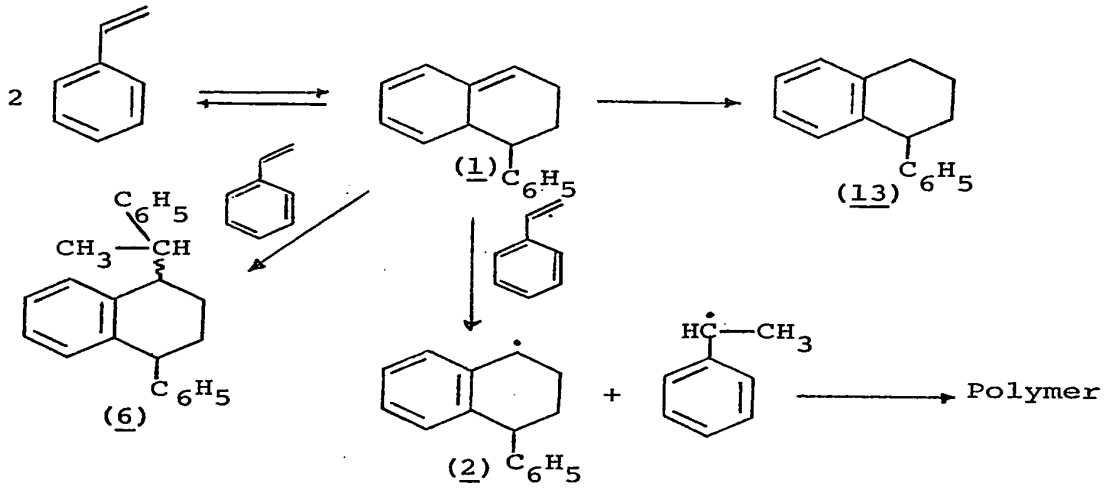
The adduct 1 can give rise to 3 and 4 either directly by ring contraction or via the diradical 5. Mayo (10,12) has suggested the formation of cyclobutanes to be an independent non-radical process. However, if orbital symmetry is to be conserved, a one step process from styrene is theoretically not allowed (26). Kirchner and Bucholz (16) carried out a kinetic investigation of the rates of formation of the dimeric and trimeric products formed in the thermal polymerization of styrene in bromobenzene solution at 137°. They found that two separate reactions occur. In the first, 1,2-diphenylcyclobutanes,

3 and 4, are formed by a cycloaddition of two molecules of styrene via the diradical intermediate 5, (Scheme 2). They showed that the rate of formation of 3 and 4 was described by a second order reaction in styrene, and that this rate was not affected by addition of radical inhibitors such as iodine or quinone.



Scheme 2

The second reaction, formation of trimeric adducts, 6, (Scheme 3), was found to be third order in styrene and the formation was completely suppressed by iodine. The yield of 1-phenyltetralin, one of the dimeric components,



Scheme 3

was found to be greatly increased by the addition of iodine, in agreement with earlier work (13). They propose an iodine catalyzed isomerization of 1 to 4-phenyltetralin in the presence of iodine.

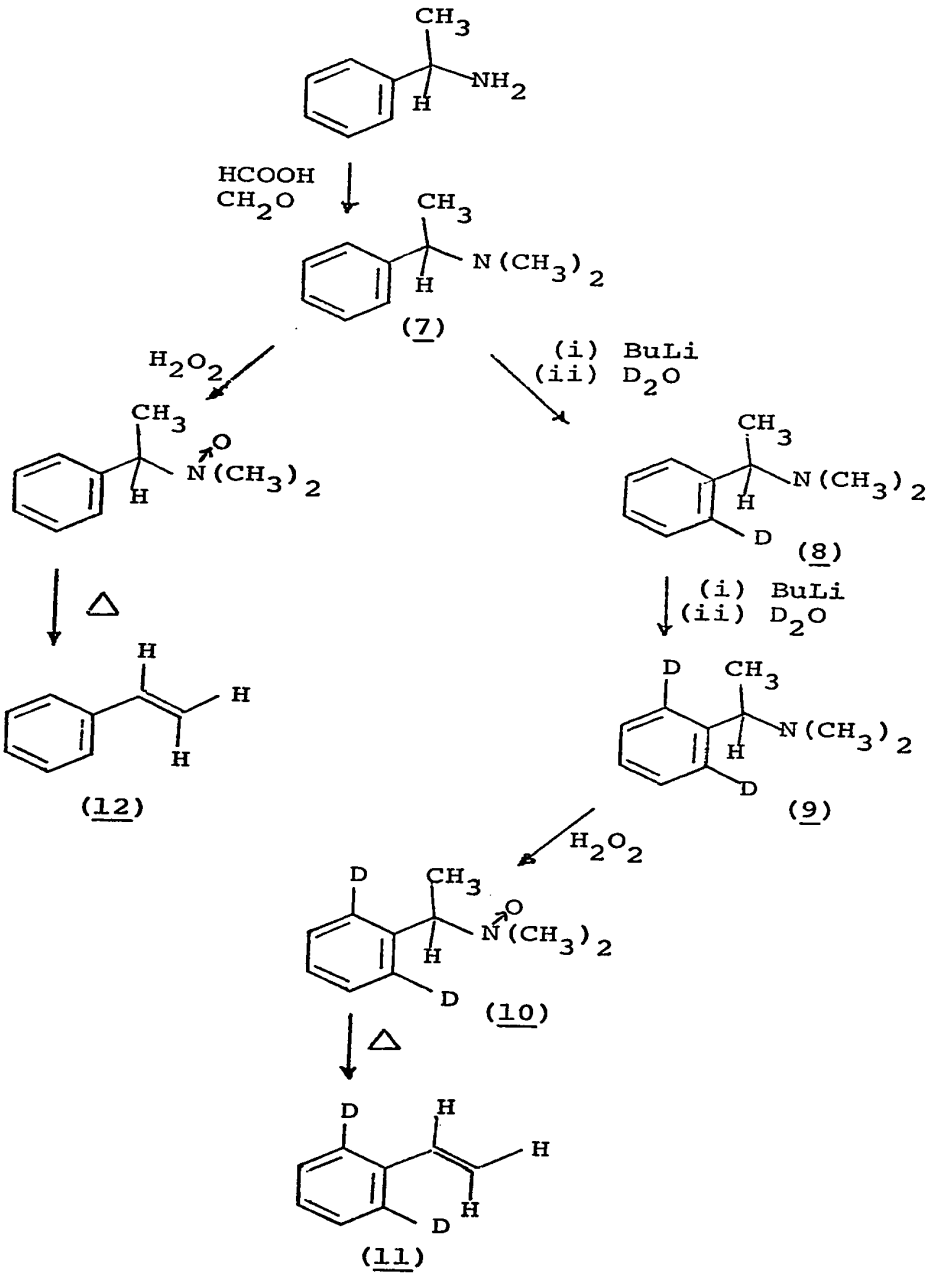
Analysis of the dimeric components formed in the presence and absence of DPPH in this work is in agreement with the findings of Kirchner and Bucholz, and supports a separate mechanism for the formation of the cyclobutanes in the thermal polymerization of styrene.

RESULTS

Preparation of Styrene-o-o'-d_2 (11)

Styrene-o-o'-d_2 (11) was synthesized according to the method of Kopecky and Evani (8). The sequence of reactions is outlined in Scheme 4. N,N-Dimethyl-(1-phenylethyl)amine (7) was prepared in 63% yield by the N-methylation of 1-phenylethylamine using formic acid and formaldehyde, according to the method of Clark (27). The nmr spectrum corresponded to the required product. The amine 7 was metalated in dry ether solution using n-butyllithium (100% excess), for 24 hours in a dry atmosphere of nitrogen. The metalated amine was treated with deuterium oxide dispersed in benzene and deuterated amine 8 was isolated in 94.6% yield. The infrared spectrum showed a C-D stretching vibration at 2270 cm^{-1}. The nmr spectrum (CCl_4) matched exactly that of 7 except that it indicated the phenyl group of 8 contained one less proton than that in 7. The mass spectrum at 11 ev had a parent peak at m/e 150 and the analysis indicated that the amine contained 92 mole % d_1-amine. The amine 8 was subjected to the metalation and deuteration sequence once more in the same manner as above and the deuterated amine 9 was isolated in 90% yield. The infrared spectrum was similar to that of 8 and the nmr spectrum matched

Scheme 4



exactly that of 7 and 8 and indicated that the phenyl group of 9 contained one proton less than that in 8. The mass spectrum of 9 at 11.5 ev had a parent peak at m/e 151 and the analysis indicated that 9 contained 68 mole % $\underline{d}_2$-amine and 24 mole % $\underline{d}_1$-amine. As the isotopic purity was less than desired, the amine 9 was subjected to the metalation and deuteration sequence once more and 9 was isolated in 78% yield. The nmr spectrum was exactly the same as before. The mass spectral analysis at 11.5 ev indicated that 9 now contained at least 95 mole % $\underline{d}_2$-amine. This figure must be in error since a second deuteration should only give a maximum of approximately 90 mole % $\underline{d}_2$-amine if the figures for the first attempt are correct. The amine 9 was converted to its amine oxide 10 by treating it with hydrogen peroxide according to the method described by Cope (28). The amine oxide 10 was decomposed to styrene-$\underline{o}$-$\underline{o}$'-$\underline{d}_2$ (11) in 70% yield. The infrared spectrum (neat) showed absorption bands at 2270 cm^{-1} and 835 cm^{-1} (C-D stretching and bending vibrations, respectively). The nmr spectrum (CCl_4) showed peaks at τ2.85 (s) due to the phenyl protons, τ3.35 (unsymmetrical quartet, $\underline{J}$ = 18 cps, $\underline{J}$ = 11 cps) due to the α-hydrogen, τ4.38 (doublet of doublets, $\underline{J}$ = 18 cps, $\underline{J}$ = 2 cps) and τ4.86 (doublet of doublets, $\underline{J}$ = 11 cps, $\underline{J}$ = 2 cps) due to the β-hydrogens. The ratio of the respective peaks was

3.0 : 1.0 : 1.0 : 1.0 and the required ratio was 3.0 : 1.0 : 1.0 : 1.0. The nmr spectrum indicates that the deuterium atoms are in the aromatic nucleus and none in the side chain. The mass spectrum at 70 ev had a parent peak m/e 106 compared to m/e 104 found in styrene. The mass spectral analysis at 10.5 ev indicated that 11 contained 91.7 mole % $\underline{d}_2$-styrene, 8.3 mole % $\underline{d}_1$-styrene and 0.0% mole % $\underline{d}_0$-styrene. The glc analysis (carbowax 20 M, 100°) indicated that the product was free from impurities.

Styrene (12)

The corresponding light styrene (12) was made in 70% yield by the decomposition of the amine oxide of 7. The infrared, nmr and mass spectra matched those of purified commercial styrene and also with those reported in the literature (29,30,31). The light styrene was made under the same conditions as 11 in order that its rate could be compared to a purified sample of commercial styrene. This ensured that the rates of disappearance of DPPH were not affected by any extraneous impurities introduced by the synthetic sequence for the preparation of 11. The deuterated styrene and the light styrene were stored in a cold, dark place. They were freshly distilled

when required for kinetic runs.

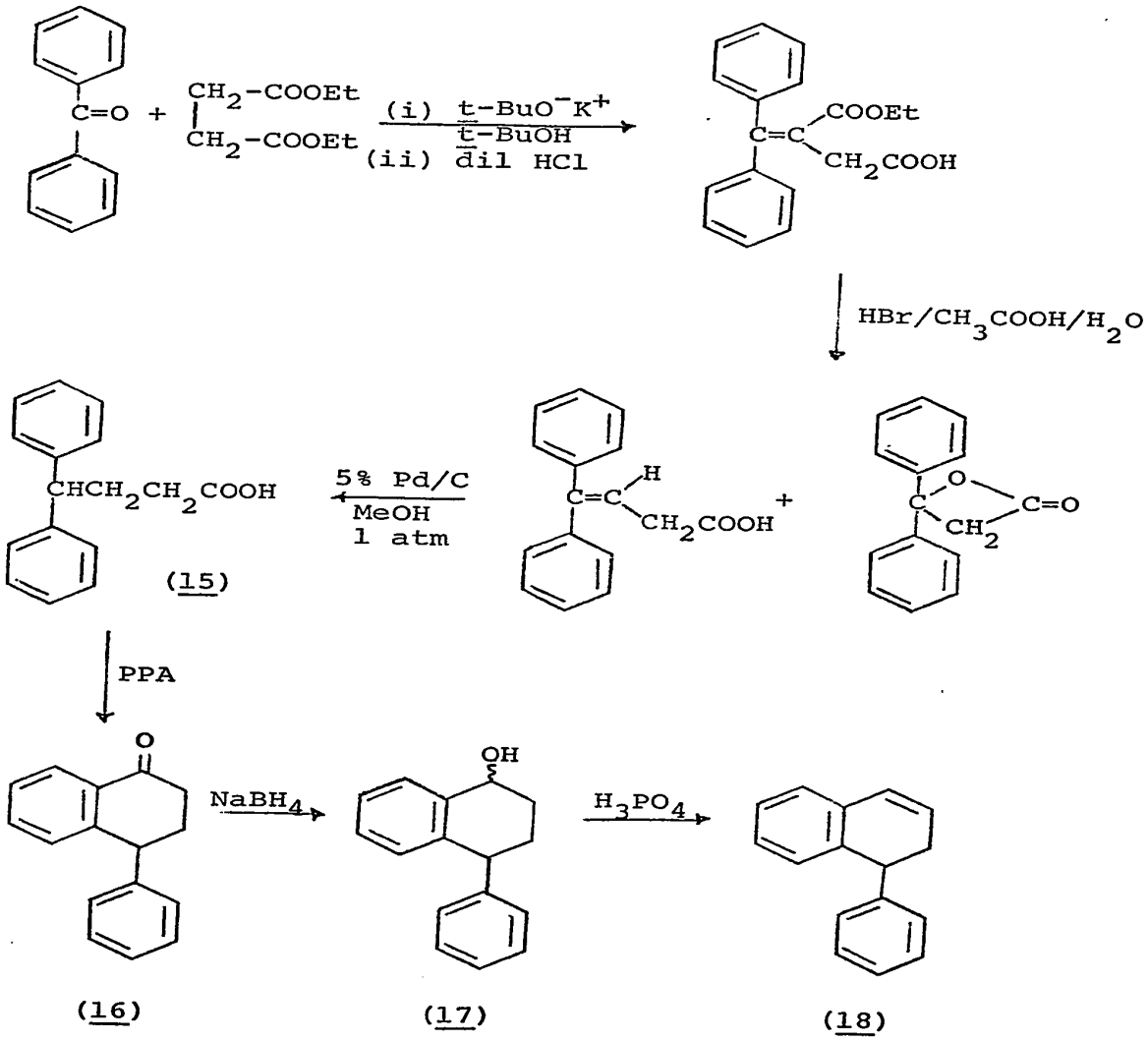
Preparation of dimeric components from the thermal and inhibited thermal polymerizations of styrene.

In order to characterize the dimer products formed in the inhibited and thermal polymerizations of styrene, authentic materials were prepared or obtained in the following manner. Pure samples of 1-phenyltetralin (13), cis- and trans-1,2-diphenylcyclobutanes (3) and (4), were obtained from S. Evani (32). 1-Phenylnaphthalene (14), was obtained from Aldrich Chemical Co. Inc. and was used without further purification.

1-Phenyl-1,2-dihydronaphthalene (18)

The preparation is outlined in Scheme 3. The Stobbe condensation reaction between benzophenone and diethyl-succinate afforded 3-carbethoxy-4,4-diphenyl-3-butenoic acid in 89% yield. Hydrolysis of the ester and subsequent decarboxylation, according to the method of Johnson (33), yielded an almost quantitative mixture of 4,4-diphenyl-3-butenoic acid and γ,γ-diphenyl-γ-butyrolactone. Wawzonek and Kozikowski (34) have hydrogenated a basic solution of this mixture to give the saturated acid 15 in 85% yield. They used a copper chromite catalyst, and the hydrogenation

Scheme 5


C=O
CH2-COOEt
CH2-COOEt
(i) t-BuO⁻K⁺
t-BuOH
(ii) dil HCl
COOEt
C=C
CH2COOH
HBr/CH3COOH/H2O
CHCH2CH2COOH
(15)
5% Pd/C
MeOH
1 atm
H
C=C
CH2COOH
+
O
C=O
C
CH2
PPA
O
NaBH4
OH
H3PO4
(16)
(17)
(18)

was carried out at a pressure of 2000 psi and a temperature of 160° for a period of two hours. A quantitative yield of 15 was obtained in this work by using a 5% palladium on charcoal catalyst in a methanolic solution of the mixed acid and lactone. The reaction was complete in two hours at room temperature and atmospheric pressure. The same yield of product was obtained after 20 minutes when the hydrogenation was carried out in the presence of acid and at 20-30 psi pressure. The acid 15 was cyclized to 4-phenyl-1-tetralone (16) in 82% yield using polyphosphoric acid. The melting point agreed with that in the literature (35) and the nmr and infrared spectra were consistent with the structure of the compound. The ketone 16 was reduced in a 96% yield to the corresponding alcohol 17, using sodium borohydride in ethanol. The alcohol 17, when recrystallized from carbon tetrachloride, formed white needles melting over the range 96-100°. A small portion was recrystallized from pentane as long white needles, mp 121.5-123°. The nmr and infrared spectra of both crystals were identical. Since the alcohol 17 contains two asymmetric carbons, the crystals from the carbon tetrachloride must be a diastereoisomeric mixture which is separated to give a pure diastereomer in pentane. The infrared spectrum ($CHCl_3$) showed an O-H absorption at 3450 cm^{-1}. The nmr spectrum was consistent

with the structure and showed a loss of the singlet peak at τ7.75 (1H) on exchange with D_2O. Treatment of 17 with orthophosphoric acid at 120° for two hours gave the expected 1-phenyl-1,2-dihydronaphthalene (18) in a 70% yield. The infrared spectrum matched that reported in the literature (13), but no reference could be found to the physical properties of pure 18.

Thermal Polymerizations

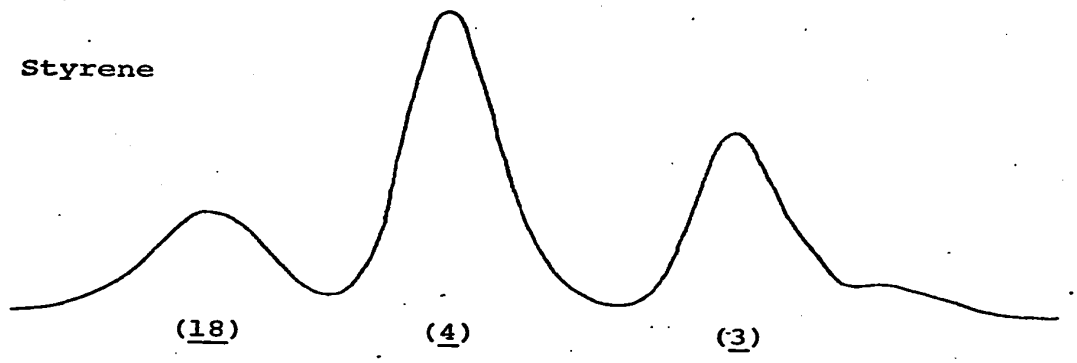
(i) Without DPPH

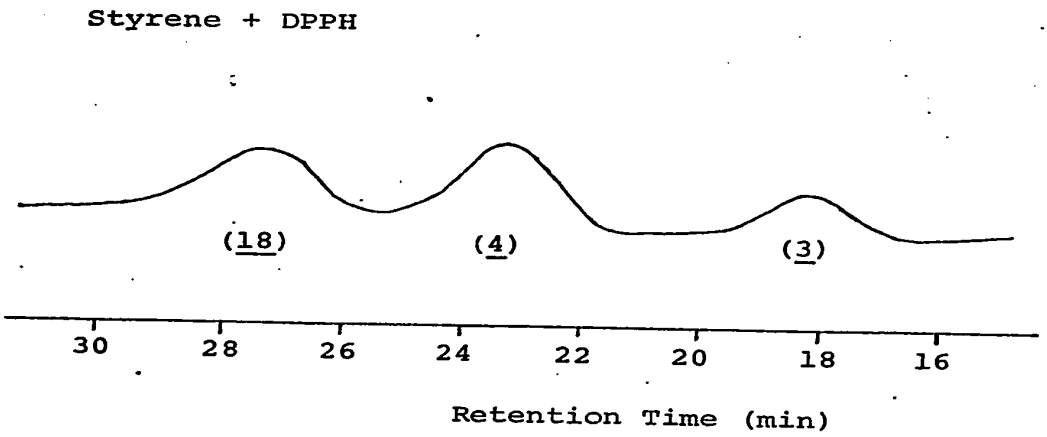
Commercial styrene was purified by shaking with base to remove the t-butylpyrocatechol inhibitor and distilled under nitrogen. A flask containing 100 ml (81.8 g, 0.786 mole) of freshly distilled styrene was carefully degassed several times to remove all traces of oxygen and placed in the dark in a thermostated water bath at 75° for 72 hours. The flask was opened, the contents dissolved in benzene and the polymeric fraction precipitated by the addition of methanol. The solvent was removed by evaporation and the residual styrene distilled at reduced pressure on a steam bath leaving a small residue in the flask. The residue was chromatographed on a short column of silica gel and yielded a pale yellow viscous liquid. Analysis of the liquid by glc (SF 96, 170°)

showed that it contained cis- and trans-1,2-diphenylcyclobutanes, (3) and (4), 1-phenyl-1,2-dihydronaphthalene (18), 1-phenylnaphthalene (14) and a small amount of a product with a retention time slightly less than observed for the former components. Identification was made by comparison of the retention times with those of authentic samples and by mixed injections of the dimer fraction with authentic samples. However, retention times themselves are not definite proof of the presence of expected products. Since the amount of dimeric fraction formed was too small to permit separate isolation of the products, a Varian 1200 gas chromatograph connected to an A.E.I. MS-12 mass spectrometer was used for further characterization. The mass spectra of the authentic materials are shown in Figures VIII and IX. Compounds 14 and 18 have parent peaks at m/e 204 and 206, respectively, and so can be easily distinguished. The most intense peak in the mass spectra of 3 and 4 appears at m/e 104 while the mass spectrum of 13 has only a very small peak at m/e 104. 13 also shows peaks of high intensity at m/e 180 and m/e 130 which are absent in the spectra of 3 and 4. The compounds 3, 4 and 13 can be identified by the difference in their mass spectra. The mass spectra of all the observed glc fractions matched exactly those for the corresponding authentic

materials. No 1-phenyltetralin could be detected under the conditions used, although there may have been some overlap with the trans-1,2-diphenylcyclobutane. A much better resolution of the products was obtained by using a column packed with 10% Apiezon L on 60/80 Firebrick. 1-Phenyltetralin was found to be present as 1.4% of the dimer fraction, calculated from measurement of the relative peak areas from the chromatogram. It is not surprising that this was not detected in the less highly resolved chromatogram using an SF 96 column. The chromatograms for the dimeric fraction from SF 96 and Apiezon L columns are shown in Figures I and II. The retention times and relative areas of the fractions are given in Table I. Glc analysis of the dimeric fraction at a higher temperature (SF 96, 200°) showed a peak at almost double the retention times of 3, 4 and 18. Although this was not identified it was probably due to trimeric products. Other workers (14,16) have identified the trimeric products as the isomeric 1-phenyl-4-(1-phenylethyl)-tetralins and 2,4,6-triphenylhex-1-ene. The former are visualized as being formed by cage recombination of the 4-phenyl-1-tetralyl radical and a 1-phenylethyl radical eq. [5], and the latter by disproportionation from a radical chain eq. [13].

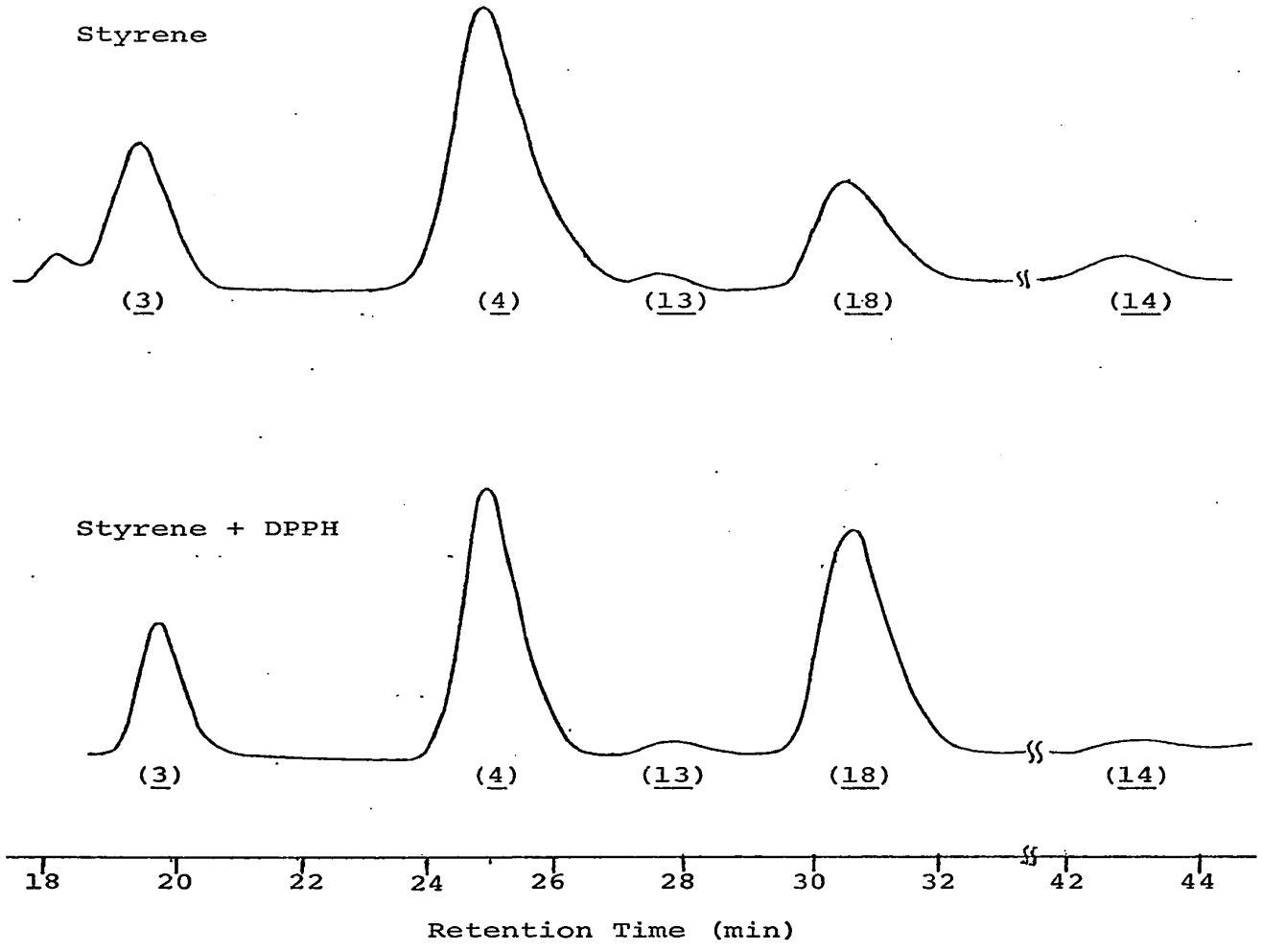
FIGURE I



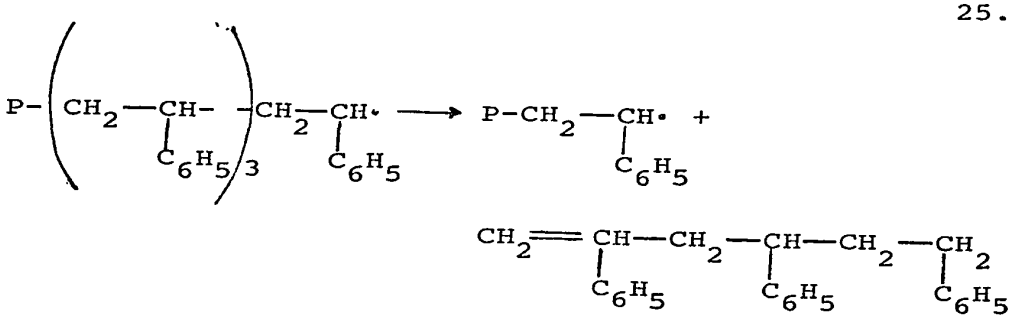


Matched chromatograms for the dimer fractions on SF96 column

FIGURE II



Matched chromatograms for the dimer fractions on Apiezon L column

[13] 

(ii) With DPPH

It has been found that DPPH reacts rapidly with styrene in the presence of oxygen (3). The styrene used in this polymerization therefore, had to be degassed and then the DPPH added in such a manner that oxygen was not introduced into the system again. The apparatus used is illustrated in Figure VII. The DPPH was placed in the reservoir C, sealed into the flask neck and styrene introduced into the flask. The contents were sealed onto a high vacuum system and thoroughly degassed before the styrene and DPPH were mixed. The styrene was purified as in (i) and an equal volume (100 ml) was mixed with 0.80 g (1% by weight) of DPPH. The thermal polymerization was carried out exactly as before. The period of heating was estimated from the kinetic measurements so that unreacted DPPH still remained at the end. This excluded the formation of any polymer. After heating for 72 hours at 75° the flask was opened and the unreacted styrene distilled at 19 mm on a steam bath. The black

residue (1.35 g) was chromatographed on a column packed with silica gel. Styrene and the dimer fraction were eluted together in the first fraction collected. The remaining fractions were isolated and will be discussed in Chapter II of this thesis. The dimer fraction was analyzed by glc (SF 96, 170°) and was found to contain cis- and trans-1,2-diphenylcyclobutanes (3) and (4), 1-phenyl-1,2-dihydronaphthalene (18) and 1-phenylnaphthalene (14). No 1-phenyltetralin could be observed under these conditions. The mass spectra of the glc fraction recorded by the MS-12 mass spectrometer coupled to the gas chromatograph were exactly identical to the mass spectra of the authentic materials. Glc analysis of the dimer fraction on the Apiezon L column under the same conditions as in (i) once again showed the presence of 1-phenyltetralin (1.4% of total dimer). There was an absence of the unknown peak present in the dimer fraction from (i). At higher temperatures using an SF 96 column under the same conditions as in (i) no trace of the peak corresponding to the trimeric fraction could be seen. The relative proportions of the products as measured from comparison of glc peak areas are given in Table I. The chromatograms are shown in Figures I and II. From the chromatograms it can be seen that there is an increase in

TABLE I

Glc Retention Times and Product Composition of the Dimeric Fractions

10% Apiezon L on 60/80 Firebrick, 10 ft x 1/8 in; Column temperature 202°; Injector 250°; Detector 275°; Helium flow 85 ml/min.

Compound	Retention Time (min)	% Composition of Dimer Fraction Thermal	Inhibited
Unknown	18.0	3.8	0.0
cis-1,2-Diphenylcyclobutane (3)	19.4	19.9	15.4
trans-1,2-Diphenylcyclobutane (4)	24.9	54.8	40.0
1-Phenyltetralin (13)	28.2	1.4	1.4
1-Phenyl-1,2-dihydronaphthalene (18)	31.2	16.4	42.1
1-Phenylnaphthalene (14)	43.3	3.5	1.1
cis-3 / trans-4		2.76	2.60

the proportion of 18 formed in the inhibited sample while the ratio of 3 to 4 remains the same for both polymerizations. The proportions of 14 and 13 are small with respect to the other dimers in both polymerizations.

Kinetic measurements

Russell and Tobolsky (3) followed the rate of disappearance of DPPH during the inhibition of the thermal polymerization of styrene by measuring the rate of loss of absorption of DPPH. This method was adopted for 11 and 12. The apparatus (see Figure IX) was constructed so that monomer and DPPH were not mixed until all the air had been removed from the system. Russell and Tobolsky observed that the presence of oxygen greatly accelerated the rate of disappearance of DPPH in styrene. A similar observation was made in earlier experiments in the work while using a ground glass joint to attach the cuvette to the remainder of the apparatus in Figure IX. Much faster and highly erratic results for the rate of disappearance of DPPH were obtained, indicating incomplete removal of air or oxygen. In the later experiments reported here, a cuvette with a graded seal, obtained from Pyrocell Manufacturing Co., was sealed directly into the apparatus. The reproducibility of the rates reported was taken as

evidence for the absence of oxygen in the system. DPPH absorbs strongly at 525 mμ and the rate of increased transmittance at this wavelength was taken as equal to the rate of disappearance of DPPH. Measurements of known concentrations of DPPH in benzene solution were found to obey Beer's Law. The concentrations were chosen so that they covered the range of those measured in the inhibited polymerizations. Small corrections were made to the kinetic rates:

(i) A blank run of DPPH in benzene at 75° to allow for thermal and/or photochemical decomposition.

(ii) A correction was made for the absorption of any DPPH-H residue formed. At 525 mμ, ε = 500 for DPPH-H compared to ε = 11900 for DPPH. It was assumed that a zero concentration of DPPH-H existed at the beginning of the run and that all the DPPH was converted to a DPPH-H type of molecule during the reaction.

Typical results obtained from these experiments are included in Table II and III and graphical plots are shown in Figures III and IV. Some kinetic runs were performed so as to allow complete consumption of DPPH and typical results from these experiments are included in Tables IV and V and graphical plots are shown in Figures V and VI. Table VI shows the rate of disappearance of DPPH at 75° for

TABLE II

Typical rate data for the disappearance of DPPH in styrene at 75°

Run 10	Time seconds	Absorbance	[DPPH] x 10^4 mole/litre
	0	2.2076	1.86
	250	2.1612	1.81
	500	2.0969	1.76
	750	2.0177	1.69
	1000	1.9469	1.63
	1500	1.7747	1.49
	1750	1.7100	1.43
	2000	1.4383	1.37
	2250	1.5607	1.31
	2500	1.5229	1.24
	3000	1.3279	1.11
	3250	1.2518	1.05
	3500	1.1772	0.99
	3750	1.0996	0.92
	4000	1.0223	0.86
	4500	0.8794	0.74
	4750	0.8097	0.68
	5000	0.7423	0.62
	5500	0.6180	0.52
	$R_{DPPH} = 2.54 \times 10^{-8}$ mole/litre/sec		

TABLE III

Typical rate data for the disappearance of DPPH in styrene-$\underline{o}$-$\underline{o}$'-$\underline{d}_2$ at 75°

Run 35	Time seconds	Absorbance	[DPPH] x 10^4 mole/litre
	0	1.1838	9.95
	500	1.1580	9.74
	1000	1.1397	9.58
	1500	1.1192	9.42
	2000	1.1024	9.25
	2500	1.0809	9.09
	3000	1.0630	8.92
	3500	1.0458	8.76
	4000	1.0295	8.66
	6000	0.9586	8.06
	6500	0.9355	7.84
	7050	0.9155	7.68
	7500	0.8979	7.52
	8000	0.8794	7.42
	8500	0.8591	7.25
	10000	0.8041	6.76

$R_{DPPH} = 3.21 \times 10^{-8}$ mole/litre/sec

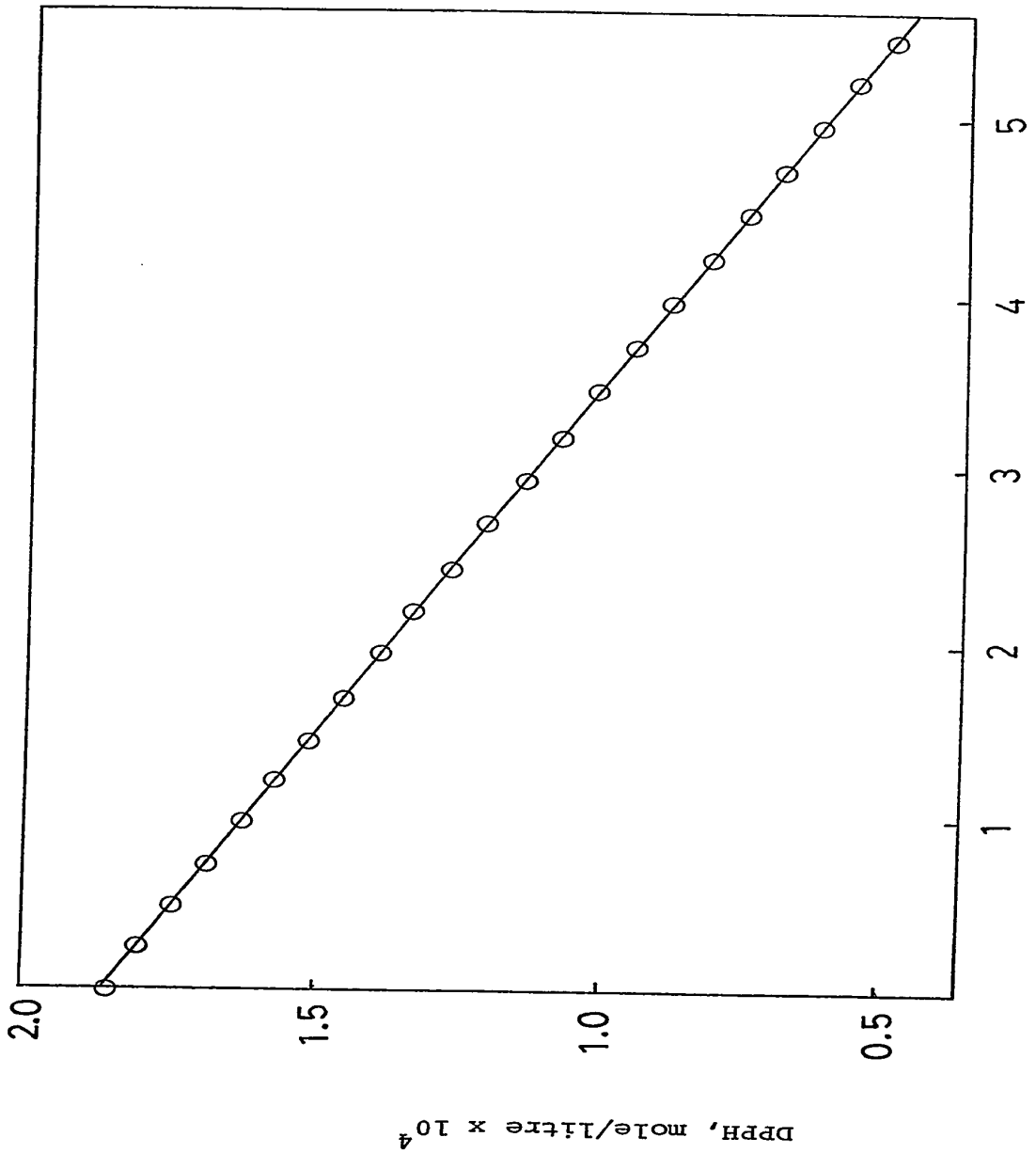


FIGURE III. Plot of [DPPH] vs time for a typical DPPH inhibited thermal polymerization of styrene at 75°. Run 10.

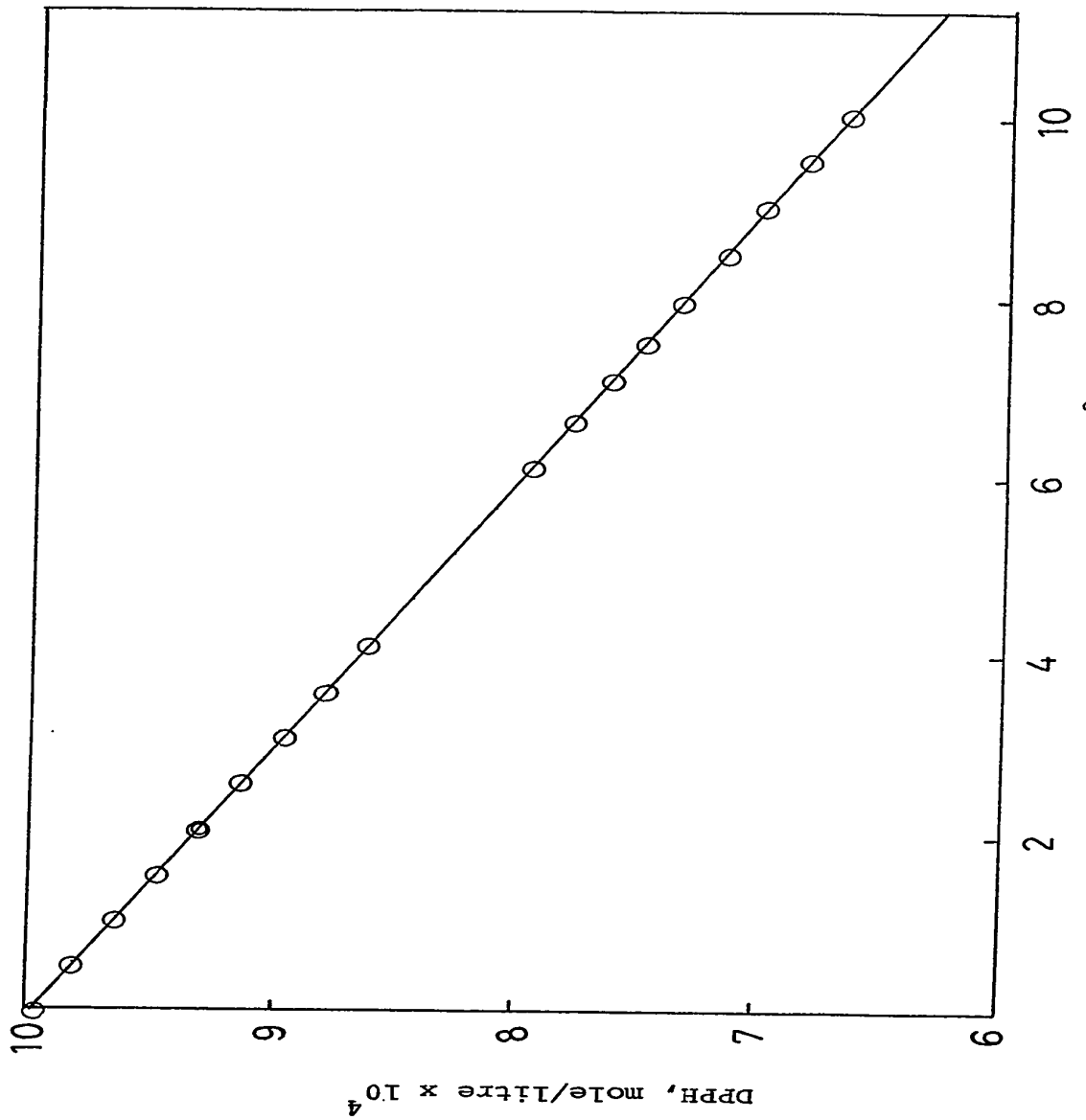


FIGURE IV. Plot of [DPPH] vs time for a typical DPPH inhibited thermal polymerization of styrene-o-o'-d_2 at 75°. Run 35.

TABLE IV

Typical rate data for the disappearance of DPPH in styrene at 75°

Run 41	Time seconds	Absorbance	[DPPH] x 10^4 mole/litre
	0	0.2168	1.82
	500	0.2062	1.73
	1000	0.1882	1.58
	1400	0.1780	1.50
	2000	0.1596	1.34
	2500	0.1450	1.22
	3000	0.1288	1.08
	3500	0.1132	0.95
	4000	0.0993	0.83
	6000	0.0533	0.45
	7000	0.0447	0.38
	8000	0.0384	0.32
	9000	0.0336	0.28
	10500	0.0299	0.25
	12000	0.0277	0.23
	14000	0.0256	0.22
	16000	0.0254	0.21

$R_{DPPH} = 2.46 \times 10^{-8}$ mole/litre/sec

TABLE V

Typical rate data for the disappearance of DPPH in styrene-o-o'-d_2 at 75°

Run 46	Time seconds	Absorbance	[DPPH] x 10^4 mole/litre
	0	0.9066	6.97
	900	0.8477	6.52
	2100	0.8168	6.28
	2500	0.8027	6.17
	3000	0.7839	6.03
	3500	0.7620	5.86
	4000	0.7399	5.78
	7750	0.5800	4.46
	9000	0.5287	4.07
	10000	0.4855	3.73
	12000	0.4056	3.12
	13000	0.3605	2.78
	15500	0.2612	2.01
	16500	0.2277	1.75
	17000	0.2111	1.62
	18000	0.1805	1.39
	19000	0.1624	1.25
	20000	0.1349	1.04
	24900	0.0605	0.47

$R_{DPPH} = 3.23 \times 10^{-8}$ mole/litre/sec

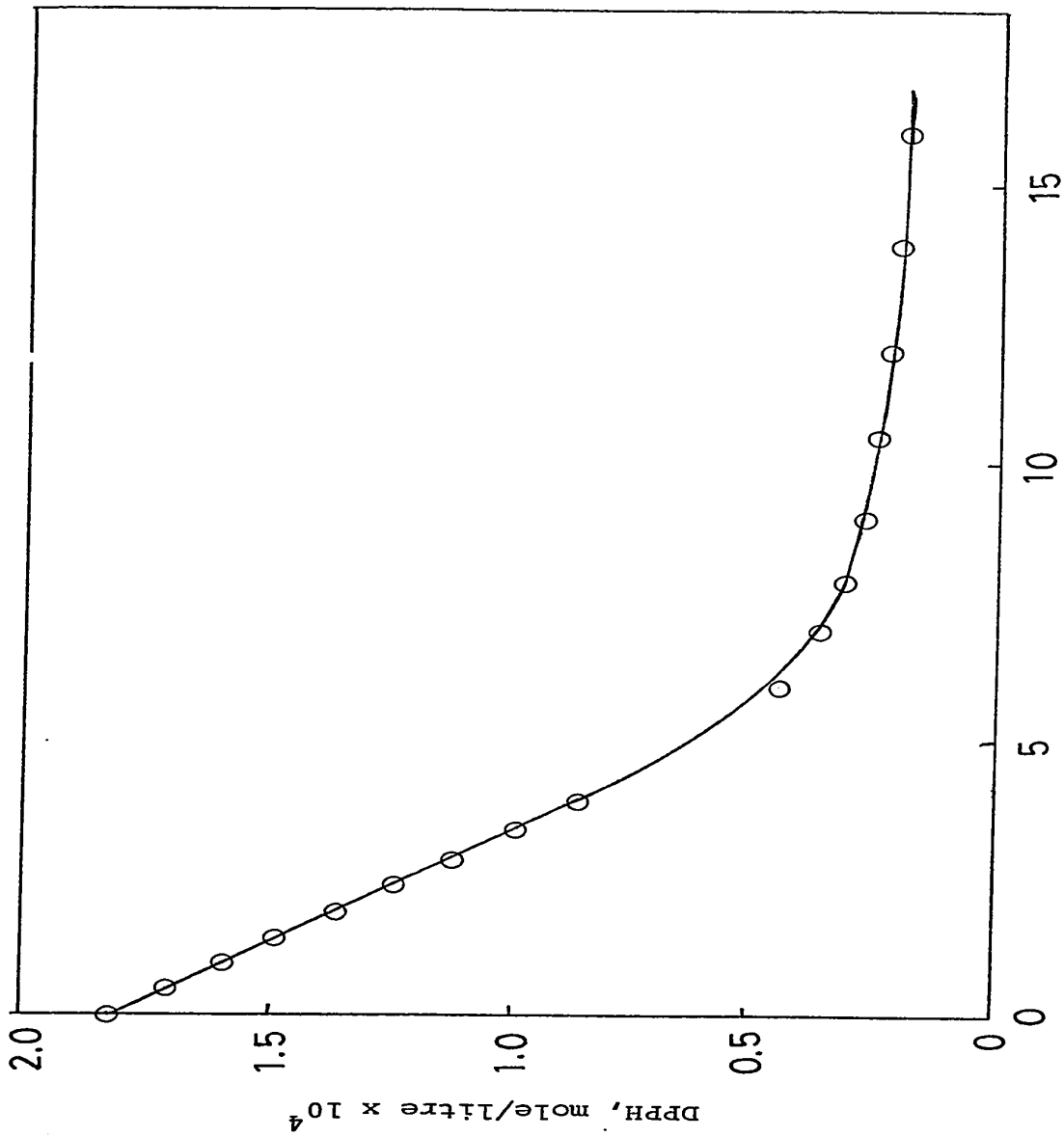


FIGURE V. Plot of [DPPH] vs time for a typical DPPH inhibited thermal polymerization of styrene at 75°. Run 41.

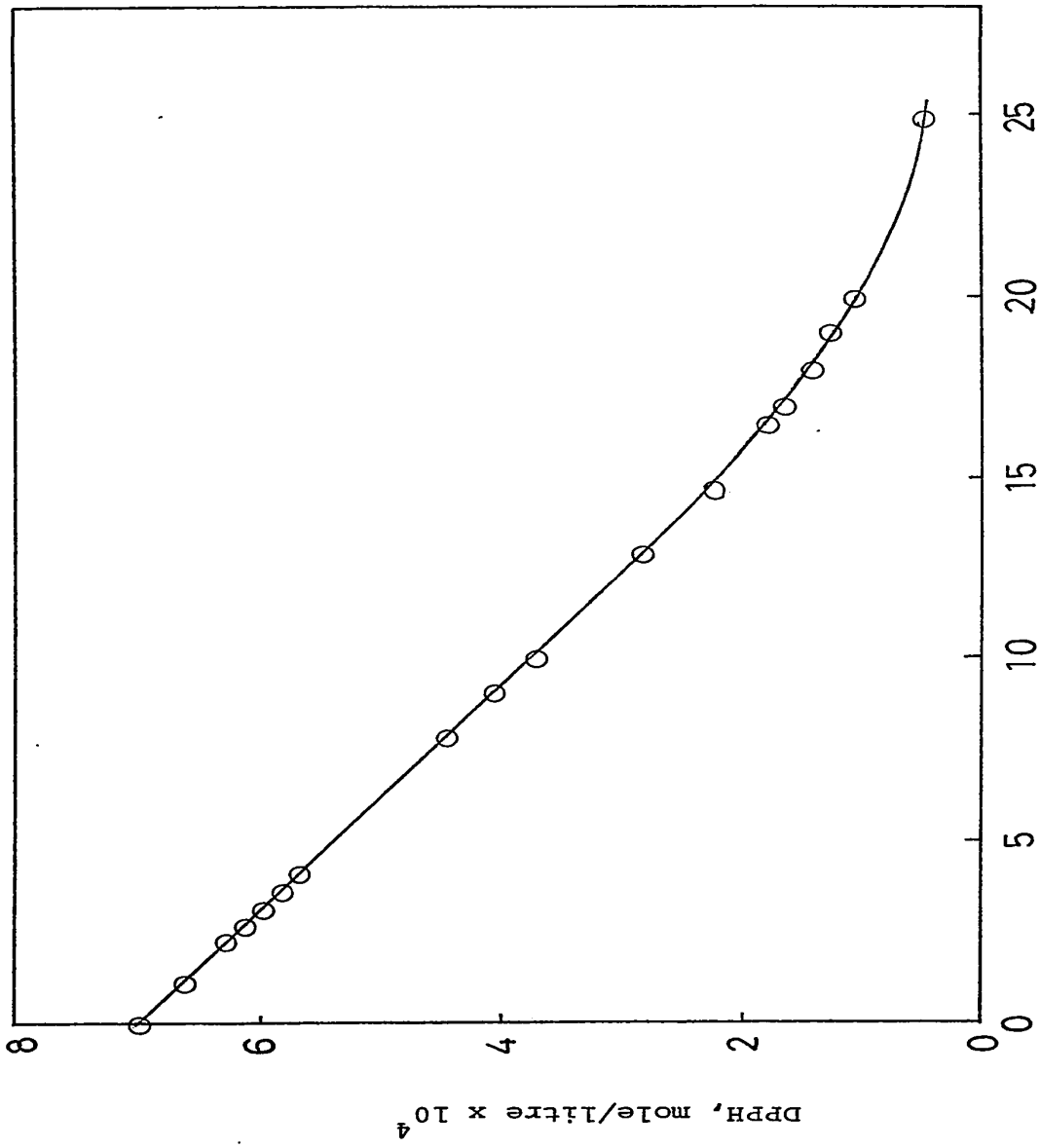


FIGURE VI. Plot of [DPPH] vs time for a typical DPPH inhibited thermal polymerization of styrene-o-o'-$\underline{d}_2$ at 75°. Run 46.

TABLE VI

Rates of disappearance of DPPH at 75°

Monomer	Run	Initial [DPPH] x 10^4 mole/litre	R_{DPPH} x 10^8 mole/litre/sec
Styrene	9	1.39	2.14
	10¶	1.86	2.54
	11	1.87	2.48
	12	1.87	2.50
	23	1.90	2.70
	41*†	1.82	2.46
	42*	1.90	2.12
			Average 2.42 ± 0.16
Styrene -o-o'-d_2	34†	8.83	3.05
	35†	9.95	3.21
	36†	6.64	3.14
	37†	8.83	3.19
	46*†	6.97	3.23
	47*†	7.17	3.35
			Average 3.19 ± 0.07

* Continuous run to end point.

† 0.1 cm cell : all others measured using 1.0 cm path length cell.

¶ Styrene prepared by the synthetic route. All other samples of styrene are commercially purified samples.

styrene and styrene-o-o'-d_2. Run 10 was carried out using styrene prepared by the same synthetic route used to prepare 11. The agreement between the values of R_{DPPH} from this styrene and the values from the purified commercial styrene show that no extraneous impurities were introduced that would affect R_{DPPH}, and demonstrates the high purity of the monomer prepared. Therefore, the isotope effects calculated from these results were not due to any extraneous impurities present in the deuterated styrene.

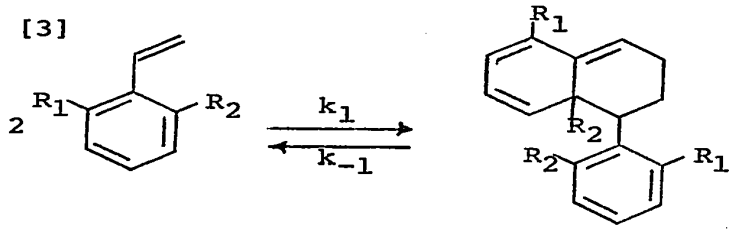
DISCUSSION

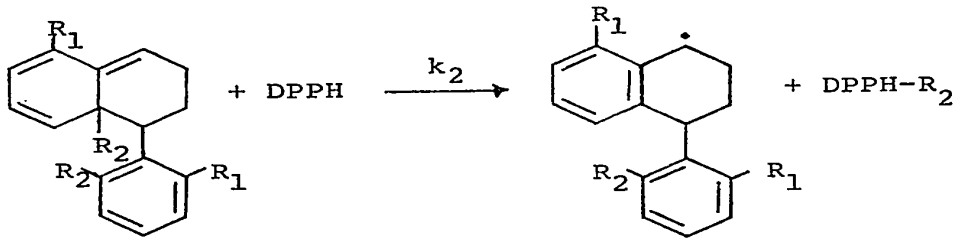
Kinetic deuterium isotope effects

Russell and Tobolsky (3) found that the rate of disappearance of DPPH in styrene was zero order with respect to DPPH between concentrations of 3.6×10^{-4} and 1.2×10^{-4} mole/litre. Below 1.2×10^{-4} mole/litre the order was found to increase. The plots in Figures V and VI confirm this and show similar deviations at low concentrations of DPPH. In the case of styrene-$\underline{o}$-$\underline{o}$'-$\underline{d}_2$ (Figure VI) this deviation occurs at $\simeq 2.3 \times 10^{-4}$ mole/litre DPPH, and for styrene (Figure V) at $\simeq 5 \times 10^{-5}$ mole/litre DPPH. The rates of disappearance of DPPH, R_{DPPH}, given in Table VII are measured from the linear portions of the curves.

In all the runs carried out using styrene-$\underline{o}$-$\underline{o}$'-$\underline{d}_2$ the value of R_{DPPH} is greater than for styrene. This increase in R_{DPPH} for styrene-$\underline{o}$-$\underline{o}$'-$\underline{d}_2$ is explained when DPPH takes the place of the third molecule of styrene in the initiation step given by eqs. [3] and [4]. We can now write eqs. [3] and [12].

[3]



[12] 

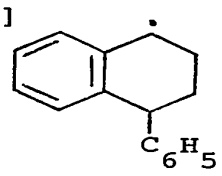
(a) $R_1=R_2=H$

(b) $R_1=R_2=D$

Here k_1 and k_{-1} are the rate constants for the reversible formation of the Diels-Alder adduct and k_2 is the rate constant for H(D) abstraction from the adduct by DPPH. The hydrogen (deuterium) abstraction by DPPH will be the fast step in this reaction since the rate of disappearance of DPPH obeys a zero order dependance. The formation of the Diels-Alder adduct will be the rate determining step. This is the converse of that seen for the termolecular initiation sequence of pure styrene in the absence of inhibitors where hydrogen atom transfer between 1 and a styrene molecule is the rate determining step (12).

Before we rationalize a kinetic scheme we must include one more reaction. Since the 4-phenyl-1-tetralyl radical 2 formulated in eq. [12] is capable of acting as

a chain initiator it must react with a second molecule of DPPH to give some non-initiating product. This is represented by eq. [14].

[14]  + DPPH ⟶ Products

(2)

The products of this reaction are described in Chapter II of this thesis. The value of R_{DPPH} measured is the rate of disappearance of DPPH for the reactions shown by eqs. [12] and [14] and so must be halved when looking at eq. [12] alone. The value of the kinetic isotope effect for the rate of formation of 1 can be obtained from these measurements. The following rate expressions can be written for the above reactions:

[15] $$\frac{1}{2}\ -\frac{d[DPPH]}{dt} = k_2[D.A.][DPPH] = 1/2\ R_{DPPH}$$

[D.A. = Diels-Alder adduct 1]

Under steady state conditions.

[16] $$\frac{d[D.A.]}{dt} = 0 = k_1[M]^2 - k_{-1}[D.A.] - k_2[D.A.][DPPH]$$

[M = Monomer]

which yields

$$[17] \quad [D.A.] = \frac{k_1[M]^2}{k_{-1} + k_2[DPPH]}$$

Substituting in eq. [15] from eq. [17] gives eq. [18].

$$[18] \quad -\frac{d[DPPH]}{dt} = 2\,\frac{k_2[DPPH]k_1[M]^2}{k_{-1} + k_2[DPPH]}$$

For the rate of disappearance of DPPH to be zero order, i.e., independant of its concentration, it is necessary that $k_{-1} << k_2[DPPH]$. This means that the adduct 1 does not dissociate reversibly to give back styrene monomer but reacts with DPPH as in eq. [12]. If the concentration of DPPH is high with respect to the dimer concentration at any time this is valid. Eq. [18] then becomes

$$[19] \quad \frac{-d[DPPH]}{dt} = 2\,k_1[M]^2$$

Since at the linear portion of the rate curve the DPPH is exhibiting a zero order dependance and k_2 represents the fast step, the slope of the curve represents a value of $2\,k_1[M]^2$. A value of k_1, the rate constant for the formation of the Diels-Alder adduct, can be easily calculated since the monomer concentration change is negligible throughout the reaction. Table VII shows the calculated values for k_1 at 75°. The average value for k_1 is found to be equal to 1.79×10^{-10} litre/mole/sec for styrene and 2.36×10^{-10} litre/mole/sec for styrene-o-o'-d_2.

TABLE VII

Rate Constants and Kinetic Isotope

Effect for the Formation of 1 at 75°

Monomer	R_{DPPH}†	$[M]^2$,¶ mole/litre	$k_1 \times 10^{10}$ litre/mole/sec
Styrene	2.42 ± 0.16	68.2	1.79 ± 0.12
Styrene-o-o'-d_2	3.19 ± 0.07	67.4	2.36 ± 0.05

$$\frac{k_{1,H}}{k_{1,D}} = 0.76 \pm 0.07$$

† values are average values from Table VI

¶ molarities are values at 70° (32).

The kinetic deuterium isotope effect for the rate of formation of the Diels-Alder adduct 1 is given by

$$\frac{k_{1H}}{k_{1D}} = 0.76 \pm 0.07$$

where the subscripts H and D represent the average value of k_1 for the normal and deuterated styrene respectively. If a correction is made for the isotopic purity of the styrene-o-o'-d_2 using eq. [20], (36)

[20] $$\frac{k_H}{k_H(1-x) + k_D(x)} = \frac{k_H}{k_D} \text{ observed}$$

where x = fraction isotopic purity

then we obtain $\frac{k_{1H}}{k_{1D}} = 0.75 \pm 0.07$

The Diels-Alder reaction leading to the formation of 1, eq. [3], involves the conversion of sp^2 centers to sp^3 centers and theoretical considerations (37) predict that the k_H/k_D ratio should be less than unity, i.e., an inverse secondary deuterium isotope effect. The value of k_H/k_D calculated here is in agreement with these predictions.

Secondary isotope effects have been reviewed in the literature by Halevi (37). The secondary isotope effects are divided into two types; (i) secondary deuterium isotope effects of the "first kind" or α-deuterium isotope effects, in which the deuterium atom is substituted on a

carbon atom which undergoes a change of hybridization as the reaction proceeds, and (ii) those of the "second kind" or β-deuterium isotope effects and γ-deuterium isotope effects, in which the deuterium is substituted on a carbon β or γ to the reaction site. The β- or γ- carbon atoms do not undergo re-orientations during the reaction. In effects of the "first kind" it has been found (38) that the substitution of a deuterium atom on a carbon atom which undergoes a hybridization from sp^3 to sp^2 produces an isotope effect of 10-15%, i.e., $k_H/k_D = 1.10 - 1.15$, and substitution of deuterium on a carbon atom undergoing a change of hybridization from sp^2 to sp^3 produces an isotope effect of similar magnitude, but in the reverse order, i.e., $k_H/k_D \simeq 0.9$ (inverse isotope effect).

Streitweiser (39) has suggested that the most important factor contributing to the magnitude of the isotope effect is the increased frequency of the out-of-plane C-H bending mode as the molecule leaves the planar trigonal configuration and moves towards the tetrahedral configuration of the product. A similar reasoning based upon the change of force constants and the geometry of the transition states has been made by Wolfsberg and Stern (40). Their conclusions support those of Streitweiser. They stress that these are only theoretical considerations and are

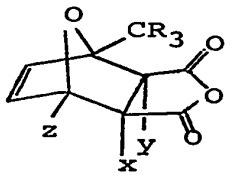
based on model reactants and transition states.

Some secondary isotope effects observed for the Diels-Alder and retro-Diels-Alder reaction (41) are listed in Table VIII. The numerical values for the inverse secondary isotope effects are small, k_H/k_D = 0.99 - 0.93 per deuterium atom, and are interpreted as indicating a small change in hybridization of the four centers of reaction in going from the starting materials to the transition state. The difference in isotope effects caused by a change of deuterium substitution from the diene to the dienophile was not adequately explained. The values observed for the retro-Diels-Alder reaction are in the normal direction as predicted (37), i.e., $k_H/k_D > 1$.

Kopecky and Evani (18) have estimated an isotope effect k_{iH}/k_{iD} = 0.91 at 75°, (see eq. [8]), for the Diels-Alder reaction between two molecules of β,β-dideuteriostyrene from the rates of polymerization of this compound and the parent styrene. Other reactions involving "concerted" additions to carbon-carbon double bonds include the reaction between diphenylketene and an olefin. Katz and Dessan (42) measured a value of k_H/k_D = 0.88 at 100° for the cycloaddition of diphenyl ketene to cyclohexene-1-d_1. Baldwin (43) observed a similar value of k_H/k_D = 0.91 for the addition of diphenyl ketene to β,β-dideuteriostyrene.

TABLE VIII

Secondary Deuterium Kinetic Isotope Effects in some Diels-Alder and retro-Diels-Alder Reactions

System	K_D/K_H per D atom at 25°	Reference
A. Diels-Alder reaction:		
Deuterated dienes:		
1,1,4,4-$\underline{d}_4$-Butadiene + maleic anhydride	1.07	(40a)
9,10-$\underline{d}_2$-Anthracene + maleic anhydride	1.06	(40a)
9,10-$\underline{d}_2$-Anthracene + tetracyanoethylene	1.06	(40b)
Deuterated dienophiles:		
Maleic anhydride-$\underline{d}_2$ + butadiene	1.01	(40a)
" " + cyclopentadiene	1.03	(40a)
" " + anthracene	1.05	(40a)
B. Retro-Diels-Alder reaction:		(41)
	i, x=y=z=R=H ii, x=y=D; z=R=H iii, x=y=R=H; z=D iv, x=D; y=z=R=H v, y=D; x=z=R=H vi, x=y=z=H; R=D	at 49.8° k_i/k_{ii} = 1.16 k_i/k_{iii} = 1.08 k_i/k_{vi} = 1.03 k_{iv}/k_v = 1.00

Both authors interpret the isotope effects in terms of the hybridization change at the reactant sites. Baldwin also measured $k_H/k_D = 1.23$ for the addition of diphenyl ketene to α-deuteriostyrene. This isotope effect is in the opposite direction to that expected for a hybridization change alone and was interpreted as due to the twisting of an sp^2 carbon out of conjugation with an adjacent p-orbital as a necessary prelude to bonding with another atom.

The k_H/k_D ratio observed in this work, while smaller than those reported previously, is still within the maximum predicted for an inverse secondary isotope effect of ≃ 0.46 (44). In the absence of any further work on isotope effects in the Diels-Alder reaction where the deuterated diene is part of an aromatic ring system, the value of $k_H/k_D = 0.75 \pm 0.07$ is taken as a value of the isotope effect in the formation of the Diels-Alder adduct 1 from styrene-o-o'-d_2.

Mayo (11,13) has suggested that if DPPH reacts directly with 1 the rate of disappearance of DPPH may be a measure of the rate of formation 1. The results obtained with DPPH are in agreement with this suggestion. Further evidence for the direct reaction of DPPH with 1 is given in the latter part of this discussion, when the analysis of the dimer fractions are examined, and in Chapter II of this thesis, where the inhibition products are identified.

The results obtained by Russell and Tobolsky (3) can now be explained if the above assumption is taken as correct. The value of $R_{i,th}$ calculated by Russell and Tobolsky is taken as a measure of the rate of formation of initiating radicals in the polymerization reaction. The analogous R_i for initiated polymerization denotes the rate of formation of initiator radicals from the added initiator. The termolecular initiation sequence in the thermal polymerization of styrene is given by eqs. [3] and [4], where eq. [4] represents the radical forming reaction which is the slow rate determining step. If DPPH takes the place of the third molecule of styrene, eq. [12], the slow step now becomes the formation of the adduct 1 and the rate is given by 1/2 R_{DPPH} as previously discussed. It is, therefore, not surprising that the values for R_i and R_{DPPH} differ by a factor of almost 10^2 as reported. A similar behaviour was noted for the inhibition by p-benzoquinone and R_{BZQ} (rate of disappearance of p-benzoquinone) was found to be 61 times greater at 60° than $R_{i,th}$ calculated as before. A similar argument may be applied here to explain the rate differences but the situation is now more complex since it has been shown (Chapter III of this thesis) that p-benzoquinone is consumed in a Diels-Alder reaction with styrene during the polymerization.

The value of k_1 for styrene dimerization calculated from eq. [19] using an average value for $R_{DPPH} = 2.42 \times 10^{-8}$ mole/litre/sec is found to be 1.79×10^{-10} litre/mole/sec. Russell and Tobolsky (3) found that $R_{DPPH} = 3.2 \times 10^{-8}$ mole/litre/sec which affords a value of $k_1 = 2.48 \times 10^{-10}$ litre/mole/sec on substitution into eq. [19]. Kirchner and Bucholz (16) have measured a value for $k_1 = 2.2 \times 10^{-6}$ litre/mole/min at 137°. An activation energy of 21 Kcal/mole for the disappearance of DPPH was measured by Russell and Tobolsky from runs at 50°, 60° and 75°. From a run at 70° in this work an estimated activation energy of 20 Kcal/mole was obtained. These figures allow an extrapolation of the value of k_1 to 137° from the value measured at 75° using eq. [21] (45).

[21] $$\log \frac{k_a}{k_b} = \frac{E_A}{2.303R}\left(\frac{1}{T_b} - \frac{1}{T_a}\right)$$

k_a and k_b rate constants at temperatures T_a and T_b respectively.
E_A activation energy Kcal/mole.
R gas constant.

A value for $k_1 = 1.06 \times 10^{-7}$ litre/mole/min from this work compares with $k_1 = 1.40 \times 10^{-7}$ litre/mole/min from the results of Russell and Tobolsky, and is a factor of 20 times slower than measured by Kirchner and Bucholz. Considering the different methods used in the measurement of k_1, these values may be considered, within experimental error, to be

in agreement.

A primary isotope effect for the rate of deuterium abstraction by DPPH from 1, as shown in eq. [12], cannot be observed under a zero order rate of disappearance of DPPH. Figures V and VI show that at long measurement times R_{DPPH} is non-linear and so no longer obeys a zero order dependance. We can now provide a kinetic scheme to evaluate k_{2H}/k_{2D}.

The loss of zero order dependance can be rationalized by assuming that at low concentrations of DPPH, the adduct 1 is not trapped completely but returns to monomer via the retro Diels-Alder reaction. If we apply this reasoning to the reaction scheme in eqs. [3] and [12], we can say that k_2 is now competing with k_{-1}. At some time, therefore, the rate of capture of dimer 1 by DPPH must be equal to the rate of 1 returning to styrene monomer. This is represented by eq. [22]

[22] $$k_{-1}\,[D.A.] = k_2\,[D.A.]\,[DPPH]^*$$

$$\text{or } k_{-1} = k_2\,[DPPH]^*$$

where $[\ ]^*$ represents the concentration when half of 1 returns to styrene.

If substitution is made into eq. [17] we obtain eq. [23]

[23] $$[D.A.] = \frac{k_1[M]^2}{2k_{-1}}$$

and eq. [18] becomes eq. [24].

$$[24] \qquad \frac{-d[DPPH]^*}{dt} = k_2[DPPH]^* \frac{k_1[M]^2}{k_{-1}} = R_{DPPH}^*$$

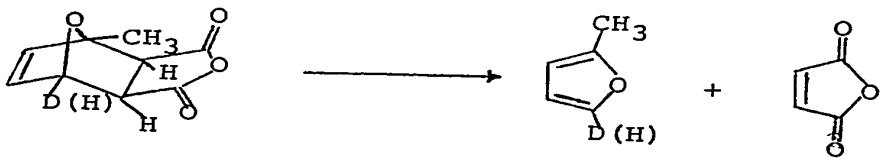
If DPPH intercepts 1 each time it is formed then we have a zero order dependance on R_{DPPH}. For eq. [22] to apply, the DPPH must be intercepting only one half of the amount of Diels-Alder adduct formed and so the rate of disappearance of DPPH is one half of that observed under zero order conditions. If a tangent is drawn to the curves such that the slope is now one half of the value observed under zero order conditions, values can be obtained directly for $-d[DPPH]^*/dt$, R_{DPPH}^*, and $[DPPH]^*$. The functions are starred so that they can be distinguished from the values used in earlier calculations. The values for the deuterated styrene can be obtained in the same manner. We can write

$$[25] \qquad \frac{R_{DPPH,H}^*}{R_{DPPH,D}^*} = \frac{k_{2H}[DPPH]_H^* k_{1H}[M_H]^2}{k_{-1H}} \frac{k_{-1D}}{k_{1D}[M_D]^2 k_{2D}[DPPH]_D^*}$$

where the subscripts H and D refer to the kinetic parameters for styrene and styrene-o-o'-d_2, respectively. A value for $k_{1H}/k_{1D} = 0.75 \pm 0.07$ has been measured in the previous section. At 70° $[M_H] = 8.26M$ and $[M_D] = 8.21M$,

and the difference between $[M_H]^2$ and $[M_D]^2$ can be neglected. Values for $R_{DPPH,H}$* and $R_{DPPH,D}$*, $[DPPH_H]$* and $[DPPH_D]$* can be obtained directly from the graphs. An estimate of the isotope effect in the retro-Diels-Alder reaction, i.e., k_{-1D}/k_{-1H}, can be made from the system

[26]



Here k_H/k_D = 1.08 at 49.8° (41) and a value of k_H/k_D = 1.07 at 75° can be calculated using the activation parameters reported for this reaction. It must be emphasized that this is a poor model for the system under consideration, where the diene is now contained partly within an aromatic ring. If the magnitude of the normal secondary isotope effect for the retro-Diels-Alder reaction was larger, inspection of eq. [25] shows that there would be an increase in the magnitude of the k_{2H}/k_{2D} ratio. The maximum theoretical value for a normal secondary isotope effect had been estimated as high as 1.40 at 70° (40).

Substitution for the rate constants in eq. [25]

yields eq. [27].

$$[27] \qquad \frac{R_{DPPH,H}^*}{R_{DPPH,D}^*} = 0.813 \quad \frac{k_{2H}}{k_{2D}} \frac{[DPPH_H]^*}{[DPPH_D]^*}$$

Table IX lists the values of $R_{DPPH,H}^*$, $R_{DPPH,D}^*$, $[DPPH_H]^*$ and $[DPPH_D]^*$ measured from the graphs.

A value for the deuterium isotope effect in the hydrogen abstraction step, $k_{2H}/k_{2D} = 1.96 \pm 0.49$, is calculated from these results. This value is interpreted as a primary isotope effect and it supports a mechanism involving reversible formation of the Diels-Alder adduct 1, eq. [3], followed by hydrogen abstraction by DPPH in a fast step to form DPPH-H and the radical 2, eq. [12]. The somewhat low value for the primary deuterium isotope effect is in accord with those observed in other free radical hydrogen abstraction reactions (46,47).

Product Analysis of Dimer Fractions

The 4-phenyl-1-tetralyl radical, (2), can react with DPPH, eq. [13], by two principal routes: (i) recombination or (ii) disproportionation. The first case is examined in detail in Chapter II of this thesis. The alternative reaction can only take place in one direction, eq. [28].

TABLE IX

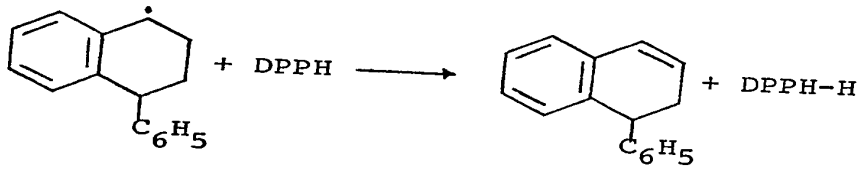
Kinetic Isotope Effects in the Hydrogen Abstraction Step

for DPPH Inhibition of Styrene Polymerization at 75°

Run	Monomer	R_{DPPH} $\underline{M}\ sec^{-1}.10^8$	R_{DPPH}^* $\underline{M}\ sec^{-1}.10^8$	[DPPH]* Mole/litre.10^5	k_{2H}/k_{2D}
41	Styrene	2.46	1.23	5.10	
42	"	2.12	1.06	5.00	
46	Styrene-$\underline{o}$-$\underline{o}'$-$\underline{d}_2$	3.23	1.62	11.05	1.98, 1.78
47	"	3.35	1.67	12.14	2.16, 1.90

Average $k_{2H}/k_{2D} = 1.96 \pm 0.49$

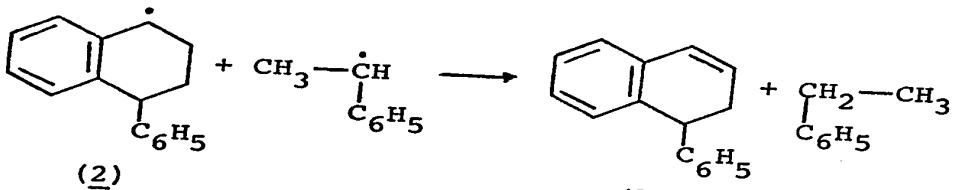
[28]



(2) (18)

Hydrogen transfer from DPPH to 2 is not possible as only aromatic hydrogens are available. The only observed product should be 1-phenyl-1,2-dihydronaphthalene (18). Analysis of the dimeric fractions formed in the presence and absence of DPPH (Table 1) shows that the proportion of 18 is increased to 42.1% of the total dimer fraction in the former from 16.4% found in the latter, in accord with eq. [28]. This increase in the proportion of 18 formed is small when compared to the proportion observed in the thermal polymerization. The formation of 18 in the uninhibited thermal polymerization of styrene, can be envisaged from disproportionation between 2 and a 1-phenylethyl radical inside a solvent cage, eq. [29].

[29]



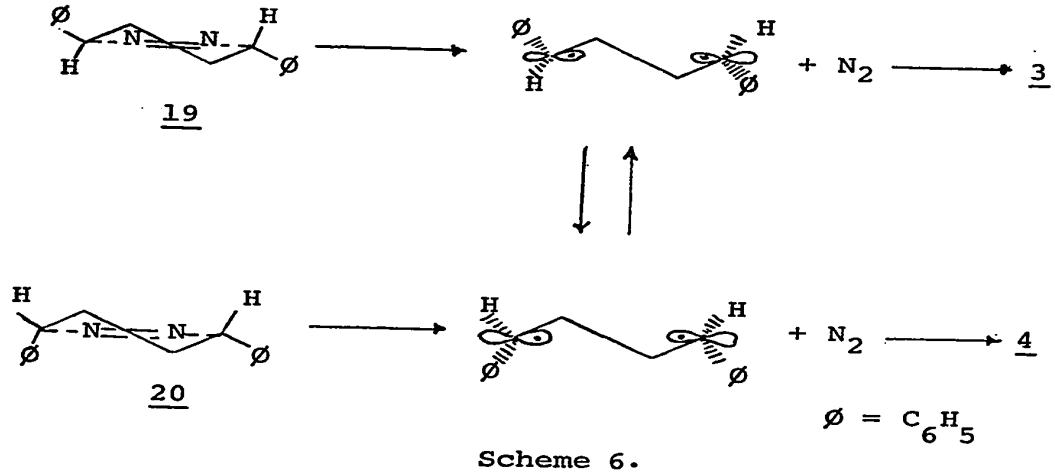
(2) (18)

However, the formation of 2 in the thermal polymerization must be greatly decreased compared to the amount formed in the presence of added inhibitor, since it is expected that 1 would revert to monomer with a greater frequency than it will react with a styrene molecule as in ea. [4] to yield the radical 2. In the inhibited polymerization, DPPH reacts with 1 each time it is formed if R_{DPPH} is to obey a zero order kinetic dependance. If disproportionation is the major route for reaction 2 with DPPH, the amount of 18 formed in the dimer fraction should have been increased at least a hundred fold with a corresponding increase in the size of the total dimer fraction. The total amount of the dimer fractions from the thermal and inhibited polymerisations were almost the same whilst the results in Table 1 show that the relative proportion of 18 is only increased 2-3 times for the inhibited polymerisation. 2 must therefore be reacting by recombination with DPPH to give a substituted DPPH molecule. The results in Chapter II of this thesis confirm that almost 90% of the radical 2 produced by eq. [12] reacts with DPPH by recombination.

The ratio of *cis*- to *trans*-1,2-diphenylcyclobutanes is not affected by the added inhibitor, in agreement with the results of Kirchner and Bucholz (16). These results also rule out the formation of 3 and 4 by way of the intermediate dimer 1, as suggested by Brown (17), (Scheme 1). As 1 must react with DPPH each time it is formed, the formation of 3 and 4 should have been completely surpressed if they were

arising from 1. Therefore, the cyclobutanes 3 and 4 must be formed by a simultaneous but separate mechanism as shown in Scheme 2.

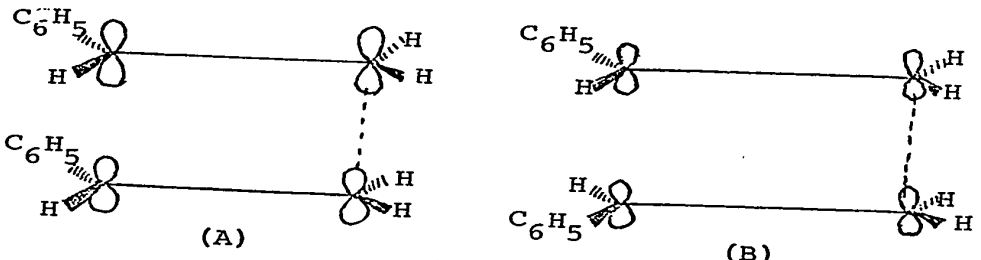
It has been shown (48) that the ratio of 3 to 4 formed from the thermal decomposition of trans-3,6-diphenyl-3,4,5,6-tetrahydropyridazine (19) is 20:1 at 133° while the ratio is 0.55:1 in the case of the cis isomer (20). The geometry of the initial diradical obviously affects the ratio of observed cyclobutane products. The stereochemistry and conformation of the diradical intermediates from the azo compounds are shown in Scheme 6.



Scheme 6.

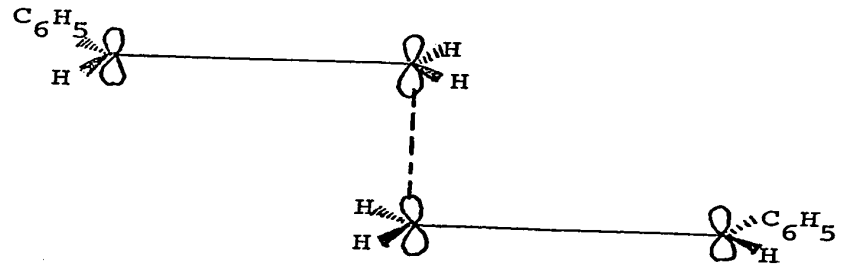
The trans/cis ratio was only changed slightly over a temperature range from 60° to 300°. The trans/cis ratio observed in this work, 2.7:1, does not correspond to either the cis or trans conformations for the diradical intermediate

from the pyridazine decomposition. These geometries could be obtained as shown in Scheme 7.



Scheme 7

Overlap of the p-orbitals on the β-carbons in A would give a geometry close to that for the diradical from cis-20, whilst the same operation for B would give a geometry close to the diradical from the trans- 19. A mixture of these geometries may be occurring as the trans/cis ratio for cyclobutane formation in styrene polymerization has been found to lie between 2/1 and 3/1 under a variety of temperature conditions (14,16,17). If overlap occurs via an "end on" geometry, Scheme 8,

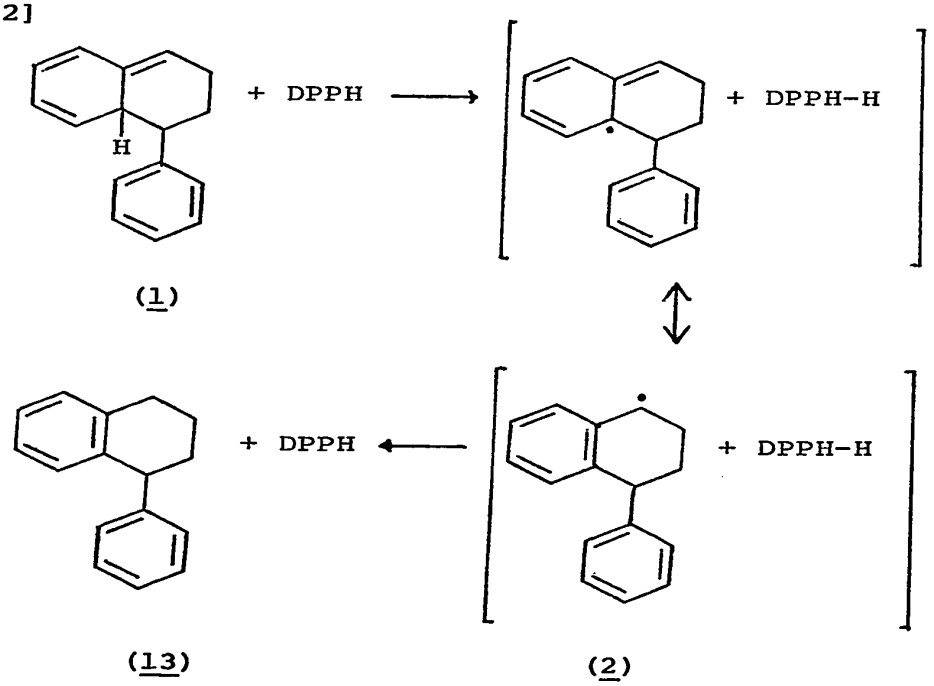


Scheme 8

rotation must occur about the newly formed C-C bond before closure can take place. The geometries of the process must be a mixture of the aforementioned possibilities.

The presence of 1-phenyltetralin in both inhibited and thermally polymerized samples can be rationalized as arising from cage reactions of radical pairs. In both cases less than 2% was observed. In the inhibited polymerization, eq. [12] describes the reaction between DPPH and the Diels-Alder adduct 1 to give DPPH-H and the radical 2. If hydrogen

[12]



(1) (13) (2)

abstraction by the radical 2 from DPPH-H occurs within the cage then 1-phenyltetralin will be the product. From the small amount of 1-phenyltetralin observed this process of hydrogen abstraction within the cage must be occurring at a much slower rate than diffusion from the cage. It has been suggested (49) that the rate determining step in hydrogen abstraction reactions from hydrocarbons involves the abstraction of a hydrogen atom by DPPH in a slow reversible step. This is in accord with an overall second order kinetics eq. [30].

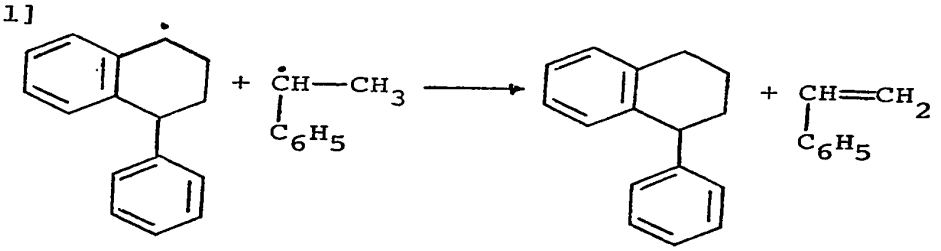
[30.1] $XH_2 + DPPH \overset{slow}{\rightleftharpoons} XH\cdot + DPPH\text{-}H$

[30.2] $XH\cdot + DPPH \longrightarrow DPPH\text{-}H + X$

It has also been shown that DPPH does not abstract hydrogen atoms from tetralin at an appreciable rate (50), indicating that the reverse reaction in eq. [30.1] must be occurring at a greater rate than the reaction in eq. [30.2]. The formation of 1-phenyltetralin in eq. [12] may then be considered irreversible under the conditions used here.

The formation of the small amounts of 1-phenyltetralin from the thermally polymerized sample must be arising from a disproportionation reaction in the cage, between the pair of initiating radicals formed in eq. [31].

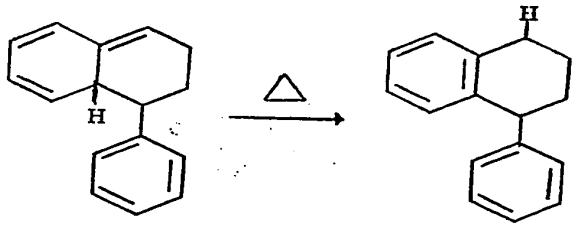
[31]



(2) (13)

The formation of 13 is unlikely to arise from an uncatalyzed thermal 1,3 sigmatropic shift of the allylic hydrogen eq. [32].

[32]



(1) (13)

The hydrogen atom must migrate in an antarafacial manner and the few reactions of this type have been found to have activation energies in the region of 50 Kcal/mole (51).

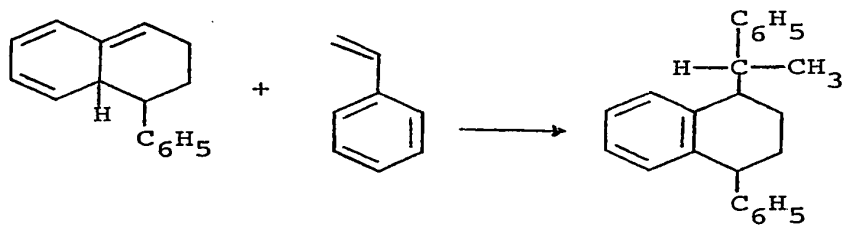
Other workers (14,15,16,17) have found 13 to be present in as high as 70% (15) and as low as 2% (14) of the total dimeric fraction. The abnormally high proportions of 13 observed must be due to an isomerization of the adduct 1 by traces of acid. This is analagous to the

iodine catalyzed isomerization proposed by Mayo (13) to explain the high yields of 13 observed in the iodine inhibited polymerization of styrene.

If DPPH reacts with 1 each time it is formed, it excludes completely any hydrogen atom transfer between 1 and styrene as in eq. [4]. There should, therefore, be an absence of any trimeric or high fractions that are formed from this sequence. A peak appears in the chromatogram of the thermally polymerized sample, with a retention time that is almost double that observed for the dimeric components, when the glc analysis of the dimer fraction was carried out at a higher column temperature. Although this peak was not identified, it must correspond to the trimeric fraction observed by other workers (14,16,17). There was an absence of this peak in the chromatogram of the inhibited sample when analyzed under exactly the same conditions. The absence of this trimeric fraction, which can only be formed by a radical recombination as in eq. [5], or by disproportionation of a growing polymer chain eq. [13] is an indication that the DPPH is trapping all the adduct 1 before hydrogen transfer to styrene, and is also trapping the radical 2 produced from this interception. Kirchner and Bucholz have estimated the activation energy for trimer formation and find a value of 20.5 $\pm$ 1 Kcal/mole. They

conclude that the 9 Kcal/mole difference between this value and the activation energy of 29 Kcal/mole estimated for the initiation step in styrene (11) must indicate another mechanism is predominant in trimer formation. They propose a concerted addition of styrene to the intermediate 1 in an "ene" fashion to give the trimer eq. [33].

[33]



(1) (6)

If DPPH intercepts 1 then this reaction is also suppressed.

EXPERIMENTAL

Physical measurements

The melting points and boiling points reported are not corrected.

Refractive indices were measured on a Bausch and Lomb Abbe-3L Refractometer.

Infrared spectra were obtained on a Beckmann IR-7 Recording Spectrophotometer.

Nuclear magnetic resonance (nmr) spectra were obtained on Varian Analytical Spectrophotometers, Models A-60 and HR-100 with tetramethylsilane (TMS) as internal standard. The τ values are reported as relative to TMS = 10. The following abbreviations are used in the text: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet.

Mass spectra were obtained on A.E.I. models MS-2, MS-9 and MS-12 mass spectrometers. A Varian Series 1200 gas chromatograph was connected to the A.E.I. MS-12 mass spectrometer, with an ion counter detector, and helium gas as the carrier.

Gas liquid chromatography (glc) analysis was carried out on an Aerograph-202 Gas Chromatograph, with thermal conductivity detectors and helium as the carrier gas.

Ultra-violet spectra were obtained on a Bausch and Lomb Spectronic 600 Spectrophotometer.

N,N-Dimethyl-(1-phenylethyl)-amine (7)

1-Phenylethylamine was N-methylated according to the method of Clarke, Gillespie and Weisshaus (27). Freshly distilled 1-phenylethylamine (136 g, 1.12 moles) was added drop by drop during one and one-half hours to 90% formic acid (287.7 g, 5.62 moles), kept in a two litre three-necked flask fitted with a reflux condenser, thermometer and dropping funnel. The temperature of the reaction mixture was maintained below 20° during addition. To the clear solution obtained, 40% formaldehyde solution (253 ml, 3.37 moles) was added. The reaction flask with its contents was placed in a preheated oil bath at 110°. When the temperature of the reaction mixture reached 65° there was a vigorous evolution of carbon dioxide. The flask was raised from the oil bath and when the evolution of gas was somewhat abated, the flask was placed again in the oil bath at 110-115° for twelve hours. The contents of the flask were then cooled and 4 N hydrochloric acid (1100 ml) was added and the slightly cloudy solution evaporated under vacuum to yield a pale yellow syrupy liquid. The latter was dissolved in 250 ml of distilled water and the organic

base liberated by addition of 17 N sodium hydroxide (280 ml). The yellow upper organic layer was separated and the lower aqueous layer was extracted twice with benzene (100 ml). The combined organic base and benzene extracts were dried over anhydrous potassium carbonate. Evaporation of the solvent and distillation of the residual oil yielded 114 g (63%) of N,N-dimethyl-(1-phenylethyl)-amine (clear colorless liquid), bp 79° (15 mm), n_D^{25} = 1.5008; lit. bp 71° (11 mm), n_D^{25} = 1.5000 (27). The infrared spectrum (neat) showed absorption bands characteristic for the compound. The nmr spectrum ($CDCl_3$) showed peaks at τ2.80 (s), τ6.88 (q, J = 7 cps), τ7.89 (s), τ8.73 (d, J = 7 cps), ratio 5.0 : 1.1 : 6.0 : 2.95, required 5 : 1 : 6 : 3.

N,N-Dimethyl-(1-phenylethyl)-amine-o-d_1 (8)

The method of Jones and Hauser (52) was used with slight modification for the ring deuteration of the amine. To a solution of freshly distilled 7 (44.7 g, 0.3 mole) in anhydrous ether (40 ml) kept in a dry one-litre three-necked flask, provided with a rubber serum cap and a magnetic stirrer, n-butyllithium solution (Foote Mineral Co. 1.6 M solution in n-hexane) (360 ml, 0.6 mole) was added with a hypodermic syringe. The addition was carried

out under nitrogen atmosphere. The solution was stirred for 40 hours at room temperature. The resulting pale yellow solution was added to a stirred mixture of deuterium oxide (Merck Sharpe & Dohme of Canada Ltd. 99.7% minimum isotopic purity) (48 ml) and sodium-dried-redistilled benzene (250 ml) under an atmosphere of nitrogen. The mixture was stirred for six hours and allowed to settle. The clear top layer was decanted from the white sludge and the sludge was washed thrice with anhydrous ether (50 ml). The combined clear layer and the ether washings were dried with anhydrous sodium sulphate. The solvents were removed and the residual oil distilled to yield 43.1 g, (94.6%) of a colorless liquid, bp 84° (21 mm), $n_D^{26} = 1.4999$; lit. bp 71° (13 mm), $n_D^{29} = 1.4986$ (8). The infrared spectrum showed an absorption band at 2270 cm^{-1} (C-D stretching vibration). The nmr spectrum (CCl_4) showed peaks at τ2.82 (s), τ6.89 (q, $\underline{J}$ = 7 cps), τ7.90 (s), τ8.75 (d, $\underline{J}$ = 7 cps), ratio 4.0 : 1.0 : 6.1 : 3.0, required 4 : 1 : 6 : 3. The mass spectral analysis (11 ev) showed a parent peak at m/e 150 and indicated that the product contained 92 mole % amine-$\underline{d}_1$ and 8 mole % amine-$\underline{d}_0$.

N,N-Dimethyl-(1-phenylethyl)-amine-$\underline{o}$-$\underline{o}$'-$\underline{d}_2$ ($\underline{9}$)

Starting with $\underline{8}$ (22.4 g), the metalation and

deuteration sequence was carried out in the same way as above to effect dideuteration of the aromatic ring of the amine. After work-up there was obtained 19.2 g (90%) of a colorless liquid bp 82-85° (35 mm), n_D^{29} = 1.4937. The nmr spectrum (CCl_4) showed peaks at τ2.80 (s), τ6.89 (q, $\underline{J}$ = 7 cps), τ7.90 (s), τ8.75 (d, $\underline{J}$ = 7 cps), ratio 3.2 : 1.0 : 6.0 : 3.0, required 3.0 : 1.0 : 6.0 : 3.0. The mass spectral analysis (11.5 ev) indicated that the product consisted of 68 mole % amine-$\underline{d}_2$ and 24 mole % amine-$\underline{d}_1$. As the isotopic purity was less than desired the metalation and deuteration sequence was repeated on the product obtained above under exactly the same conditions as in the earlier case. There was obtained 15.1 g (78%) of a colorless liquid bp 82-84° (35 mm), n_D^{28} = 1.4939; lit. bp 97° (50 mm), n_D^{29} = 1.4975 (8). The nmr spectrum (CCl_4) was exactly the same as in the previous case except the ratio was 3.1 : 1.0 : 6.0 : 3.0, required 3.0 : 1.0 : 6.0 : 3.0. The mass spectral analysis (11.5 ev) indicated greater than 95 mole % amine-$\underline{d}_2$. The product was used without further enrichment.

N,N-Dimethyl-(1-phenylethyl)-amine oxide and its decomposition to styrene (12)

The method employed was due to Cope (28). A mixture of freshly distilled 7 (22 g) and 30% hydrogen peroxide

solution (48 g) was stirred for 18 hours at room temperature (29°). A drop of the reaction mixture, diluted with distilled water, when tested with phenolphthalein indicator, showed the absence of base, indicating the completion of the reaction. The excess hydrogen peroxide was decomposed with 0.007 g of palladium black. When the gas evolution stopped the solution was filtered. The filtrate and washings were concentrated under vacuum in a current of nitrogen and the distillate was collected in a dry-ice acetone bath. When all the water was removed the residual syrupy liquid was heated to 100° and the distillate collected in the same trap. The decomposition was quite spontaneous and was over in 15-20 minutes leaving no residue in the distillation flask. The distillate in the trap was warmed to room temperature and the organic layer was separated. This was washed three times with cold 5% hydrochloric acid (25 ml), three times with cold 10% sodium hydroxide solution and finally with saturated sodium chloride until free from alkali. It was then dried with anhydrous sodium sulphate and distilled under vacuum through a vigreaux column in a current of nitrogen to obtain 10.8 g (70%) of styrene bp 32° (13 mm), n_D^{26} = 1.5441. The infrared spectrum (neat) and nmr spectrum (CCl_4) matched exactly with those of commercial styrene.

The glc analysis (SF 96 at 100°C) indicated that the product was free from impurities.

N,N-Dimethyl-(1-phenylethyl)-amine oxide-o-o'-d_2 (10) and its decomposition to styrene-o-o'-d_2 (11)

Decomposition of 10 to 11 was carried out exactly as described above. Starting with 9 (95 mole % d_2-amine, 30.0 g) there was obtained 14.6 g (70%) of styrene-o-o'-d_2 bp 38° (13 mm). The nmr spectrum (CCl_4) showed peaks at τ2.85 (s), τ3.35 unsymmetrical quartet (J = 18 cps, J = 11 cps), τ4.38 (q, J = 18 cps, J = 2 cps), τ4.85 (q, J = 11 cps, J = 2 cps), ratio 3.0 : 1.0 : 1.0 : 1.0, required 3.0 : 1.0 : 1.0 : 1.0. The glc analysis (SF 96 at 100°C) indicated the product was free from impurities. The mass spectral analysis (10.5 ev) indicated that the product contained 91.7 mole % d_2-styrene, 8.3 mole % d_1-styrene, 0.0 mole % d_0-styrene.

γ,γ-Diphenylbutyric acid (15)

The method employed was a modification of that due to Johnson (33). To a cooled solution of 4.30 g (0.11 mole) of potassium in 90 ml dry t-butyl alcohol was added 26.1 g (0.15 mole) of diethyl succinate and 18.2 g (0.10 mole) benzophenone. The system was evacuated, filled with dry

nitrogen and protected from the atmosphere by a mercury trap. The mixture was heated under gentle reflux for 30 minutes, and after cooling was acidified with 10% hydrochloric acid. The t-butanol was removed at reduced pressure, water was added and the residue extracted with two 200 ml portions of ether. The combined ether extracts were washed several times with 2% sodium hydroxide solution. Acidification of these alkaline extracts afforded 27.5 g (89%) of almost colorless crystalline 3-carbethoxy-4,4-diphenyl-3-butenoic acid, mp 118-122°. A small portion was recrystallized from benzene-petroleum ether to give colorless needles mp 125-126°; lit. mp 124.5-125.5° (33). The crude half-ester was used immediately in the next step.

A solution of 27.5 g of the half-ester (mp 118-122°) in a mixture of 420 ml glacial acetic acid, 280 ml hydrobromic acid (48%), and 140 ml water was heated under reflux until no more gas was being evolved (six hours). The solvent mixture was removed under vacuum, water was added, and the residue was extracted with ether. Removal of the ether gave 20.1 g (96%) of a mixture of 4,4-diphenyl-3-butenoic acid and γ,γ-diphenyl-γ-butyrolactone.

To 10 g (0.045 moles) of the above mixture in 150 ml methanol, was added 500 mg of 5% palladium on charcoal catalyst and the mixture was hydrogenated at atmospheric

pressure until no more uptake in hydrogen occurred (three hours). The catalyst was removed by gravity filtration and the solvent removed under vacuum to yield 10 g (100%) of a pale cream solid. Recrystallization from benzene-petroleum ether gave 9.2 g (92%) large prisms mp 107°; lit. mp 107° (53). The infrared spectrum (CCl_4) showed absorptions for C=O 1710 cm^{-1}, and O-H 3300 cm^{-1}. The nmr spectrum (CCl_4) showed peaks at τ1.15 (s), τ2.99 (s), τ6.20 (m), τ7.75 (m) in ratio 1 : 10 : 1 : 4, required 1 : 10 : 1 : 4. The peak at τ1.15 disappeared on D_2O exchange.

4-Phenyl-1-tetralone (16)

The acid 15 preheated to 60-70° was added in one lot to polyphosphoric acid (40 g) kept at 90° and the mixture kept at steam bath temperature for three minutes. The mixture was removed and stirred vigorously by hand for a further four minutes. More polyphosphoric acid (40 g) heated to 90° was added with stirring and the mixture kept at 80-90° for one hour and then allowed to cool to 60°. Ice water (200 ml) was added and stirred until the reaction mixture was completely dispersed. The mixture was extracted twice with ether (100 ml). The ether extracts were combined and washed successively with water, 5% sodium hydroxide solution, water, 3% acetic acid

solution, 5% sodium bicarbonate, water and finally dried over anhydrous magnesium sulfate. The solvent was evaporated and the resulting off-white solid recrystallized from methanol to yield 7.6 g (82%) of white needles mp 76-77°; lit. mp 75.5-76° (35). The infrared spectrum (CCl_4) showed a carbonyl absorption at 1695 cm^{-1}. The nmr spectrum (CCl_4) showed peaks at τ2.41 (m), τ5.80 (t) τ7.52 (m) in the ratio 9.1 : 1 : 4.1, required 9 : 1 : 4.

4-Phenyl-1,2,3,4-tetrahydro-1-naphthol (17)

To 5.0 g (0.02 mole) of 16 dissolved in 50 ml of 95% ethanol was added 0.5 g (100% excess) of sodium borohydride powder and the solution stirred for 20 hours at room temperature. The excess solvent was removed by rotary evaporation and the product diluted with distilled water (100 ml). The organic soluble product was extracted with three portions of ether (50 ml) and the combined extracts dried over anhydrous magnesium sulfate. Removal of the solvent under vacuum yielded 4.8 g (96%) of a white powder. Recrystallization from carbon tetrachloride gave white needles melting over a range 96-100°. A small portion recrystallized from pentane gave long white needles mp 121.5-123°. The needles from carbon tetrachloride were concluded to be a mixture of isomers of 17. Both types

of crystals showed identical spectral characteristics. The infrared spectrum ($CHCl_3$) showed an absorption at 3450 cm^{-1} (O-H stretch). The nmr spectrum ($CDCl_3$) showed peaks at τ2.72 (m), τ5.16 (m), τ5.91 (m), τ7.75 (s) overlapping τ8.0 (m) in the ratio 9 : 1 : 1 : 5, required 9 : 1 : 1 : 5. The peak at τ7.75 disappeared on D_2O exchange.

Analysis: Calculated for $C_{16}H_{16}O$: C, 85.68; H, 7.19: Found C, 85.98: H, 7.11.

1-Phenyl-1,2 -dihydronaphthalene (18)

A mixture of 4.8 g 17 and 10 g orthophosphoric acid was heated at 120-130° for two hours. At the end of this time the homogeneous tan-colored liquid was cooled and poured into 250 g ice-water. The organic compound was extracted with two 50 ml portions of ether and the combined extracts washed with 5% sodium carbonate solution and then water until free from base. After drying over anhydrous magnesium sulfate, the solvent was removed to yield 4.0 g (83%) of a tan-colored viscous liquid. Distillation at reduced pressure gave 3.4 g (70%) of a viscous colorless liquid, bp 87° (0.08 mm), $n_D^{25} = 1.6225$. The infrared spectrum (neat) showed an absence of an O-H absorption and matched that reported in the literature (13). The

nmr spectrum (CCl_4) showed peaks at τ3.01 (s) overlapping τ3.45 (m), τ4.27 (m), τ6.00 (t, J = 8.5 cps) τ7.50 (m) in the ratio 10 : 1 : 1 : 2, required 10 : 1 : 1 : 2.

Analysis: Calculated for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.45; H, 6.94.

Dimeric components

Pure samples of cis-1,2-diphenylcyclobutane (3), trans-1,2-diphenylcyclobutane (4), and 1-phenyltetralin (13) were obtained from S. Evani (32). 1-Phenylnaphthalene (14) was obtained from Aldrich Chemical Co. Inc. and was used without further purification.

Isolation of the dimeric fraction from the thermal polymerization of styrene.

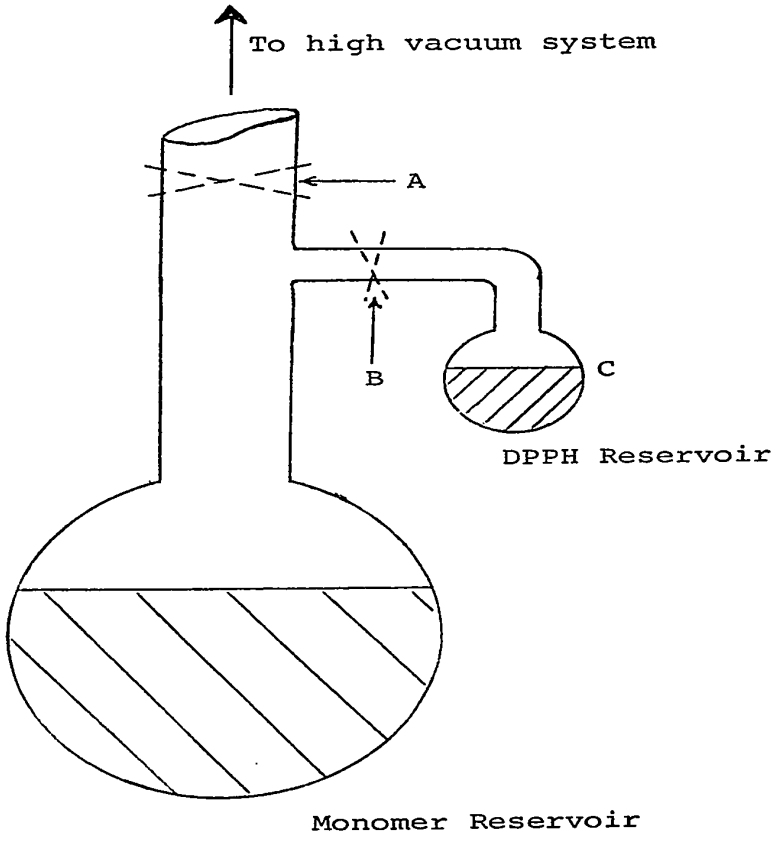
All glassware used for handling of styrene was carefully cleaned in the same manner as mentioned under the kinetic measurement portion of this experimental report.

(i) Inhibited thermal polymerization

The apparatus used for the polymerization is illustrated in Figure VII. The reservoir C containing 0.80 g of DPPH-benzene complex was carefully sealed into a long-necked 250 ml round-bottomed flask. The flask was carefully

FIGURE VII

Apparatus for DPPH Inhibited Polymerization of Styrene



filled with 100 ml (81.8 g, 0.786 mole) of freshly distilled styrene, taking care not to introduce any into the side arm C, and then sealed to a high vacuum system. The styrene was thoroughly degassed by three freeze-thaw cycles under high vacuum to less than 20 μ pressure, and the apparatus sealed at point A. Inversion of the apparatus allowed solution of the DPPH in the styrene. After freezing the flask and its contents, the apparatus was finally sealed at point B and allowed to warm to room temperature. The apparatus was immersed completely in a thermostatted water bath, and heated for 30 hours at 75° in the dark. At the end of this time the flask was broken and its contents poured into a 250 ml flask in preparation for distillation. The styrene was removed by distillation at 23 mm and the almost black residue (1.35 g) was placed on a 3 cm X 60 cm column of silica gel (150 g, 70-325 mesh ASTM, E. Merck & Co.) made up in acetone-petroleum ether (1:4 by volume). The residue was eluted with acetone-petroleum ether (1:4 by volume). The fractions were collected in 20 ml portions and analyzed by TLC (silica gel) using the same composition eluent. The fractions containing similar products were combined and each was rechromatographed on a 1 X 25 cm column of silica gel, using a 1:100 compound:silica gel ratio. Acetone-petroleum ether (1:4) was used as eluent.

The following fractions were obtained pure as analyzed by this method:

Fraction 1. (0.520 g) contained some unreacted styrene as well as the dimeric fraction from the polymerization reaction.

Fraction 2. (0.054 g) identified in Chapter II as a mixture of 1,1-diphenyl-2-[2,6-dinitro-4-(4-phenyl-1-tetralyl)phenyl]hydrazine and 1,1-diphenyl-2-picrylhydrazine.

Fraction 3. (0.408 g) consisted of 1,1-diphenyl-2-picrylhydrazine.

Fraction 4. (0.190 g) identified in Chapter II as 1-(4-nitrophenyl)-1-phenyl-2-picrylhydrazine.

Isolation of any further fractions was not attempted as 1.172 g (87%) of the total materials had been recovered from the column. Fractions 2, 3 and 4 were all dark-red or red-brown solids or gels. Fraction 1 was a pale yellow viscous liquid and was identified from its nmr spectrum and glc analysis (SF 96, 170°C). The identification is described below. From the nmr integration it could be estimated that the sample contained almost 90% styrene. The weight of dimers was then ~50 mg. Fraction 3 was identified from its nmr spectrum and melting point. There was no depression of melting point when mixed with

an authentic sample.

(ii) Thermal polymerization

Freshly distilled styrene (100 ml, 81.8 g, 0.786 mole) was thermally polymerized at 75° for 30 hours under exactly the same conditions as in (i). The degassing procedure was repeated exactly as reported in (i). After opening the flask the contents were dissolved in 250 ml benzene and twice the volume (500 ml) of methanol was added so as to precipitate any polymer formed. The sticky polymeric residue was filtered at the pump and leached several times with methanol. The combined methanol extracts and the benzene-methanol filtrate were concentrated under vacuum and the styrene removed by distillation at 23 mm on a steam bath. The yellow viscous residue was chromatographed on a 3 x 40 cm column containing 100 g silica gel using acetone/petroleum ether 1:4 as eluent. There was recovered 0.36 g of pale yellow viscous liquid. From the nmr spectrum (CCl_4) it was found to contain approximately 85-90% styrene and the remainder was dimer hydrocarbons.

Glc analysis and mass spectral measurements

Preliminary analysis of the dimeric fractions isolated from the thermal polymerizations in the presence and absence of DPPH were carried out on an Aerograph-202

gas chromatograph. A 5 ft x 0.25 in column with 20% SF 96 fluid on 60-80 mesh Chromosorb P at 200° with a helium flow rate of 60 ml/min was used with an injector temperature of 225° and a detector temperature of 285°. The dimer fractions were usually injected as solutions in benzene. The matched chromatograms are shown in Figure I, and the retention times are in Table I. Identification of the compounds was made by comparison of retention times of authentic materials and by mixed injections of authentic materials with the dimer fraction. A much better resolution of components was made using a 10 ft x 1/8 in Apiezon L on 60/80 Firebrick. The column temperature was 202° with a helium flow rate of 85 ml/min. The matched chromatograms are shown in Figure II. The retention times of the compounds under these conditions are: cis-1,2-diphenylcyclobutane, 19.4 min; trans-1,2-diphenylcyclobutane, 24.9 min; 1-phenyltetralin, 28.2 min; 1,2-dihydro-1-phenylnaphthalene, 31.2 min; 1-phenylnaphthalene, 43.3 min. The thermal response factors for all the materials were assumed to be approximately the same since all the compounds were either isomeric hydrocarbons or hydrocarbons of almost the same molecular weight. The area of the peaks was measured by using a planimeter (Gelman Instrument Co.) or by cutting out and weighing the curves. Similar

results were obtained by both methods. The relative proportions of the components in the isolated dimeric fractions are given in Table I

Mass spectral analysis of the dimer fraction was made using a Varian Series 1200 gas chromatograph connected to an A.E.I. MS-12 mass spectrometer. The SF 96 column was used with a column temperature of 200° and a helium flow rate of 50 ml/min. The collection port of the gas chromatograph was joined directly to the ionizing chamber of the mass spectrometer by means of a sintered glass Watson-Biemann separator. An ion-counter detector was used to monitor the fractions eluted. The gas chromatogram was also recorded using a Honeywell recorder. A scanning time of 2 or 4 sec was used for the mass spectra and several spectra were recorded as each component was eluted. Background spectra were recorded at convenient intervals as there was some bleeding of the stationary phase in the column. The background was subtracted from the recorded mass spectra in each case. Mass spectra of the authentic materials were recorded under the same conditions after injection into the chromatograph. The mass spectra of 3, 4, 13 and 14 were also recorded by using a direct probe inlet and are shown in Figures VIII (a) and VIII (b). The mass spectra of the glc fractions matched exactly those recorded for the authentic materials.

FIGURE VIII (a)

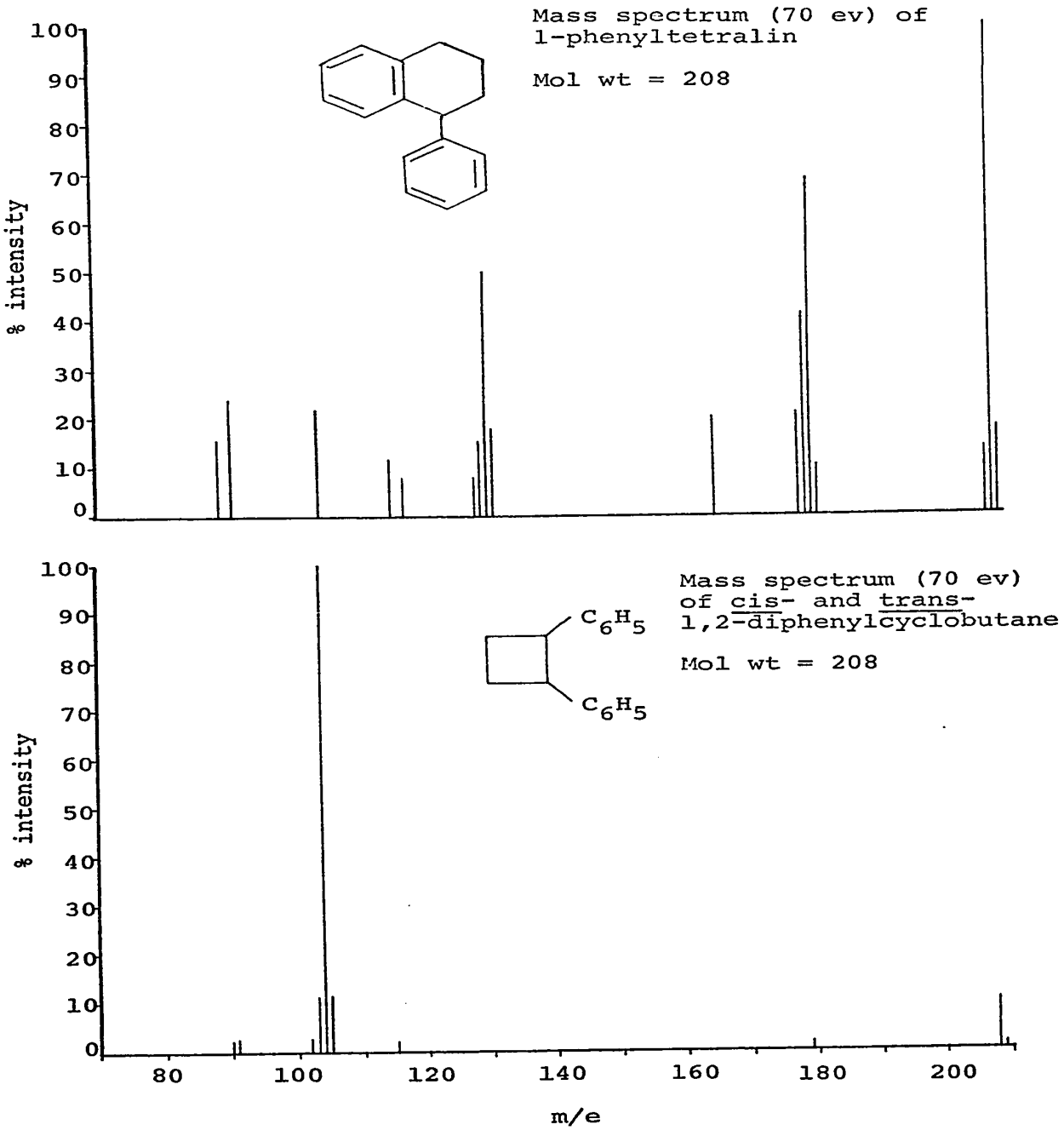
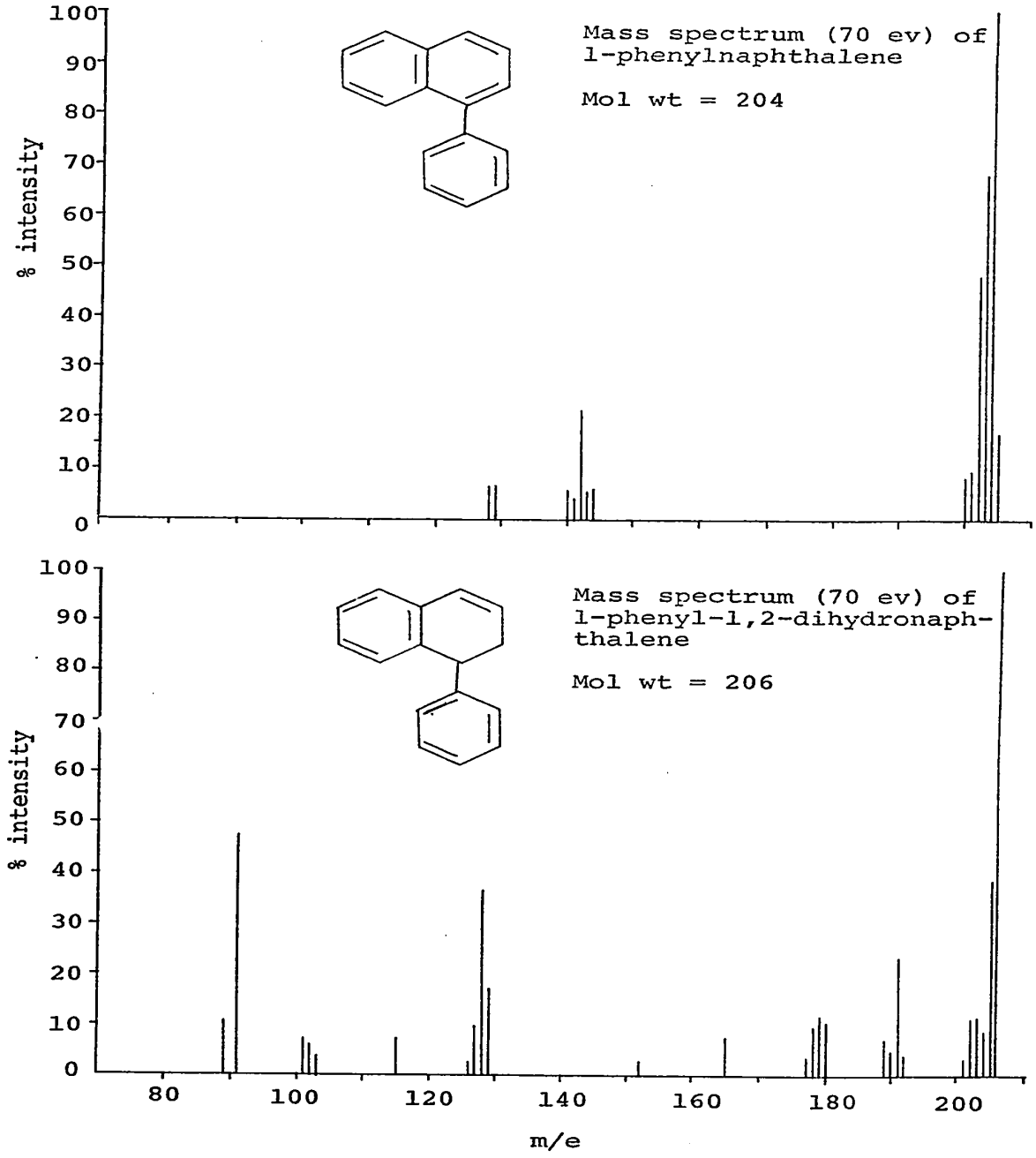


FIGURE VIII (b)



Kinetic measurements:

Glassware

All glassware used in distillation of monomers and in kinetic measurements was carefully neutralized before use. The glassware was cleaned in a mixture of concentrated nitric and sulphuric acids (mixed in a ratio 1 : 3, respectively, by volume), washed thoroughly several times with distilled water, placed in ammonium hydroxide solution for 3-4 hours, washed again several times with distilled water and finally dried in an oven at 110°. The cuvette used for kinetic measurements was washed with benzene and rinsed with acetone after each kinetic run prior to the neutralization procedure.

Purification of commercial styrene:

Styrene (Eastman Kodak, practical grade) was washed three times with cold 10% sodium hydroxide solution (1 : 1 on volume) and then washed with saturated sodium chloride solution until free from alkali. The styrene was then dried with anhydrous magnesium sulfate and distilled through a vigreaux column in a current of nitrogen. A middle cut of the distillate was collected in a clean dry flask, bp 41° (14 mm), $n_D^{26} = 1.5439$; lit. bp 40° (14 mm), $n_D^{20} = 1.5462$ (54).

Monomers

All monomers were distilled through a 12 inch vigreaux column under reduced pressure in a current of nitrogen before each kinetic run.

2,2-Diphenyl-1-picrylhydrazyl (22)

2,2-Diphenyl-1-picrylhydrazyl (Aldrich Chemical Co., Inc.) was recrystallized before use by dissolving 50 mg in a minimum amount of spectro-grade benzene, which had been redistilled from sodium, and adding 4-5 drops of ligroine (distilled over potassium permanganate). The solution was allowed to stand at room temperature in an open flask to induce crystallization. After one day crystals were seen adhering to the sides of the flask and were removed by filtration through a sintered glass funnel (4-8 μ mesh) and dried under vacuum for eight hours. There was obtained 45 mg of a bright violet crystalline DPPH : benzene complex mp 128-129°; lit. mp 128-129° (55). The uncomplexed crystals have a dull brown color before recrystallization. A correction was made for the 1 : 1 complex in measuring the crystals by weight since the composition is given as 83.5% by weight of DPPH (56).

Preparation of samples for kinetic measurements

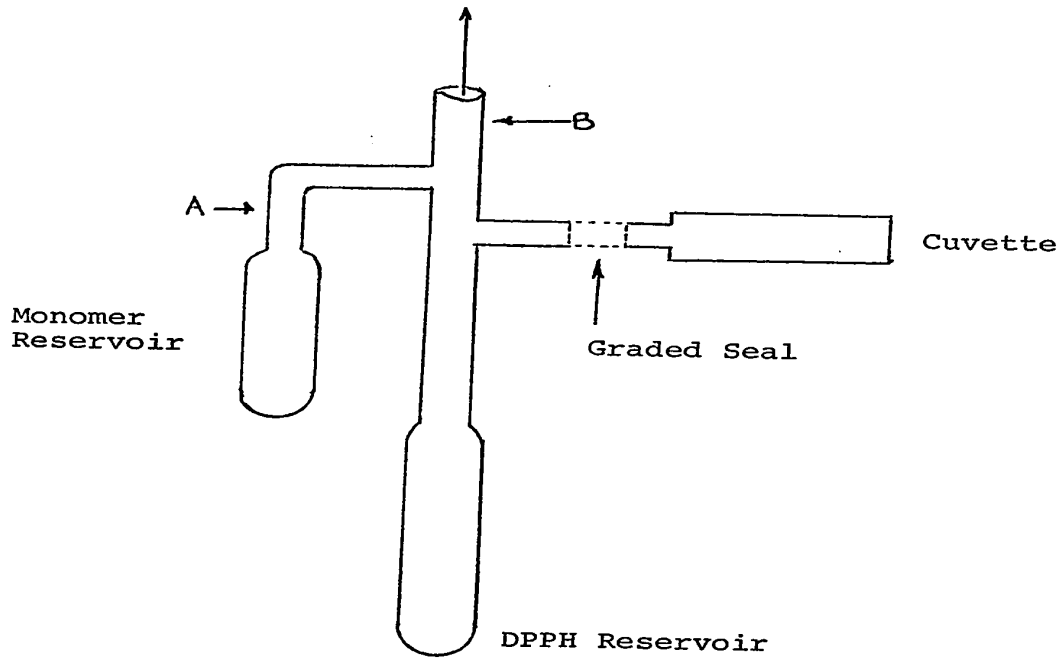
The apparatus used is illustrated in Figure IX. A solution of DPPH in spectro-grade benzene (0.0123 g of DPPH : benzene complex made up to 25 cc with benzene) was measured out using a 1 cc syringe (1/2 cc) and transferred to the DPPH reservoir. The apparatus was sealed onto a high vacuum rack and the benzene removed by careful evaporation at 200 μ pressure. The side arm was broken at point A and the monomer reservoir was filled with 2 cc of monomer. The arm was resealed and the monomer thoroughly degassed by three freeze-thaw cycles. Finally the monomer was distilled under high vacuum into the DPPH reservoir and the solution degassed once more before sealing off the apparatus at points A and B. The DPPH-monomer solution was allowed to warm to room temperature and the solution inverted into the 0.1 mm cuvette (Pyrocell Manufacturing Co.). The cuvette was affixed into a Bausch and Lomb dual cell constant temperature holder through which water from a constant temperature water bath was circulated. The cell temperature was maintained at 75°.

Kinetic measurements: Rates of initiation

The reaction was followed by the decay in absorbance at λ = 525 mμ for the DPPH. A plot of absorbance vs concentration of DPPH for several standard solutions gave a straight line and verified that Beer's Law is obeyed.

FIGURE IX

Apparatus for Kinetic Measurements



Prepared solution [DPPH] mole/litre.10^4	Measured value [DPPH] mole/litre.10^4
0.50	0.52
1.34	1.26
16.5	16.4

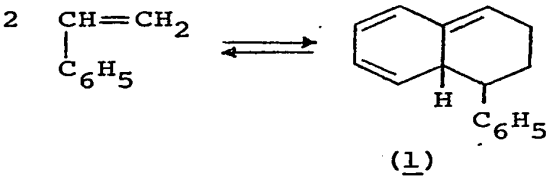
In all the runs the concentration of DPPH at any instant was calculated directly from the absorbance of the DPPH-styrene solution, using Beer's Law.

CHAPTER II

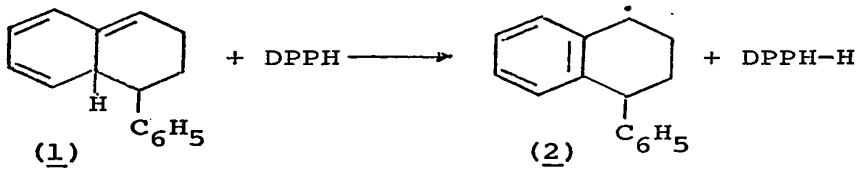
The Chemistry of 2,2-Diphenyl-1-picrylhydrazyl Free Radical

INTRODUCTION

Values for the deuterium isotope effect in the DPPH inhibited thermal polymerization of styrene-o-o'-d_2 have been calculated in Chapter I. A mechanism for the inhibiting action of DPPH was proposed, involving hydrogen abstraction from the Diels-Alder adduct 1, followed by reaction of a second molecule of DPPH with the resulting 4-phenyl-1-tetralyl radical, (2), eqs. [3], [12] and [14].

[3] 

(1)

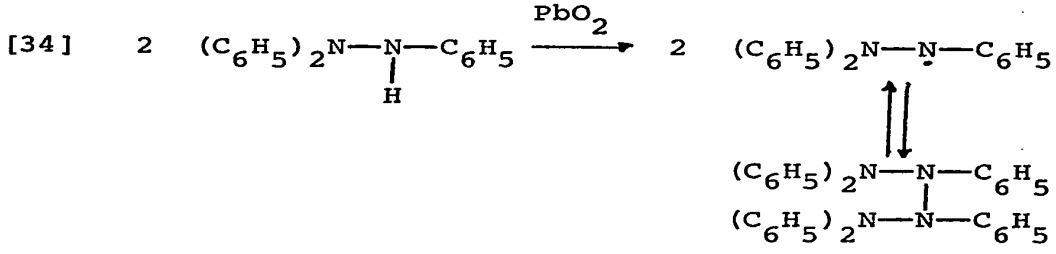
[12] 

(1) (2)

[14] (2) + DPPH ⟶ Products

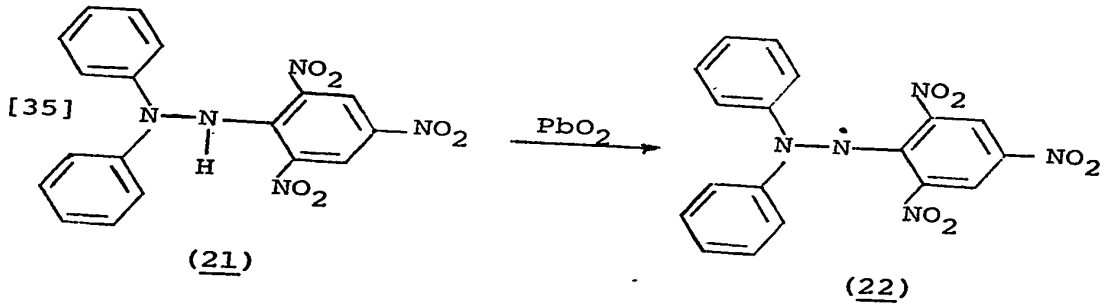
A survey of available literature showed that the products from the reactions of radicals with DPPH have not been investigated, other than by esr or ultra-violet spectroscopy. These techniques only offer information regarding the possible site of radical capture. The identification and characterization of the products from the DPPH inhibition of the thermal polymerization of styrene was made so that a better understanding of the inhibition mechanism and nature of the dimeric intermediate in the initiation step could be obtained.

The discovery and investigation of hydrazyl radicals were made entirely by Stefan Goldschmidt and his collaborators during the period 1920-1929. From his original observation (57), that treatment of triphenylhydrazine with lead dioxide in ether gave a deep blue solution which rapidly changed to green and then to brown-red, Goldschmidt deduced, by analogy with the oxidation of diphenylamine, that the labile blue intermediate was triphenylhydrazyl and the final product hexaphenyltetrazine, eq. [34].

[34] 

On cooling to -60°C he obtained from the blue solution a pale green solid which was stable for several days at -80°C. The solid gave blue solutions in organic solvents which readily oxidized hydroquinone to p-benzoquinone, reacted with nitric oxide to yield a N-nitrosamine, were decolorized by triphenylmethyl radicals, and did not obey Beer's Law.

Goldschmidt also prepared and characterized several other triarylhydrazyls (58). The remarkably stable violet 2,2-diphenyl-1-picrylhydrazyl free radical (22), eq. [35], (59,60),

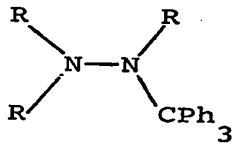


(21) (22)

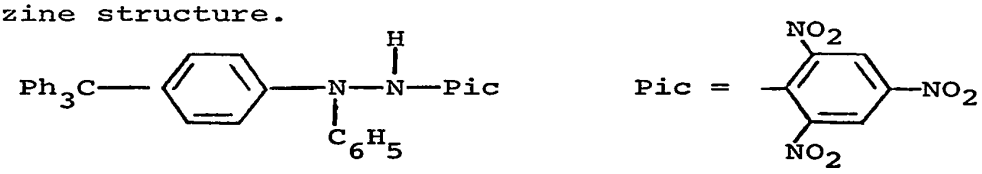
was obtained from the lead oxide oxidation of a chloroform solution of 1,1-diphenyl-2-picrylhydrazine (21). The DPPH free radical is very stable at room temperature and its monomolecular nature can be demonstrated in solution by molecular weight determinations. Even at liquid air temperatures the substance exhibits paramagnetic properties of a molecule containing one unpaired electron (61). Although

it is quite stable in solution, it instantaneously converts hydroquinone to p-benzoquinone and hydrazobenzene to azobenzene, in quantitative yields at room temperature. These reactions are still being used to titrate this radical (59,62). Because of its several applications and excellent stability, interest in hydrazyl chemistry has been focused mainly on this radical. In particular it has been used since 1950 as a radical scavenger, mainly in polymer chemistry and decomposition of azo compounds, and to a lesser extent in general organic work. It is also used as a standard in esr studies for spin concentrations, line position and field scale. Although esr measurements of the many hydrazyls, especially substituted diarylpicrylhydrazyls prepared in recent years, have revealed a detailed picture of the distribution of electron density throughout these radicals, knowledge of their organic chemistry has advanced little since the work of Goldschmidt.

In the absence of air, hydrazyls usually combine with triphenylmethyl radicals in benzene solution to give adducts, usually sufficiently stable to be isolated and are assigned (57,58,63) tetrasubstituted hydrazine structures.

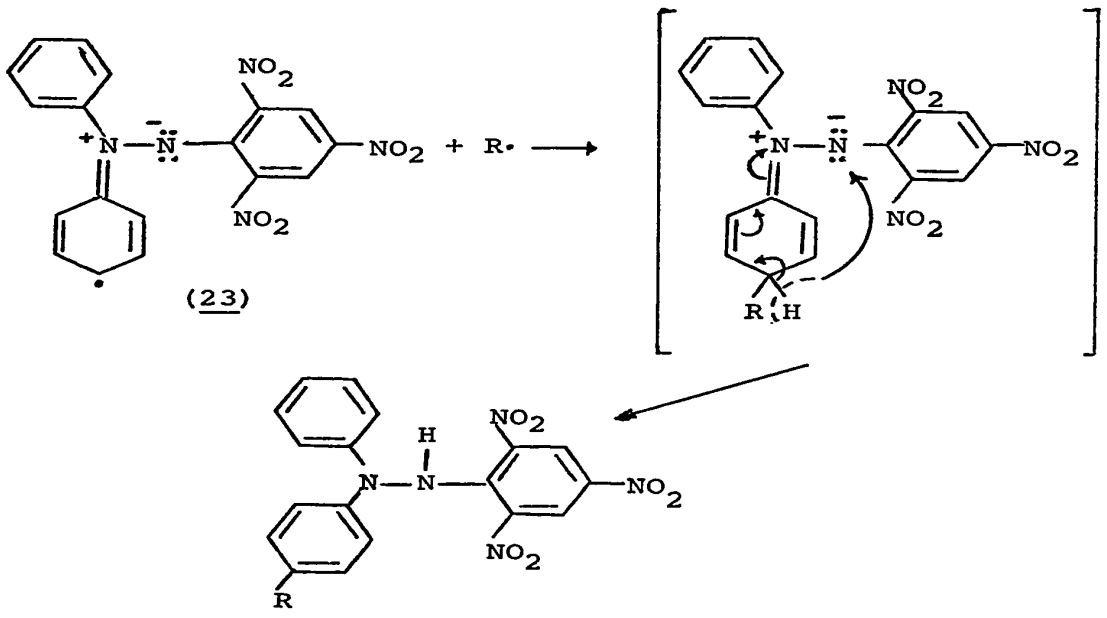


However, DPPH reacts with triphenylmethyl radical (59) to yield an adduct which could be easily oxidized to a violet solution, and was postulated as having a trisubstituted hydrazine structure.



Although Goldschmidt and Renn proposed first addition at the "radical" nitrogen of DPPH followed by a migration to the para position of the phenyl ring, it was later pointed out by Poirer, Kahler and Benington (55) that because of the steric hinderance at the β-nitrogen addition probably took place at the phenyl ring. This was represented by using the resonance structure 23, eq. [36]

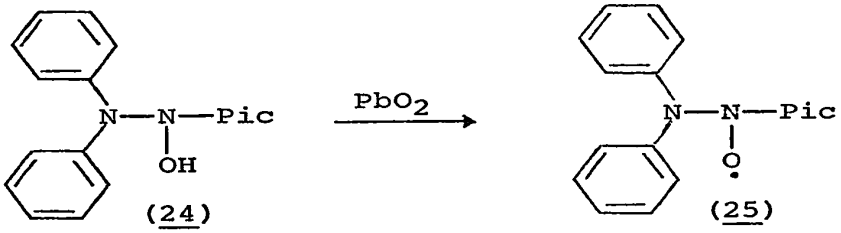
[36]



DPPH does not react with nitric oxide, in contrast to many hydrazyls which combine to form the corresponding N-nitrosamine. These vary in stability and cannot always be isolated (57,58). The apparent failure of DPPH to react is probably due to the reversibility of the reaction. The equilibrium is expected to lie far to the left because of the relatively high stabilities of DPPH and nitric oxide, eq. [37].

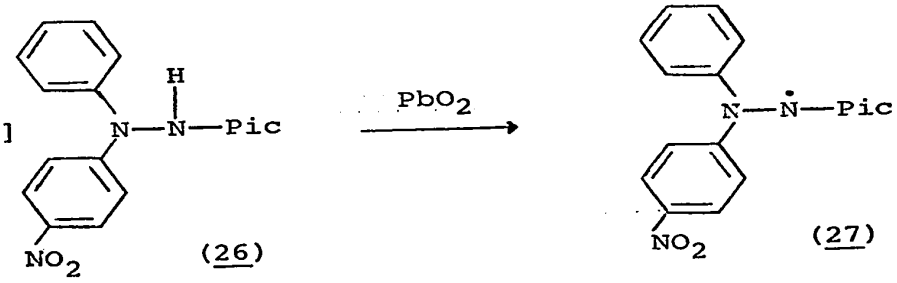
[37] $$DPPH + NO \rightleftharpoons DPPH - NO$$

The reaction of DPPH and nitrogen dioxide in benzene solution at room temperature was thought to give rise to the hydroxylamine, ("hydroxyhydrazine"), 24 (55,59,64),

[38] 

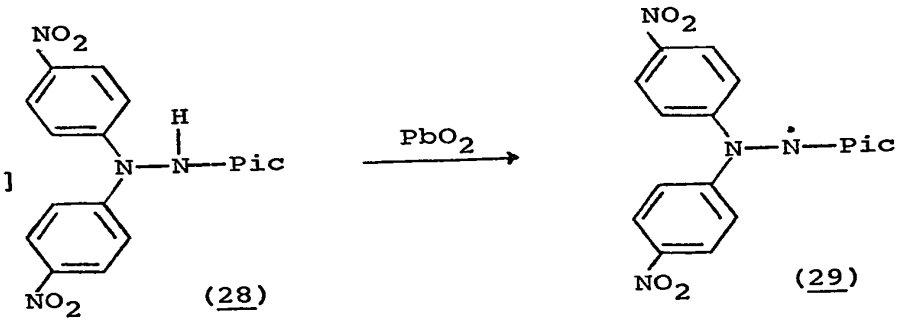
(24) (25)

which on oxidation gave the cherry-red "oxyhydrazyl" free radical (25), eq. [38]. The product of this reaction has since been shown to be 1-phenyl-1-(p-nitrophenyl)-2-picryl-hydrazine, (26), on the basis of analytical and spectroscopic (uv, ir, nmr) evidence (65). The oxidation product would then be the corresponding hydrazyl 27, eq. [39].

[39] 

(26) (27)

Prolonged treatment of a benzene solution of DPPH with nitrogen dioxide gives 1,1-bis-(p-nitrophenyl)-2-picryl-hydrazine, (28), which yields the corresponding hydrazyl 29 on oxidation, eq. [40].

[40] 

(28) (29)

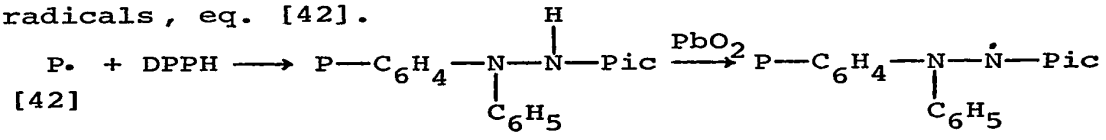
Mrzewinski and Okon have suggested the formation of 28 in the DPPH inhibition of the thermal decomposition of nitrocellulose (66).

Although DPPH does not undergo a chemical reaction with oxygen, there is however, a physical interaction with reversible formation of a molecular complex, eq. [41], (67).

[41] $$DPPH + O_2 \rightleftharpoons [DPPH\text{-}O_2]$$

The formation of such a complex with oxygen accounts for the poorly resolved esr spectra obtained from solutions of DPPH which have not been thoroughly degassed (68).

Henglein (69) has used ultra-violet and visible spectroscopy in the determination of free radicals produced during the ultrasonic degradation of polymethylmethacrylates in benzene solution. He has shown that approximately one half of the DPPH consumed during degradation becomes built into the polymer and cannot be removed by repeated precipitation from solutions. Polymers containing the built-in DPPH were yellow and showed absorption spectra in benzene solution similar to that for DPPH-H. After treatment with lead dioxide, the solutions of the yellow polymers became violet. The ultra-violet spectra showed an absorption similar to solutions of DPPH itself. Henglein suggested that polymer free radicals produced during ultrasonic degradation reacted with DPPH to yield substituted DPPH-H molecules containing an easily oxidizable N-H bond, and that on treatment with lead dioxide gave stable free radicals, eq. [42].



[42]

Similar work by Ovenall (70), using esr absorption spectroscopy, showed that polymeric hydrazines prepared from initiated polymerization of methylmethacrylate in the presence of DPPH-H, eqs. [43.1] and [43.2],

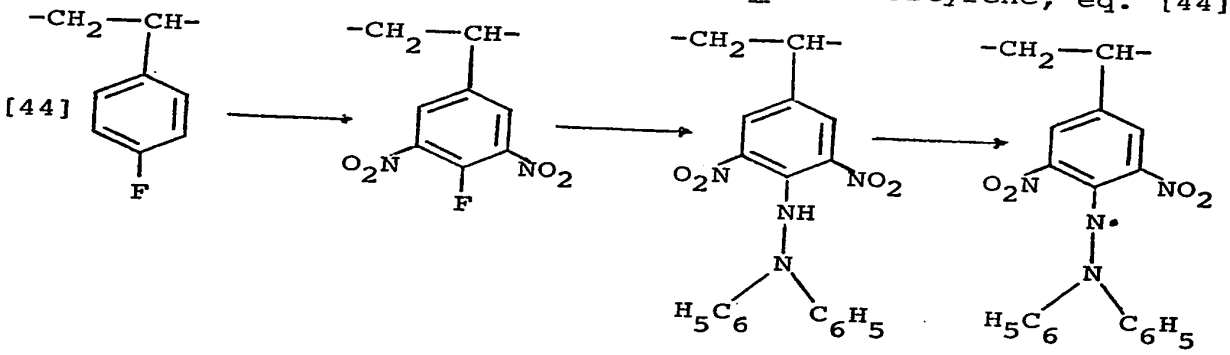
[43.1] $P\cdot + DPPH\text{-}H \longrightarrow PH + DPPH$

[43.2] $P\cdot + DPPH \longrightarrow P\text{—}DPPH$

contained N-H bonds which were oxidized to the corresponding hydrazyls, whereas those from styrene contained no oxidizable N-H bond. He proposed addition of polymethylmethacrylate propagating radicals to the aromatic rings of the DPPH and addition to the β-nitrogen for the polystyrene adduct. However, it appears that both the polymethylmethacrylate and polystyryl radicals should be subject to the steric hinderance of the o-nitro groups in the picryl ring, if addition took place at the β-nitrogen atom.

A related polymeric hydrazyl has been synthesized (71), by the following sequence, from p-fluorostyrene, eq. [44]

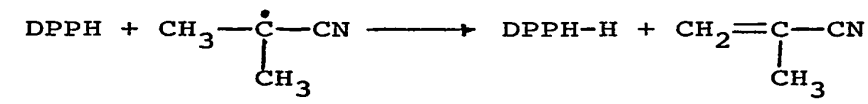
[44]



The polyhydrazine was easily oxidized to a stable polyhydrazyl which like DPPH, oxidizes hydrazobenzene and hydroquinone and inhibits the polymerization of styrene.

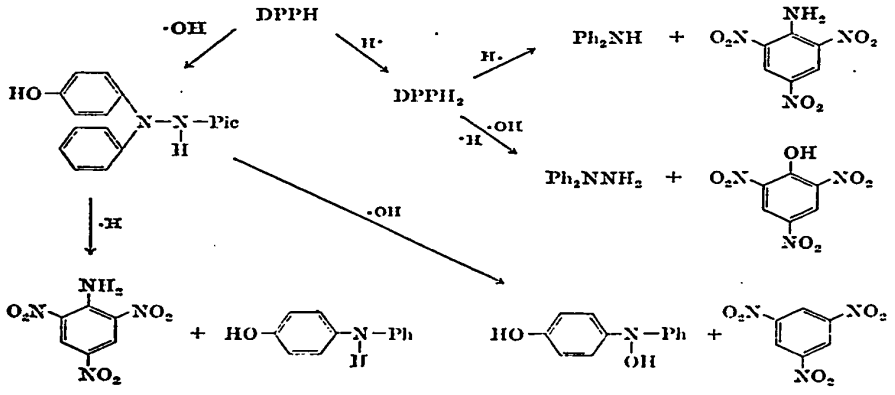
DPPH may also be used to measure the efficiency of radical formation from initiators in the absence of monomers. The most common class of initiators are symmetrical azo compounds of the general formula R-N=N-R (22).

Bawn and Verdin (72) concluded that in the absence of oxygen DPPH, at relatively high concentrations, acted as an effective radical scavenger during the decomposition of azo-bis-isobutyronitrile (AIBN). All the products derived from DPPH contained N-H bonds, shown from their easy oxidation to the characteristic violet color, and were concluded to be probably <u>para</u>-substituted diphenyl-picrylhydrazines. Bevington (73) and Hammond, <u>et al</u>, (74) considered that DPPH-H was formed by disproportionation of DPPH and cyanoisopropyl radicals, eq. [45]

[45] 

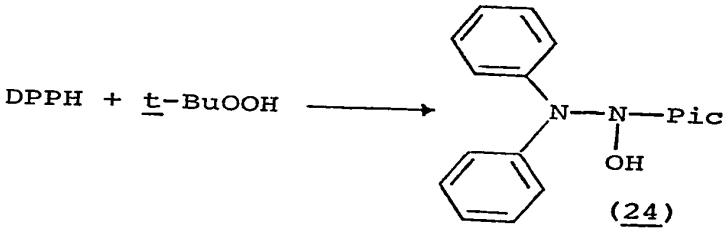
to account for discrepancies in the amounts of DPPH consumed based on the number of cyanoisopropyl radicals formed from AIBN decomposition. Bawn and Verdin recalculated Bevington's results using their own data and found

that complete consumption of DPPH by cyanoisopropyl radicals had taken place. They concluded that no DPPH-H could be formed by this route. In the presence of oxygen, DPPH has been shown to be unsuitable as a scavenger for cyanoisopropyl and other radicals (74). This has been attributed to the formation of cyanoisopropyl-peroxyl radicals which Verdin (75) considers react at the picryl nitrogen of DPPH. This adduct then undergoes further unspecified reactions. This reaction is obviously related to that between DPPH and hydroperoxides which has also been found to be complex and non-stoichiometic. Tarladgis and Schoenmakers (76) have studied the treatment of DPPH with fatty acid hydroperoxides in heptane at 70°C and have suggested the following scheme involving exclusive attack of the decomposition products of the hydroperoxide at the phenyl groups (Scheme 9).



The scheme is based upon ultra-violet, visible and mass spectral measurements of the partially separated mixture of products. After thin layer chromatography, none of the products was obtained pure. The proposed participation of hydrogen atoms was visualized "as being abstracted from any of the known labile sites of the long chain unsaturated fatty hydroperoxide". More recently Dulog and Baum (77) have shown that the reaction between DPPH and t-butylhydroperoxide gives the hydroxylamine 24, eq. [46].

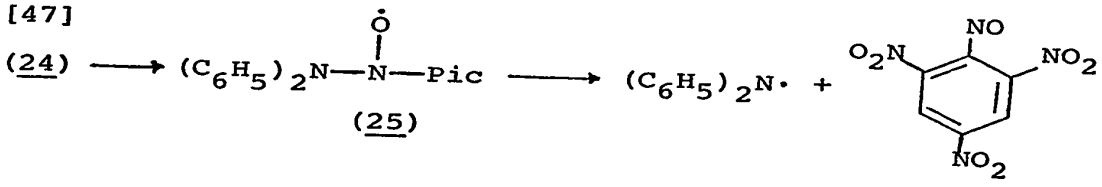
[46]



(24)

The structure of 24 was based upon an elemental analysis and isolation of only diphenylamine from the reductive cleavage products. Oxidation and cleavage of 24 to give the diphenylamino radical and a nitroso compound could account for some of the observed products of Tarladgis and Schoenmakers, eq. [47].

[47]



Maruyama and Otsuki (78,79) have isolated trinitronitrosobenzene and diphenylamine from the reaction of DPPH-H with t-butylhydroperoxide, and observed diphenylnitroxide in the esr spectra of the reaction products. Diphenylamine and hydroperoxides readily give diphenylnitroxide (80), eq. [48].

[48]

$$(C_6H_5)_2NH \text{ or } (C_6H_5)_2N\cdot + \underline{t}\text{-BuOOH} \longrightarrow (C_6H_5)_2NO + \underline{t}\text{-BuOH}$$

In all the work to date no identification of the seemingly complex products obtained by trapping radicals with DPPH has been made, except in the case of hydroperoxide decomposition. It appeared that use of modern techniques, e.g., thin layer and gas chromatography and nmr spectral analysis could serve as tools in identifying the products of radical capture by DPPH. The use of azo compounds as a source of free radicals was chosen because of their ready decomposition at low temperatures, easy accessibility and because this area of hydrazyl chemistry still remained unsolved. The choice of compounds was directed by the need to determine the products of DPPH inhibition of the thermal polymerization of styrene.

1,1'-Diphenylazoethane (32) and 4,4'-diphenylazo-1-tetralin (35) were synthesized and the products of decom-

position products in the presence of DPPH were identified. These were used in the identification of the products of DPPH inhibited thermal polymerization of styrene. A mechanism for radical capture by DPPH is proposed and further evidence for the Diels-Alder mechanism in the thermal initiation of styrene polymerization is presented.

RESULTS

Product analysis of reaction mixtures containing products derived from DPPH and free radicals is extremely difficult and has usually been avoided. In order to minimize any difficulties in the isolation procedure, the product analysis of the decomposition of 1,1-diphenylazoethane (32) in the presence of DPPH was carried out first. The 1-phenylethyl radical is a much simpler system than the 4-phenyl-1-tetralyl radical derived from thermal decomposition of 35. These two radicals were chosen as they are proposed to be the initiating radical pair formed in the thermal initiation sequence of styrene polymerization, eq. [4]. The results obtained from the decomposition of 32 were entirely unexpected in the light of the previously proposed mechanisms for radical capture by DPPH, but careful analysis furnished methods for preliminary analysis of DPPH-radical adducts as well as isolation and characterization of these products. These methods were then applied to the isolation of the products from the thermal decomposition of 35 in the presence of DPPH and to the isolation of the products from the DPPH-inhibited thermal polymerization of styrene.

Preparation of Azo Compounds:

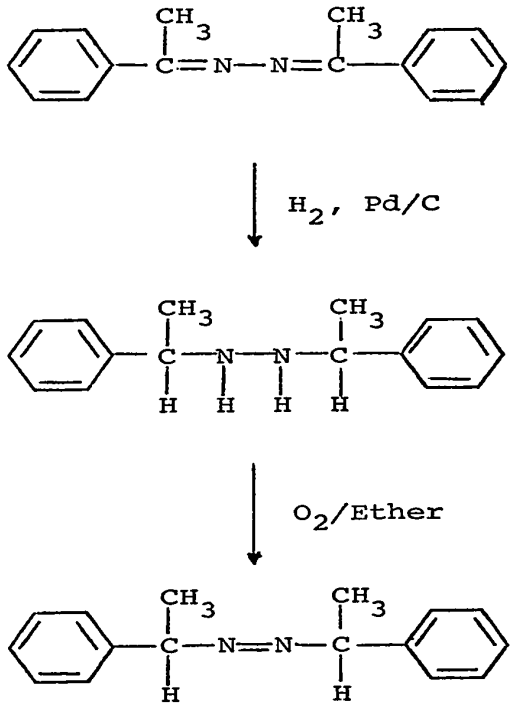
1,1-Diphenylazoethane (32)

The preparation of 32 is outlined in Scheme 10. Acetophenone azine was hydrogenated over palladium on charcoal to yield the saturated hydrazine 31. 31 was not isolated but oxidized immediately in ether solution, using oxygen gas at 5 psi pressure, to yield 32 as white needles mp 71-72°. The physical properties matched those reported in the literature (81). The infrared and nmr spectra were consistent with the structure of the compound. The ultra-violet spectrum (EtOH) showed λ_{max} = 335 mμ in agreement with the value reported in the literature (81).

4,4'-Diphenylazo-1-tetralin (35)

35 was prepared by a route analagous to that for 32. The synthetic sequence is outlined in Scheme 11. 4-Phenyl-1-tetralone ketazine (33), was prepared in an 84% yield by treating 16 with hydrazine hydrate. 33 was hydrogenated over palladium on charcoal in benzene solution and the resulting hydrazine 34 immediately oxidized in the same way as described for 31. The azo compound 35 precipitated out of solution as a fine white powder, mp 121-124°, with decomposition. The infrared spectrum showed an absence of an N-H stretch. The nmr spectrum was in accord with the

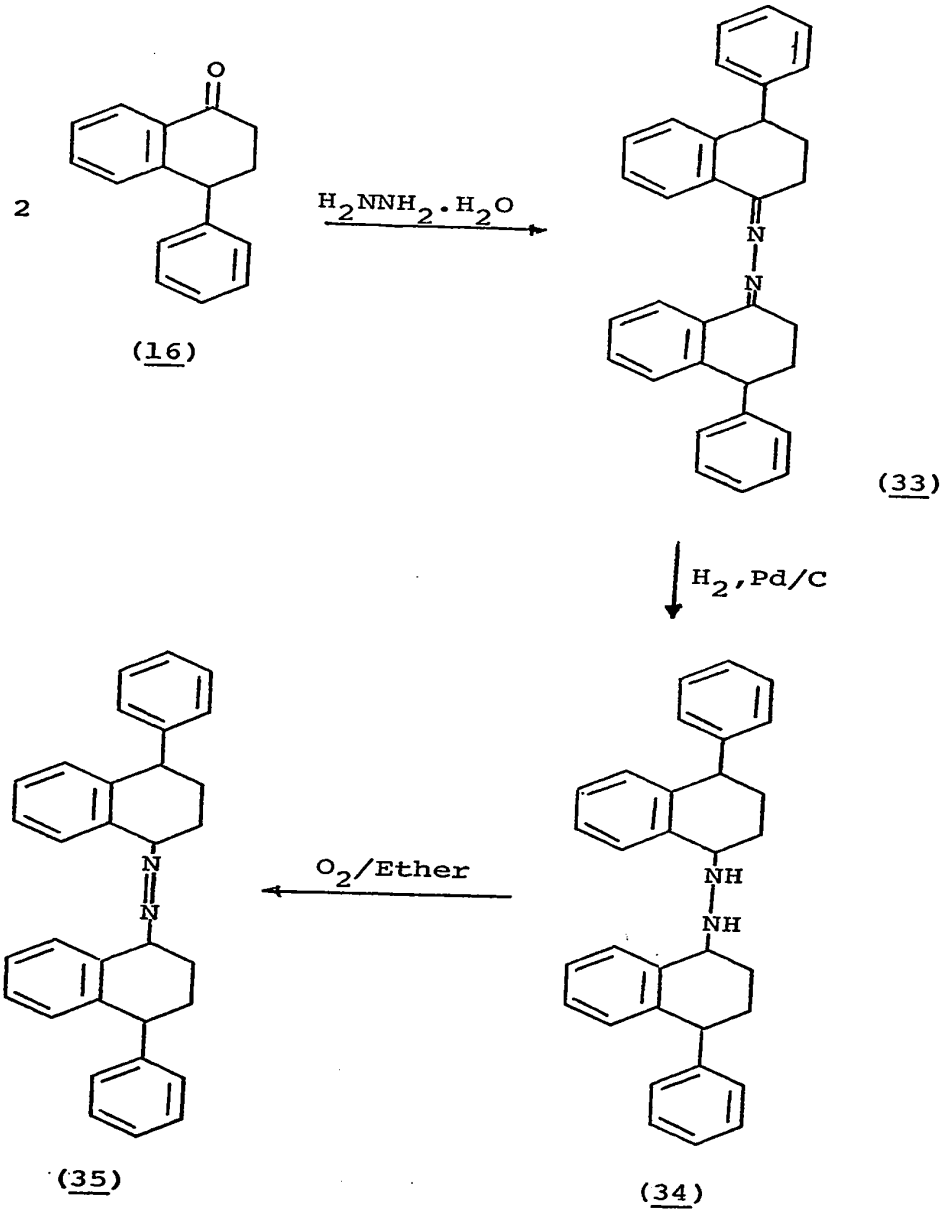
Scheme 10



(31)

(32)

Scheme 11



structure of the compound. The ultra-violet spectrum (ether) showed λ_{max} = 362 mμ (ε 110), consistent with the n→π* transition for aliphatic azo compounds (82). The hydrazone, formed by the addition of dilute acid to an ether solution of the azo compound, showed λ_{max} = 286 mμ (ε 11000). From the ultra-violet spectrum of the azo compound it could be ascertained that the compound contained <0.1% hydrazone.

Thermal Decomposition of 32 and 35 in Benzene Solution in the Presence of DPPH

Azo compounds are decomposed thermolytically with an ease that varies with the expected stability of the free radical of the groups attached to nitrogen (83). It is generally agreed for symmetrical azo compounds, R-N=N-R, that a concerted two bond scission occurs to yield molecular nitrogen and two radicals, without any intermediate diazoalkyl radical formation (84). The fate of the two radicals generated is determined largely by the "cage" effect; the two radicals have a greatly enhanced probability of reacting with each other, either by coupling or disproportionation, as a consequence of being generated in a solvent "cage". Alternatively the radicals may diffuse from the solvent "cage" and react in the normal manner by coupling or disproportionation

with themselves, or they may react with the solvent or an added radical scavenger. These reactions are outlined in Scheme 12.

Scheme 12

(i) $R-N=N-R \longrightarrow [R\cdot\ N_2\ \cdot R]_{cage}$

(ii) $[R\cdot\ N_2\ \cdot R]_{cage} \longrightarrow R-R$ + disproportionation products + N_2

(iii) $[R\cdot\ N_2\ \cdot R]_{cage} \longrightarrow 2R\cdot + N_2$

(iv) $2R\cdot \longrightarrow R-R$ + disproportionation products

(v) $R\cdot + SH(solvent) \longrightarrow RH + S\cdot$

(vi) $R\cdot$ + Scavenger $\longrightarrow$ Products

The reaction (vi) in Scheme 12 was of interest to this work as it represents the capture of the generated radicals by DPPH.

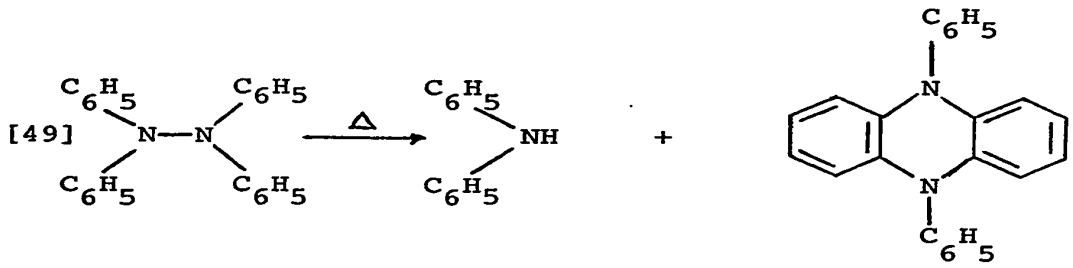
Benzene solutions of 32 and 35, containing a weighed amount of DPPH were thoroughly degassed by three freeze-thaw cycles under 15 μ pressure. The ampoules were sealed under vacuum and heated in a thermostated oven at 84° for 72 hours. This time period allowed complete decomposition of the azo compound. Although the half-life of decomposition of 35 was not measured it was assumed to be of the same order as that for 32, (81). Both materials will yield a secondary benzylic

radical on thermal decomposition and so should be of approximately equal thermal stability. In the case of 32 a 4 : 1 molar ratio of DPPH : 32 was used. For 35 a 2 : 1 molar ratio of 35 : DPPH was used. This, however, still represents an excess of DPPH as all the radicals formed from the decomposition of 35 will not escape the initial solvent cage.

Analysis of the Products of Decomposition of 32

The first decomposition was carried out using 21 mg 32 and 134 mg DPPH dissolved in 2 ml benzene. It was of interest to measure the scavenger efficiency of DPPH for the decomposition of 32 and to estimate the cage effect by this method. With this in mind a sample of the decomposition product was injected into the gas chromatograph in order to measure the proportions of coupling and disproportionation products formed between the two 1-phenylethyl radicals in the presence of DPPH. The analysis using a 5 ft column of 15% SF 96 on 60/80 Chromasorb P at 220° showed that there were four fractions with retention times of 6.0 min; 14.4 min; 25.4 min and 43.5 min. Since, under these conditions, styrene and ethylbenzene had retention times less than 1 minute these fractions must have included radical - DPPH products. The retention time of the first fraction corresponded with the retention

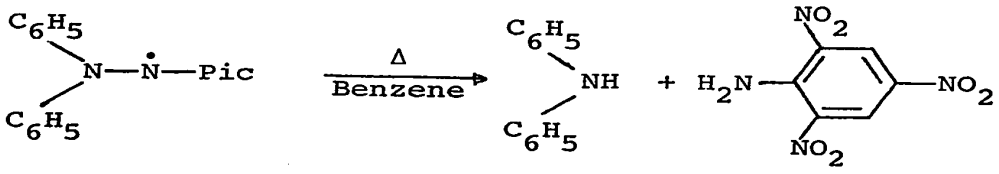
times of meso- and dl-2,3-diphenylbutane. These are the coupling products produced from the recombination of a pair of 1-phenylethyl radicals. The other three fractions must, therefore, be derived from the reaction between DPPH and a free 1-phenylethyl radical from the decomposition of 32. Since substituted hydrazines are known to undergo thermal decomposition in solution (85), it appeared that some of these fractions may correspond to decomposition products from DPPH or DPPH-radical adducts. The thermal decomposition of DPPH has not been reported but Wieland found that tetraphenylhydrazine underwent N-N bond fission to give diphenylamine and 9,10-diphenyl-9,10-dihydrophenazine (85), eq. [49].



The formation of the latter material has, however, been disputed (86,87) and the structure of the product has still not been elucidated. Injection of diphenylamine into the gas chromatograph increased the size of the peak observed

at 6.0 min, showing that under the conditions used, diphenylamine and the 2,3-diphenylbutanes have the same retention time. By using a 5 ft column of 20% PDEAS on 60/80 Chromasorb W, diphenylamine was completely separated from the two hydrocarbons, proving the presence of all three materials in the original product mixture.

The second fraction from the SF 96 column was collected by repeated injections of the product mixture and analyzed by nmr spectroscopy. The nmr spectrum showed a sharp singlet overlapping a broad singlet both centered at τ1.02. The spectrum was exactly identical to the spectrum of 2,4,6-trinitroaniline, and the isolated fraction gave the correct melting point for this material. It appeared that DPPH was undergoing a similar cleavage to that proposed for tetraphenyl hydrazine and the corresponding amines were being produced, eq. [50].

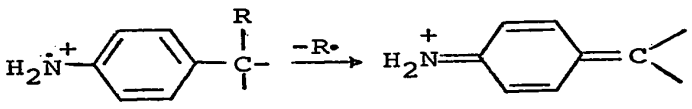
[50] 

To verify this assumption a solution of DPPH in benzene was injected into the gas chromatograph using the same conditions as for the analysis of the azo decomposition products. There were observed three well separated peaks with retention times that corresponded to the retention times of the first three fractions for the glc analysis of the azo decomposition products. The same result was obtained when DPPH-H was used, except the proportions of the fraction was changed slightly. The presence of the first two fractions, corresponding to diphenylamine and 2,4,6-trinitroaniline was expected. However, the presence of the third fraction in the azo decomposition and both DPPH-H and DPPH decompositions was entirely unexpected. This meant that only fraction four in the azo decomposition could have arisen from a possible DPPH-radical adduct.

Isolation of the remaining two fractions from the azo decomposition by preparative glc analysis was not practical because of their longer retention times, and the fractions were analyzed by coupling the gas chromatograph to an AEI mass spectrometer using the technique described in Chapter I.

The mass spectrum of the third fraction indicated a parent peak at m/e 214 and was exactly identical to the mass spectrum of 4-nitrodiphenylamine (88). The mass

spectrum of the fourth fraction indicated a parent peak at m/e 287 and peaks at m/e 272 (P - 15), 180 (P - 107) and 152 (P - 135). The most intense peak was m/e 272 indicating a loss of a methyl group. The odd molecular weight indicated that the compound contained an odd number of nitrogens. The peak at m/e 180 was attributed to a loss of CH_3 followed by two nitro groups [15+(2x46)]. Other small peaks corresponding to (P - 17) and (P - 48) indicated the presence of an amine group on an aromatic ring with two ortho-nitro groups. These were deduced by analogy with the cracking pattern of a sample of 2,4,6-trinitroaniline. The loss of CH_3 indicated a benzylic carbon, probably para-substituted to the amine, carrying a methyl substituent. Compounds of this structure undergo ready loss of benzylic substituents to give a quinoidal species (89).

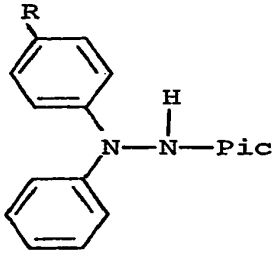


This prompted the assignment of 2,6-dinitro-4-(1-phenylethyl)aniline (42) to the fraction four. The mass spectrum

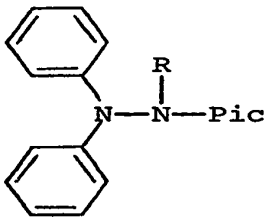
of authentic 42 matched exactly that of fraction four and confirmed that it was indeed the same compound.

Although 42 may have arisen from cleavage of a substituted DPPH molecule, the possibility of it being a rearrangement product formed after injection into the gas chromatograph could not be ruled out. The formation of 4-nitrodiphenylamine from the decomposition of DPPH in the gas chromatograph must have arisen from a displacement of a nitro group in the DPPH molecule. When an internal standard, ditertiarybutylbenzene, was added to the DPPH, only 25% of the hydrazyl was accounted for in the form of decomposition products, indicating a complex decomposition route.

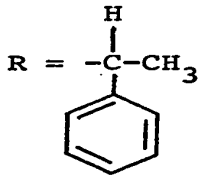
Radical capture by DPPH has previously been proposed to take place at the para-position of the phenyl ring or at the radical nitrogen. In the present case this would afford the hydrazines 61 or 62.



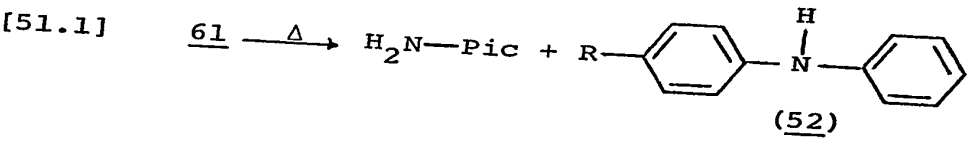
(61)



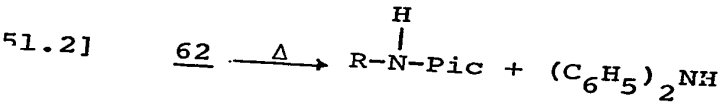
(62)



If these compounds were present in the product mixture from the decomposition of 32 they would be expected to undergo cleavage after injection into the gas chromatograph and yield either a substituted diphenylamine 52 or an N-substituted picramide 51, eq. [51].

[51.1] 

(52)

[51.2] 

(51)

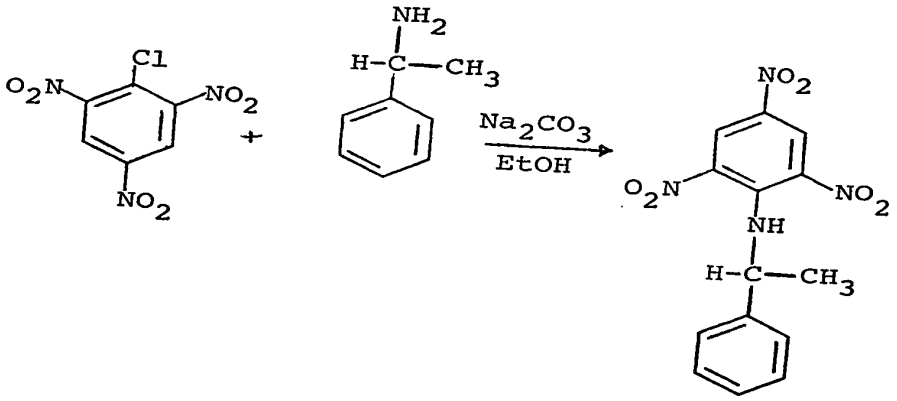
Preparation of 51 and 52

The synthetic routes to these materials are shown in Scheme 13. 51 was prepared in 89% yield by treating picrylchloride with 1-phenylethylamine in the presence of base. The nmr spectrum and elemental analysis were consistent with the structure of 51.

52 was prepared by heating a mixture of diphenylamine, 1-phenylethylchloride and zinc chloride until evolution of HCl ceased. Chromatography of the product mixture gave 52 in a low yield. The nmr spectrum was consistent with the structure of the material and the infrared spectrum

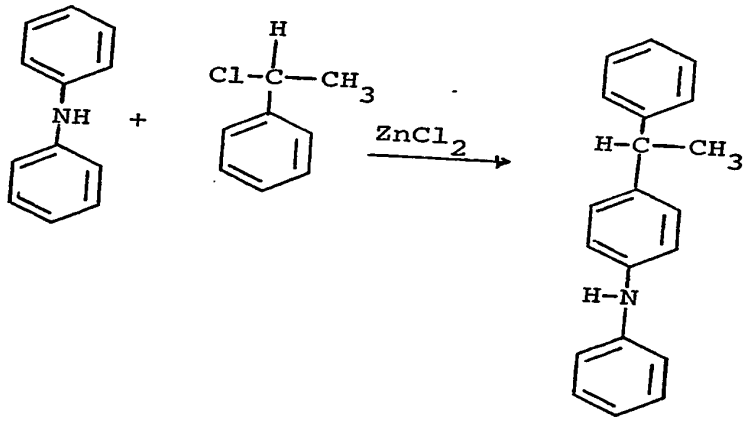
Scheme 13

(i)



(51)

(ii)



(52)

showed the presence of an -N-H stretching frequency. The material was not characterized any further. The procedure employed was based on the method of Meldola (90) for the preparation of 4-benzyl-N-phenylaniline, from benzylchloride, diphenylamine and zinc chloride.

Samples of N-(1-phenylethyl)-2,4,6-trinitroaniline (51) and N-phenyl-4-(1-phenylethyl)aniline (52) were injected into the gas chromatograph using a 10 in x 1/4 in column of 5% SF 96 on 60/80 Chrom P at 180° with a helium flow rate of 50 ml/min. Samples of the azo decomposition products from 32 were injected under the same conditions and no peaks could be observed corresponding to the retention times observed for the above two materials.

Although the glc analysis was effective as a preliminary analysis, and indicated that radical capture was probably taking place in the picryl ring, the isolation of the hydrazine products was necessary to confirm this assumption. The use of preparative thin-layer chromatography appeared attractive after analytical tlc of the products from the decomposition of 32 showed at least four well resolved spots. Also, it had been reported (64) that separation of 1-(p-nitrophenyl)-1-phenyl-2-picrylhydrazine (26), DPPH and DPPH-H could be obtained on a cellulose column. A combination of these techniques was used on a

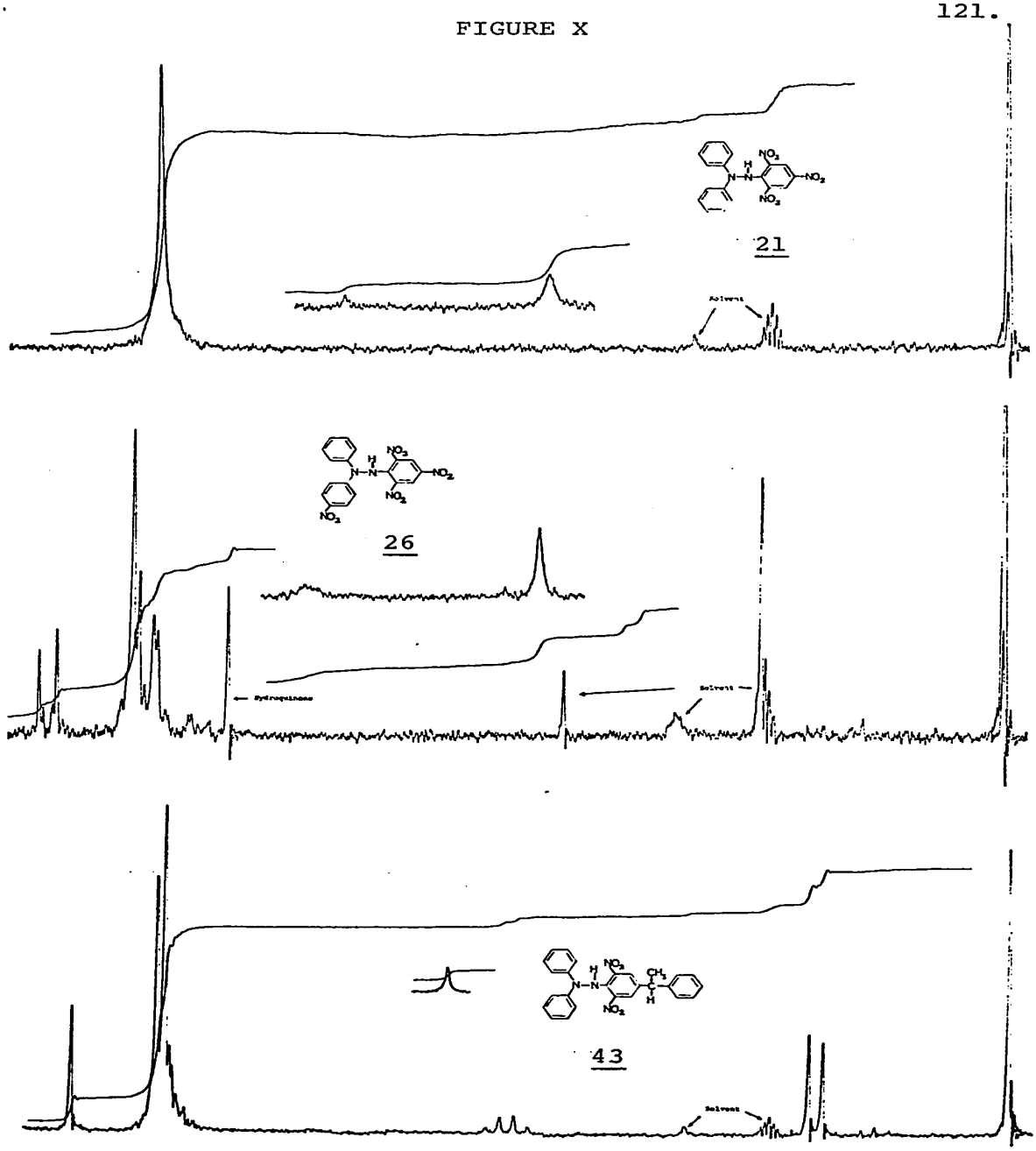
second decomposition of 32 in the presence of DPPH.

The second run was a duplicate of the first but all the materials were scaled up by a factor of ten to facilitate identification of isolated materials. The heating time for the decomposition was kept the same.

The benzene solvent was removed from the reaction mixture and approximately one half of the residue, 750-850 mg, was chromatographed on a 5 cm x 38 cm column packed with microcystalline cellulose. Elution with heptane gave 400 mg of a mixture of DPPH, DPPH-H and a third compound identified as 1,1-diphenyl-2-(2,6-dinitro-4-(1-phenylethyl)-phenyl)-hydrazine (43). The mixture was separated by preparative tlc on 2 mm silica gel plates to yield 178 mg 43 and 146 mg DPPH and DPPH-H. The compounds were identified by their nmr spectra, mass spectra and infrared spectra which were all identical to those of authentic materials. 43 was also identified by its melting point which was the same as that of an authentic sample. The nmr spectra are shown in Figure X.

The eluent was changed to heptane-benzene (1:1 by volume) and further elution gave a mixture consisting mainly of 1-phenyl-1-(4-nitrophenyl)-2-picrylhydrazine (26), identified from its nmr spectrum which matched that of the authentic material and that reported in the literature

FIGURE X



Nuclear magnetic resonance spectra of 21, 26 and 43 in acetone-d_6. All offsets are 300 Hz.

(65,91), and the corresponding hydrazyl. Once again the compounds were separated by chromatography on preparative tlc plates. When 85 mg of the crude mixture was chromatographed there was obtained 48 mg 26 and 33 mg of 27. A compound with a retention time slightly less than that observed for 26 was identified as 1-(p-nitrophenyl)-1-phenyl-2-(2,6-dinitro-4-(1-phenylethyl)-phenyl-hydrazine from its nmr spectrum. This compound could not be separated completely from the other products of the azo decomposition and was not characterized further.

The remainder of the material on the column was very dark and further elution with benzene-heptane gave only traces of a black solid. Further identification was not attempted.

The isolation of the products of the decomposition of 32 confirmed that radical attack was occurring at the para-position of the picryl ring. It also indicated that under the conditions of the glc analysis the hydrazines were being cleaved at the N-N bond to give the respective diphenylamine and picramide derivatives. This confirms that preliminary glc analysis is a useful tool in determining the products of DPPH - radical reactions, providing that the products have reasonable retention times under

the glc conditions that are being used.

Analysis of the Products of the Decomposition of 35

The decomposition of 35 was carried out using 76 mg (1.7 mmole) 35 in 3 ml benzene containing 134 mg (3.4 mmole) DPPH.

Preliminary glc analysis of the products from the decomposition of 35, showed only the presence of diphenylamine, 4-nitrodiphenylamine, picramide and the coupling and disproportionation products, 1-phenyltetralin and 1-phenyl-1,2-dihydronaphthalene formed from the 4-phenyl-1-tetralyl radical. No trace of the substituted picramide corresponding to 42 was observed under the glc conditions, which were the same as for the analysis of 32. Using shorter columns and higher temperature and flow rate conditions still only yielded the three components named above. Since the substituted picramide expected in this case has a high molecular weight (mol wt = 389) it is not surprising that it was not readily observed.

The benzene solvent was removed to yield 194 mg of black residue. After dissolving in a small amount of acetone, 186 mg of the residue was chromatographed on 2 mm preparative tlc plates to yield five fractions consisting of the following:

Fraction 1, 40 mg of colorless hydrocarbon products, which were identified as containing approximately 20 mg of 1-phenyltetralin and 1-phenyl-1,2-dihydronaphthalene from their retention times on glc analysis. The presence of a third hydrocarbon product, 20 mg, which was slightly separated from the above after preparative tlc analysis was assumed to be the coupling product two 4-phenyl-1-tetralyl radicals, although no positive identification was made. All of the hydrocarbons above are the normal products expected from the decomposition of 35 in the absence of a scavenger.

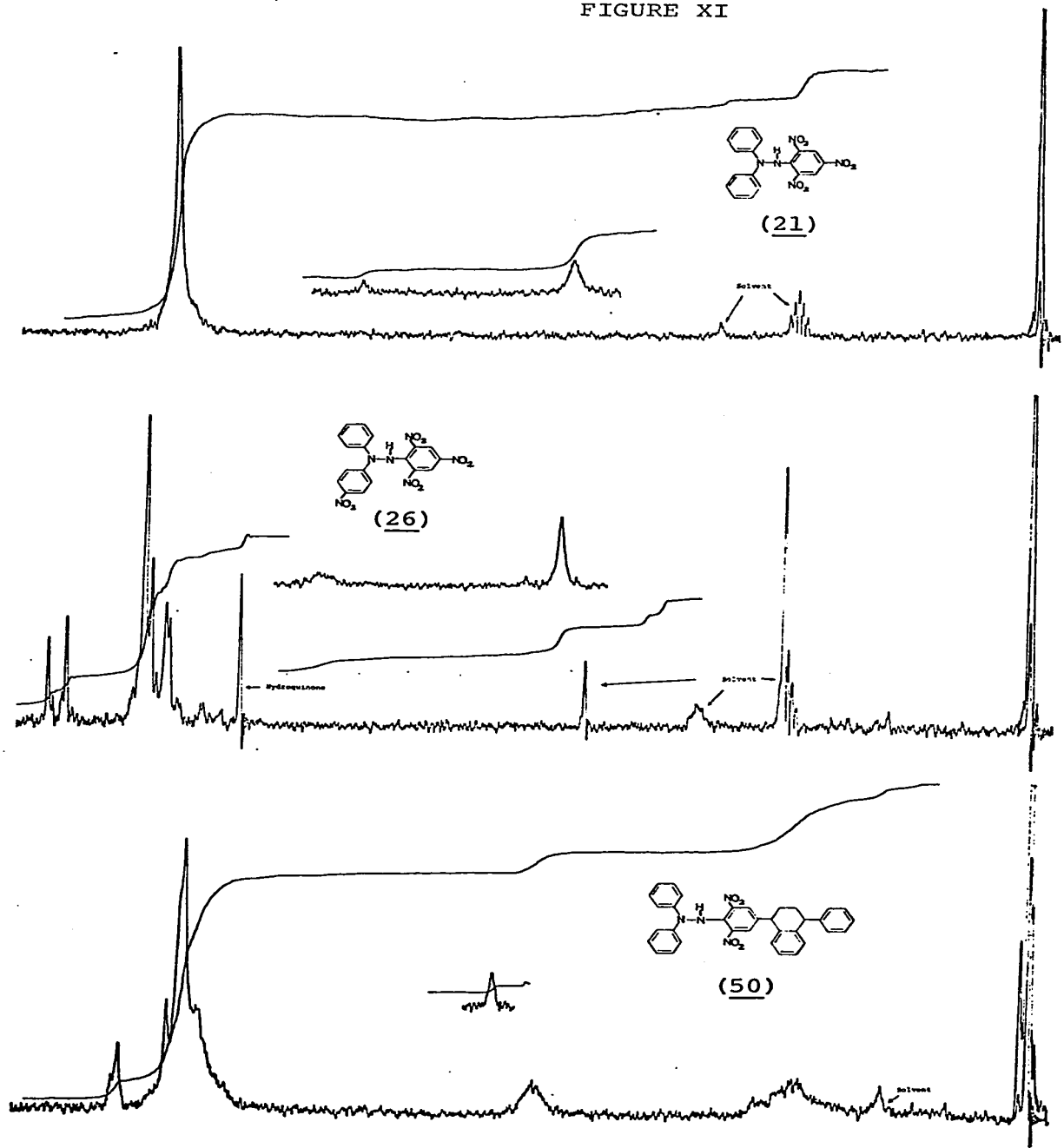
Fraction 2, 38 mg of 1,1-diphenyl-2-(2,6-dinitro-4-(4-phenyl-1-tetralyl)-phenyl)-hydrazine (50).

Fraction 3, 47 mg of DPPH-H.

Fraction 4, 23 mg of a red-brown solid which was tentatively assigned as 1-(4-nitrophenyl)-1-phenyl-2-(2,6-dinitro-4-(4-phenyl-1-tetralyl)-phenyl)-hydrazine (57b) from its nmr spectrum. The spectrum was almost identical to that of 50 except that the aromatic region now contained an A_2B_2 system that was identical to that observed for the p-nitrophenyl system in the spectrum of 26.

Fraction 5, 40 mg of 1-phenyl-1-(4-nitrophenyl)-2-picrylhydrazine (26).

FIGURE XI



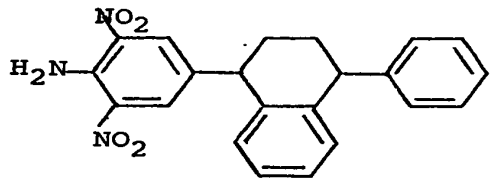
Nuclear magnetic resonance spectra of 21 and 26 in acetone-d_6, and 50 in CCl_4. All offsets are 300 Hz.

A residue of 8 mg remained on the plates concentrated at the original baseline. Discounting the residue, a total of 188 mg of material was recovered indicating a complete product analysis had been obtained.

The identification of fractions 2, 3 and 5 was made by comparison of their nmr and infrared spectra with those of authentic samples. The nmr spectra are shown in Figure XI.

The nmr spectra of 43 and 50, shown in Figures X and XI, show that the hydrogens adjacent to the nitro groups of the substituted picryl ring have been shifted upfield to approximately τ2.0 and τ2.4 from their position of τ1.0 in the spectrum of DPPH-H and (26). This reflects the decrease in the electron withdrawing inductive effect produced by the replacement of one of the nitro groups of the picryl ring. The substitution must be at the para-carbon of the picryl ring as substitution at an ortho carbon would still leave one hydrogen flanked by nitro groups and it would still appear at low field. Only a singlet is observed for those hydrogens in the spectrum of 43 while the spectrum of 50 shows two unequal singlets almost overlapping. This could be caused by the presence of diastereoisomers since the 4-phenyl-1-tetralyl system contains two asymmetric benzylic carbons.

The electron impact mass spectra of 43 and 50 did not show any parent peaks, but only peaks corresponding to fragments of the molecule. The fragmentation appeared complex as these peaks could not be assigned to any simple mode of fission such as N-N bond cleavage. Chemical ionization mass spectroscopy, using CH_5^+ as a proton source, gave mass spectra with the corresponding M+1 peaks required for the protonated hydrazines from 43 and 50. For 43 the parent peak was at m/e 455 corresponding to $C_{26}H_{23}N_4O_4^+$. Peaks were observed at P - 46 corresponding to a loss of NO_2 and P - 63, loss of NO_2 followed by loss of NH_3 and the most intense peak was at m/e 288 corresponding to protonated form of 42 formed from N-N bond cleavage of the hydrazine 43. The spectrum of 50 showed the parent peak at m/e 557 corresponding to $C_{34}H_{29}N_4O_4^+$. Once again peaks were observed at P - 46 and P - 63 as for 43, and the most intense peak was at m/e 390 corresponding to the protonated amine from 67.



(67)

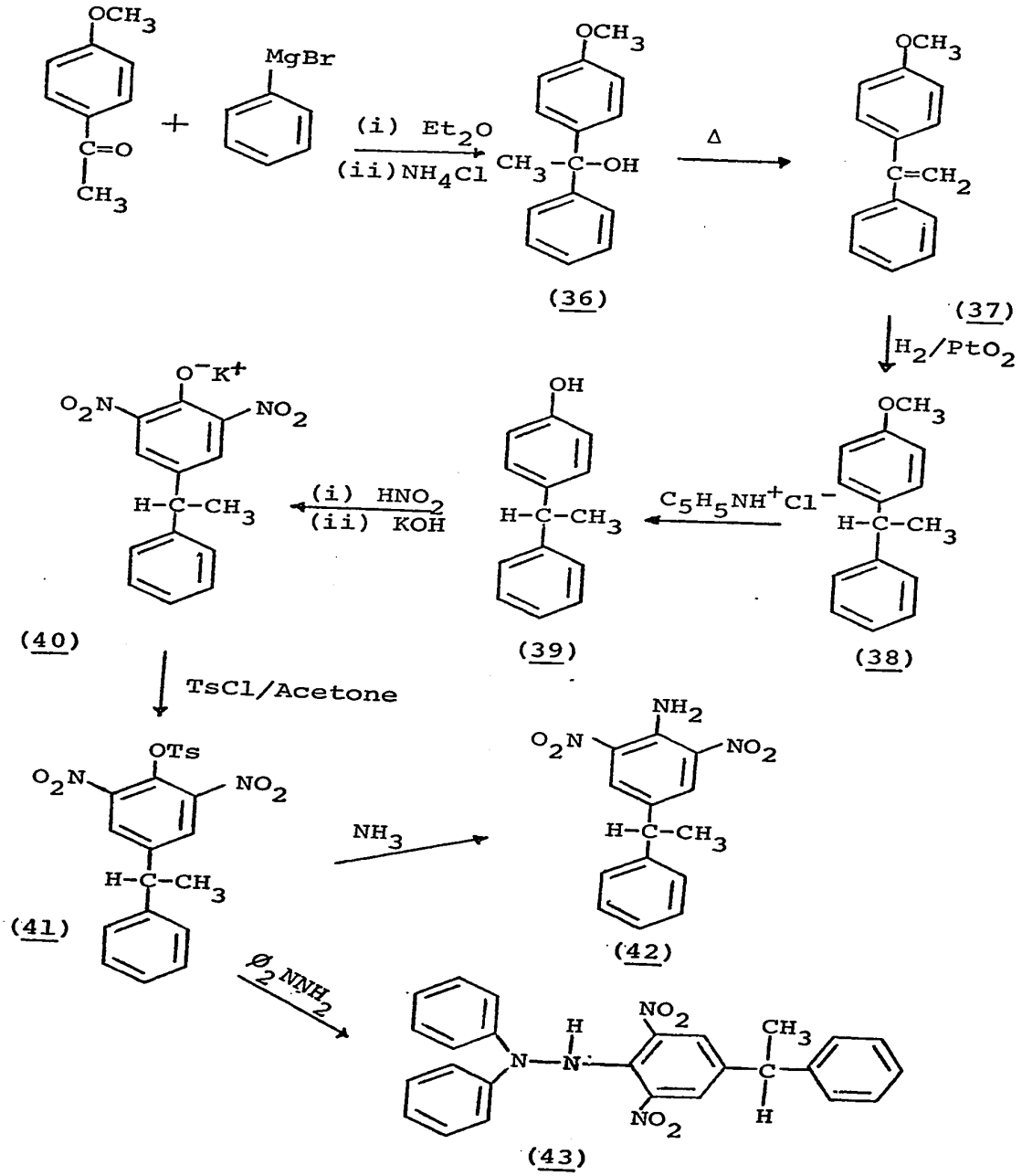
The chemical ionization spectrum of fraction four from the decomposition of 35 showed a peak at m/e 556 which was assigned as P - 46 and would then correspond to the protonated hydrazine $C_{34}H_{28}N_5O_6^+$ in agreement with the proposed structure. The most intense peak appeared at m/e 390 as for 50 indicating the presence of the picramide 67 structure in the molecule. The presence of a P - 64 peak was also seen, although this may be in error because of the difficulty in counting at these high values in the mass spectrum. It could have therefore been P - 63 in accordance with the observed cracking pattern of the other hydrazines 43 and 50.

Preparation of Authentic DPPH-Radical Adducts

1,1-Diphenyl-2-(2,6-dinitro-4-(1-phenylethyl)-phenyl)-hydrazine (43)

The synthesis of 43 is outlined in Scheme 14. (37) was prepared from the Grignard reaction between phenylmagnesium bromide and 4-methoxyacetophenone, followed by dehydration of the crude alcohol product (36)upon heating to 210°. (37) was obtained in an overall yield of 74% from the ketone and crystallized as giant white prisms from

Scheme 14


OCH3
MgBr
(i) Et2O
(ii) NH4Cl
CH3-C-OH
Δ
C=CH2
(36)
(37)
H2/PtO2
O-K+
O2N
NO2
H-C-CH3
(i) HNO2
(ii) KOH
OH
C5H5NH+Cl-
(40)
(39)
(38)
TsCl/Acetone
OTs
NH3
NH2
(41)
(42)
Ø2NNH2
H
N
NO2
CH3
(43)

pentane, mp 73-74° in agreement with the literature value (92). The infrared and nmr spectra matched the structure of the material. Hydrogenation of 37 over platinum gave 38 in a 99% yield. The physical properties agreed with the literature values (93). The ether linkage of 38 was cleaved according to the method of Curphey, Hoffman and McDonald (94) using pyridine hydrochloride, to give the phenol 39 in a 91% yield. The compound boiled at 133-134° (0.5 mm) and on cooling in ice water set to a crystalline white solid mp 54-56°. The literature values for the boiling and melting points of 39 covered a wide range, being reported as bp 185-190° (10 mm) (95); bp 133-134° (5 mm) (96); mp 64° (97). The compound reported as mp 64° (97) was prepared by the reaction of phenol with 2-phenylethanol in the presence of zinc chloride. The authors proposed that since the product was not the expected 4-(2-phenylethyl)-phenol it must have rearranged to yield 39. They offer no further explanation nor give an analysis of the product. The other two authors use similar methods for preparing these materials, i.e., by a Friedal-Crafts type of reaction. In one case (95) the reaction between 1 mole of acetophenone and 2 moles of phenol in the presence of concentrated hydrochloric acid gave a mixture of phenols, which were separated by

fractional distillation to yield 39 as one of the components. The analysis given is not quite correct for the compound. In the second case a reaction between anisole and styrene in a 5 : 1 molar ratio in the presence of boron trifluoride etherate yields the ether 38 which was cleaved to the phenol 39 with HBr-acetic acid mixture. The bp 133-134° (5 mm) may have been a misprint since in this work it was found to be the same boiling range but at 0.5 mm. The original literature, however, was not available. Since the synthesis of 39 presented here is unambiguous, it must be assumed that the material has been prepared in a pure form for the first time. 39 analyzed correctly for the molecular formula, and the nmr and infrared spectra were consistent with the proposed structure.

39 was converted to 40 according to the method of Gasparic (98). After dissolving 39 in a buffer solution of acetic acid and potassium acetate it was treated with sulfuric acid and sodium nitrite at 60° to yield the nitrophenol which was extracted as its potassium salt 40.

40 was treated with p-toluenesulfonyl chloride in boiling acetone to give the tosylate 41 which melted sharply at 114-115°. 41 was treated with 1,1-diphenylhydrazine in ethanol solution to yield a dark-red gel which could not be crystallized from a chloroform-ethanol

solvent mixture normally used for these types of hydrazines. Recrystallization from 98% ethanol yielded 43 as brick-red prisms, mp 133° (charred at 131°). The infrared spectrum ($CHCl_3$) showed an absorption at 3310 cm^{-1} indicating an N-H stretching mode. The nmr spectrum (acetone-d_6) shown in Figure X, showed peaks at τ0.30 (s) due to the hydrogen on N_2, τ1.99 (s) due to the two aromatic protons adjacent to the nitro groups, τ2.76 (m) due to the aromatic protons in the phenyl rings on N_1 and the phenyl ring at the para-position of the substituted picryl ring, τ5.75 (q, J = 7 cps) due to the benzylic proton, and τ8.50 (d, J = 7 cps) due to the methyl group, in the ratio 1.0 : 2.0 : 17.0 : 1.0 : 3.0, required 1.0 : 2.0 : 17.0 : 1.0 : 3.0.

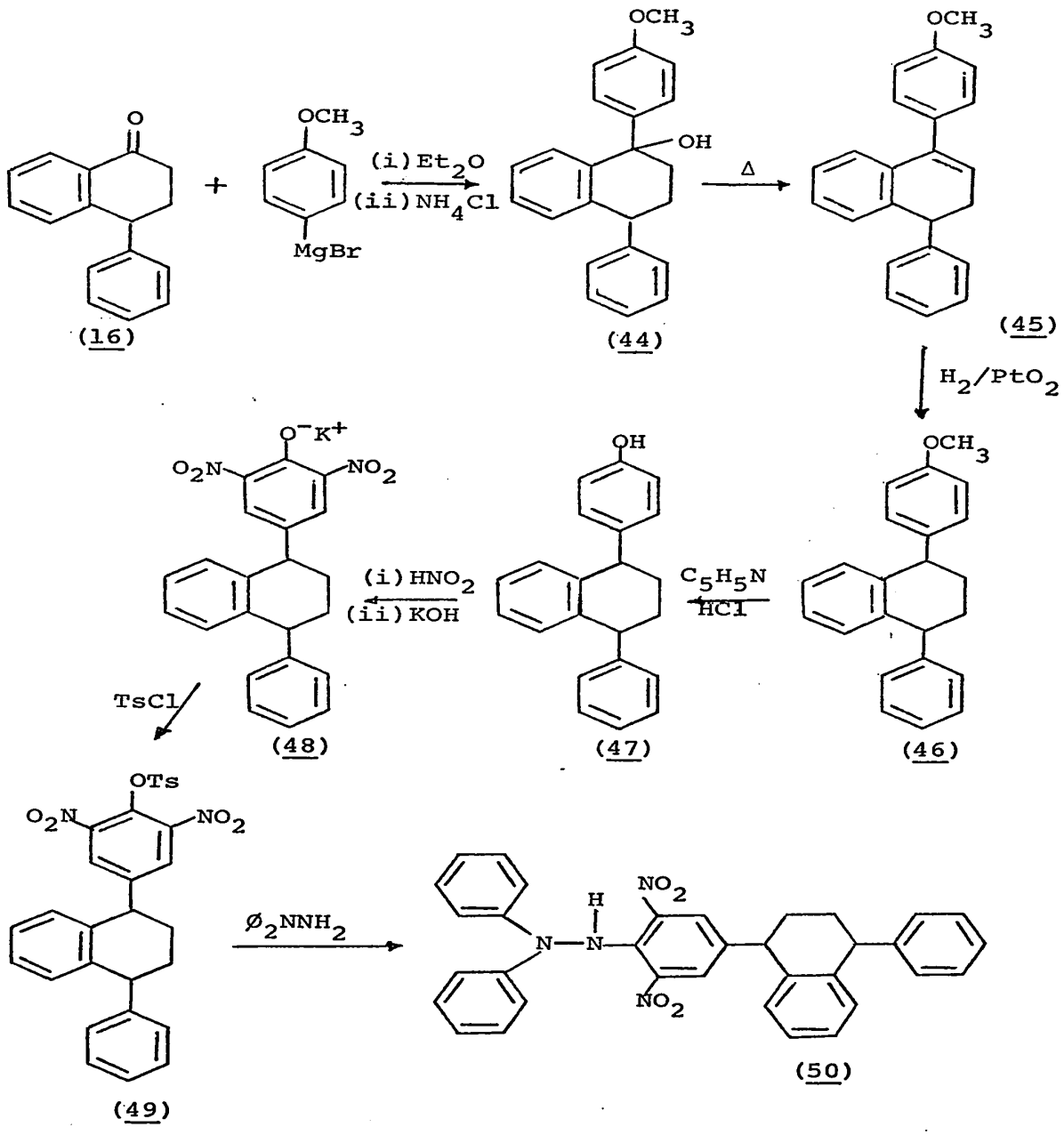
2,6-Dinitro-4-(1-phenylethyl)-aniline (42)

Treatment of 41 in diglyme solution with anhydrous ammonia gas gave 42 in an 81% yield. The bright orange prisms melted at 115° and analyzed correctly for the molecular formula. The nmr spectrum ($CDCl_3$) showed a peak at τ1.58 (broad singlet, overlapping a sharp singlet). The broad singlet was due to the protons on nitrogen, and disappeared on D_2O exchange, and the sharp singlet was due to the aromatic protons adjacent to the nitro groups on the aromatic ring. Other peaks were observed at τ2.70 (m)

due to the aromatic protons of the monosubstituted phenyl ring, τ5.89 (q, $\underline{J}$ = 7.5 cps) due to the benzylic proton and τ8.33 (d, $\underline{J}$ = 7.5 cps) due to the methyl group. The ratio of peaks was 4.0 : 5.0 : 1.0 : 3.0, required 4.0 : 5.0 : 1.0 : 3.0. After D_2O exchange the ratio changed to 2.2 : 5.0 : 1.0 : 3.0. The infrared spectrum showed absorptions at 3485 cm^{-1} and 3370 cm^{-1} (N-H stretch) and 1647 cm^{-1} (N-H band). The mass spectrum (70 ev) had peaks at m/e 287 (P), 272 (P - 15), 180 (P - 107) and 152 (P - 135).

1,1-Diphenyl-2-(2,6-dinitro-4-(4-phenyl-1-tetralyl)-phenyl)-hydrazine (50)

The synthesis 50 was carried out by a route exactly analagous to that for 43 and is outlined in Scheme 15. Unfortunately, all of the compounds were obtained either as very viscous liquids or glass-like materials, which could not be crystallized. In every case the nmr spectra showed the compounds to be pure materials as deduced from the integrations of the relative peak areas. Attempts to distil these materials was not practical because of the very high temperatures needed even at low pressures. Also the compounds appeared to become more viscous if distillation was attempted. Elemental analyses were carried out


O
OCH3
MgBr
(i) Et2O
(ii) NH4Cl
OH
Δ
(16)
(44)
(45)
H2/PtO2
O2N
NO2
O−K+
(i) HNO2
(ii) KOH
C5H5N
HCl
TsCl
OTs
(48)
(47)
(46)
Ø2NNH2
H
N
NO2
(49)
(50)

on the ether 45 as it was the first compound isolated in the synthetic route and on 50, the final product. The analyses were not within the required ±0.3% error from the calculated values for some of the elements. Since the compounds could not be recrystallized, the difficulty in removing all traces of solvents or impurities, could have been a source of error for the analyses. All the compounds have two asymmetric centers except 45 which only has one, and the possibility of forming a mixture of diastereoisomers could be the cause of the failure of the compounds to crystallize. However, the combination of nmr and infrared spectra, the proven synthetic pathway and the exact duplication of the spectra of 50 with the spectra of the materials obtained from the decomposition of 35 and the DPPH inhibited thermal polymerization of styrene, were taken as convincing evidence that the structure of 50 was correct.

The Grignard reaction between 16 and a three-fold excess of p-methoxyphenylmagnesium bromide, afforded, after dehydration of the intermediate alcohol 44, a glassy solid in an 85% yield, which could not be crystallized. Attempts to distil the compound only increased the viscosity of the product. Use of less than a three-fold excess of Grignard with 16 gave some unreacted ketone after the

dehydration step. A similar excess of the same Grignard reagent has been used in the addition to 2-phenyl-1-tetralone (99). The nmr spectrum of 45 was consistent with the structure and integration of the relative peak areas showed the compound to be pure. Several analyses of a thin film only agreed within 1.3% with the calculated values for the carbon analysis although the hydrogen analyzed correctly. 45 was used without further purification and was hydrogenated over platinum oxide to afford 46 in a 99% yield. Once again a glassy solid was obtained but the nmr spectrum showed the compound to be pure, as indicated by the integration of the relative peak areas. No further characterization was made and 46 was cleaved directly to the phenol 47 using pyridine hydrochloride. The phenol was pure, as deduced from the nmr spectrum, and was obtained as a viscous straw-colored liquid. Attempts to make a benzoate derivative gave only a sticky product which would not crystallize. The phenol was nitrated in the same manner as for the nitration of 39, and 48 was obtained in an 18% yield as a dark-red sticky solid which was directly converted to 49 with p-toluenesulfonyl chloride in acetone. The fawn colored crude tosylate was treated immediately with 1,1-diphenylhydrazine in ethanol to yield a dark-red oil. Preparative tlc on 2mm

silica gel plates gave 73 mg of an orange-red sticky solid. The nmr spectrum (CCl_4) showed peaks at τ0.50 (s) due to the proton on nitrogen, τ2.35 (overlapping singlets) due to the aromatic protons adjacent to the nitro groups, τ2.90 (m) due to the remaining aromatic protons, τ5.85 (broad multiplet) due to the two benzylic protons and τ8.10 (broad multiplet) due to the four methylene ring protons, in the ratio 1.0 : 2.0 : 19.3 : 2.0 : 4.0, required 1.0 : 2.0 : 19.0 : 2.0 : 4.0. The infrared spectrum (CCl_4) showed a peak at 3310 cm^{-1} (-N-H stretch). The nmr and infrared spectra were exactly identical with the spectra of 50 isolated from the decomposition of 35, and 50 isolated from the DPPH inhibited thermal polymerization of styrene. The elemental analysis of 50 prepared above was not in agreement with the calculated figures although it may have retained some solvent of recrystallization in the molecule. A similar discrepancy was observed in the analysis of 43 after it was recrystallized from a chloroform-ethanol mixture. A subsequent recrystallization from ethanol gave a crystalline solid which analyzed correctly. Attempts to recrystallize 50 from ethanol failed because of lack of compound.

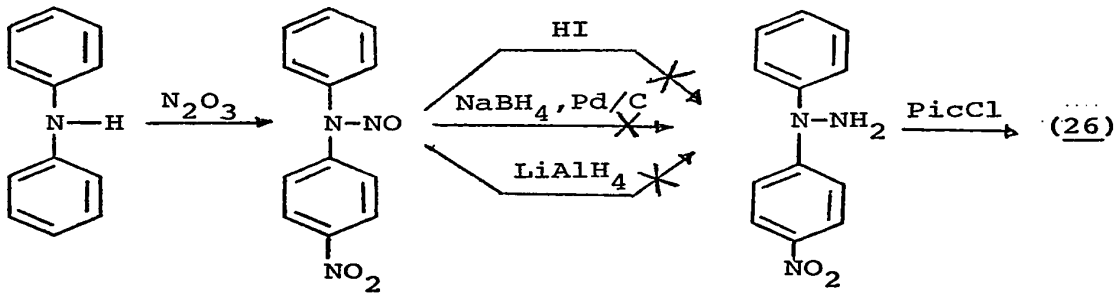
1-Phenyl-1-(4-nitrophenyl)-2-picrylhydrazine (26)

The preparation of 26 was carried out as described by Poirier (55). After passing nitrogen dioxide through

a benzene solution of DPPH, 26 was obtained as a brick-red powder, mp 146-148°. A large amount of 1,1-bis-(4-nitrophenyl)-2-picrylhydrazine (28) was also obtained. The compound was identified by its nmr spectrum which showed an A_2B_2 system centered at τ2.10 (J = 9 cps) and broad singlets at τ-1.16 and τ0.97 matching the reported nmr spectrum (65,91). Poirier obtains none of (28) and reports a high yield of 26 although later workers (65) report the isolation of the same type of product mixture as obtained here.

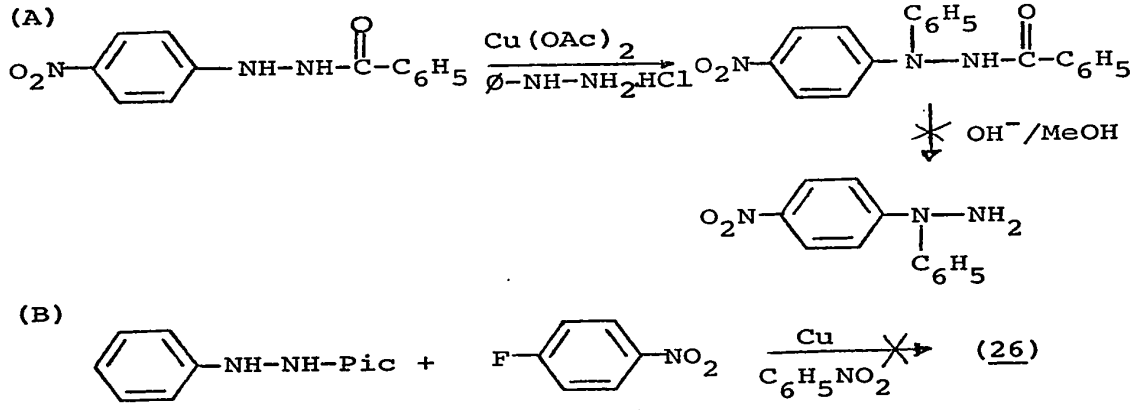
Several attempts were made to prepare 26 by another route involving the preparation of p-nitrophenylhydrazine as shown in Scheme 16.

Scheme 16



Attempts to selectively reduce the nitroso group of N-nitroso-4-nitrodiphenylamine under a variety of conditions only gave 4-nitrodiphenylamine indicating a reductive cleavage of the N-N bond had taken place. Other methods of preparation (Scheme 17)

Scheme 17



via (A) the Tafler-Gatterman reaction (100) and (B) the Ullman reaction (101) were also unsuccessful. Similar results have been reported (102) for the attempted preparation of 1,1-bis-(4-nitrophenyl)-2-picrylhydrazine using all of these methods.

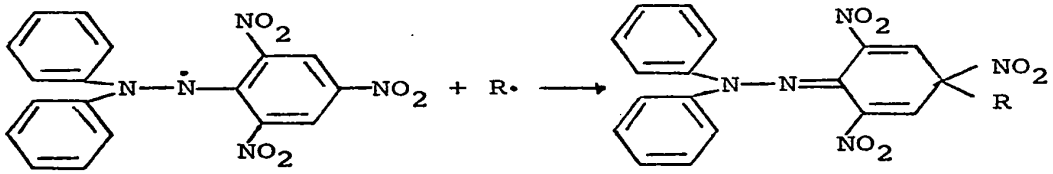
Isolation of 50 from DPPH Inhibited Styrene Polymerization

The experimental procedure and conditions for the isolation of 50 were reported in Chapter I of this thesis. The material was identified from its nmr, infrared and chemical ionization mass spectra, which matched those of the product from the decomposition of 35 in the presence of DPPH. The nmr and infrared spectra were also identical to those of the authentic material.

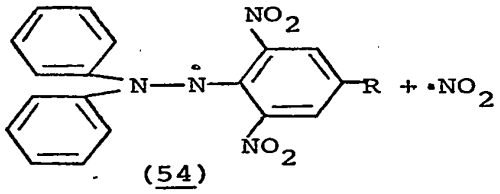
DISCUSSION

Radical Capture by DPPH

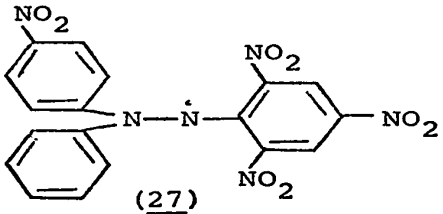
The isolation of 43 and 50 from the decompositions of the respective azo compounds 32 and 35 in the presence of DPPH, now provides a basis for a mechanism for radical capture by DPPH. This is represented by eqs. [52] to [55].

[52] 

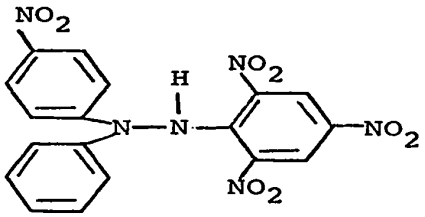
(22) (53)

[53] (53) 

(54)

[54] (53) + DPPH → → (54) + 

(27)

[55] $\cdot NO_2$ + DPPH → → 

(26)

Eq. [52] represents the initial capture of a radical R· to form the stable quinoidal species 53. 53 may now decompose by two routes to give the observed hydrazine 54. These are shown in eqs. [53] and [54]. We cannot tell whether the route in eq. [53] or that in eq. [54] is operating, or indeed if there is a mixture of both taking place.

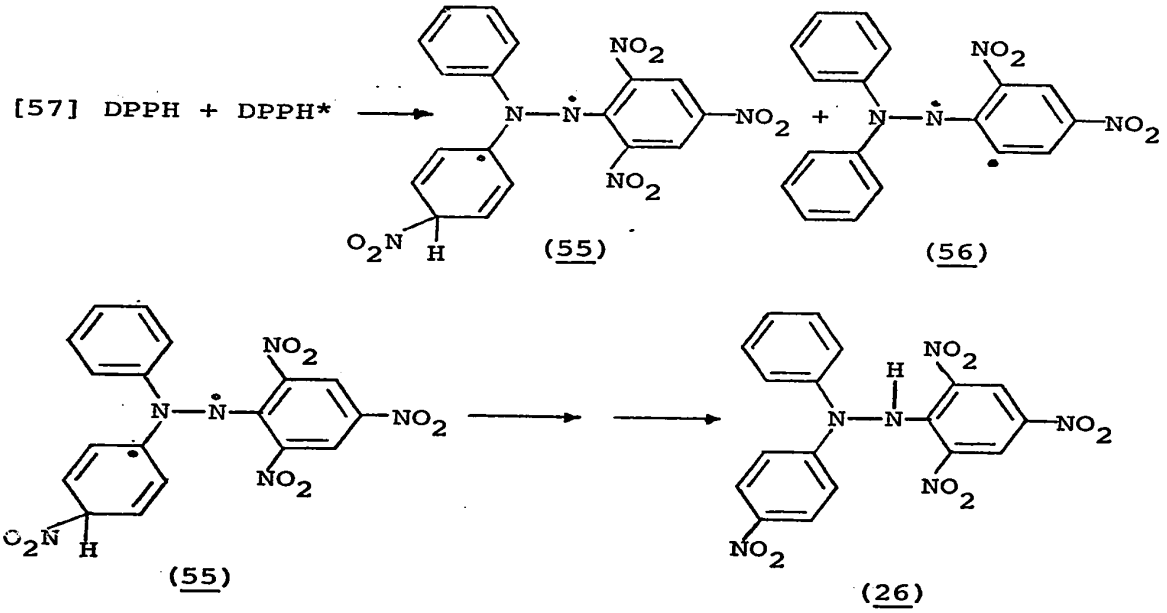
Eq. [53] represents a unimolecular decomposition to give the hydrazyl 54 and nitrogen dioxide. The hydrazyl 54 must subsequently abstract a hydrogen atom or exchange with a hydrazine molecule, as the product of the reaction that was isolated is the hydrazine. The production of 26 is now given in eq. [55] by the reaction of DPPH with nitrogen dioxide. This reaction has been used in this thesis and by other workers (55,65) for the preparation of 26.

Eq. [54] represents a bimolecular route to the formation of 27 and 54 involving intermolecular transfer of nitrogen dioxide between 53 and a second molecule of DPPH. As before, subsequent hydrogen abstraction must occur to form the corresponding hydrazines which were the products of the azo compositions.

A similar mechanism to that in eq. [54] has been proposed for the photochemical decomposition of DPPH.

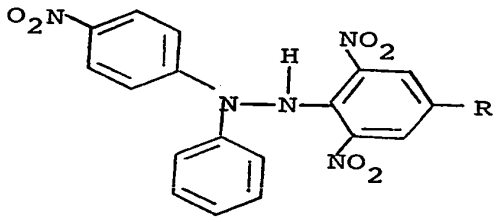
An intermolecular transfer of nitrogen dioxide between two molecules of DPPH has been suggested to explain the formation of 26 from a solution of DPPH in benzene that had been exposed to sunlight (103). The other products of this reaction were DPPH-H and an unidentified product thought to be a phenazine derivative. A reaction scheme was proposed in which the NO_2 group is transferred from an excited DPPH molecule to an unexcited one to give the hydrazine 26, eqs. [56], [57] and [58].

[56] DPPH $\xrightarrow{h\nu}$ DPPH*



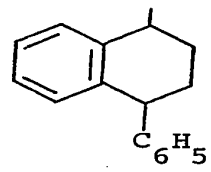
The other product 56 from eq. [57] is postulated as yielding cleavage products and ultimately phenazine derivatives.

Eqs. [53] and [55] both show reaction of 53 or $\cdot NO_2$ with a second molecule of DPPH to give 54 and 26. Reaction could occur as easily with 54 in place of DPPH giving a hydrazine of the structure 57.



(57a,b)

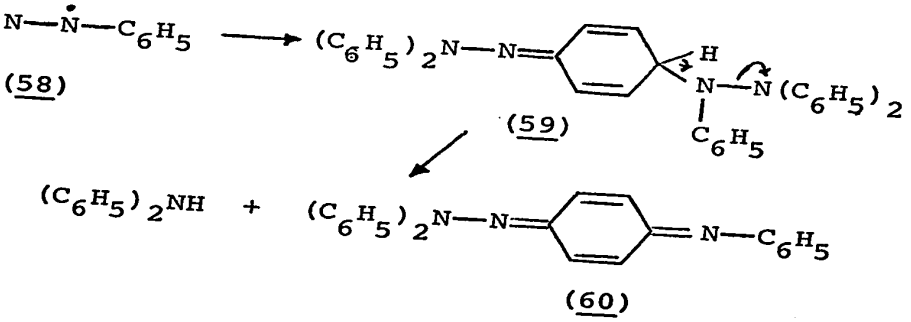
(a) R = $-CH(C_6H_5)-CH_3$

(b) R = 

In the case of the decomposition of 35, a compound of the structure 57b was identified from its nmr spectrum and chemical ionization mass spectrum. The corresponding hydrazine 57a was identified in the product mixture from the decomposition of 32. Identification was made only from its nmr spectrum, as it could not be separated completely from the other components. The proportion of 57a was very much less than the proportion of 57b in the respective total product mixtures. The higher

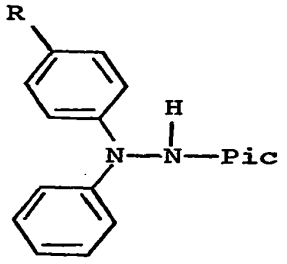
proportion of 57b compared to the proportion of 57a isolated from the respective product mixtures can be rationalized from the amount of DPPH used in each of the decompositions. For 35 an equivalent amount of DPPH was used and so the hydrazyl 54b can be expected to compete favorably with DPPH, as the concentration of 54b increases during the reaction while that of DPPH will decrease. In the decomposition of 32, a 100% excess, i.e., two equivalents of DPPH, were used and the DPPH will now be predominant throughout the reaction. The corresponding amount of 54a will be proportionally smaller as observed.

It is of interest to note that triphenylhydrazyl (58) derived from oxidation of the corresponding hydrazine undergoes a rapid decomposition to diphenylamine and the di-imine 60, probably by the route shown in eq. [59] (57,104).

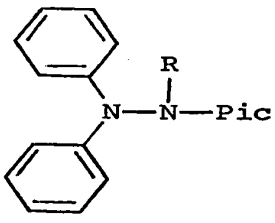
[59] 

This para-coupling at the phenyl ring attached to the "radical" nitrogen to give a neutral quinoidal species 59 is analagous to the radical attack proposed in eq. [52] for DPPH. It was found that introduction of para-substituents into the N_1 phenyl ring of 58 slowed down the rate of decomposition of the hydrazyl.

The absence of any products derived from attack at either of the phenyl rings attached to the second nitrogen atom or from attack at the radical nitrogen is further support for the mechanism proposed in eq. [52]. Injection of DPPH and DPPH-H into the gas chromatograph at temperatues of about 280° showed that they underwent N—N bond fission to give diphenylamine and picramide. A similar decomposition was observed for 43 which decomposed to give diphenylamine and 42. It therefore seems likely that if radical capture had occurred at either of the phenyl rings or at the "radical" nitrogen, giving the hydrazines 61 and 62



(61)



(62)

the corresponding substituted diphenylamine or picramide should have been observed in the glc analysis. 4-(1-Phenylethyl)-N-phenylaniline (52) and 2,4,6-trinitro-N-(1-phenylethyl)-aniline (51) were synthesized and their retention times on the gas chromatograph were compared with the retention times of the product mixture from the decomposition of 32 in the presence of DPPH. No products were observed with retention times that matched either 51 or 52. This evidence then supports attack at the picryl ring of DPPH and excludes attack at either of the phenyl rings or the "radical" nitrogen of DPPH.

In all the other reactions between DPPH and radicals found in the literature, radical capture has been assumed to take place at the para-position of one of the phenyl rings, or by direct recombination at the DPPH radical nitrogen. In the instances where radical capture is speculated to occur at the phenyl ring, the only evidence cited was that the hydrazine product still contained an oxidizable N-H bond (59,69). The mechanism proposed in eqs. [52], [53] and [54] yields a hydrazine that contains an oxidizable N-H bond and is therefore consistent with the above observations.

In only a few cases has radical capture been proposed to take place at the "radical" nitrogen of DPPH. Henglein (59) has proposed that the radicals

produced from the ultrasonic degradation of polystyrene add to the nitrogen of DPPH, while those from a similar degradation of polymethylmethacrylate are substituted in the phenyl ring. The apparently contrasting behavior of these polymer radicals has been criticized in the introduction of this Chapter. From the results of the decomposition of 32, which yields a 4-phenylethyl radical, with a structure analogous to the end group of a polystyryl radical, substitution must have occurred in the picryl ring and Henglein's observation was incorrect.

The only case in which there is some evidence for radical capture at the nitrogen is in the work of Dulog and Baum (77), on the decomposition of t-butylhydroperoxide in the presence of DPPH. The structure of 24 isolated from the reaction mixture was assigned on the basis of an elemental analysis and a reductive cleavage of 24 to give only diphenylamine. The last reaction excludes attack in the phenyl rings of DPPH. Recent experimental evidence (105) indicates that t-butylhydroperoxide undergoes unimolecular decomposition as in eq. [60].

[60] $$\text{t-BuOOH} \longrightarrow \text{t-BuO}\cdot + \cdot\text{OH}$$

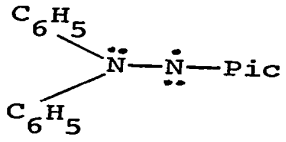
DPPH would be expected to react with the hydroxyl and

t-butoxyl radicals produced to form adducts. It is quite possible that the •O-H radical is small enough to enter the highly hindered reaction sphere of the DPPH "radical" nitrogen and give the product 24.

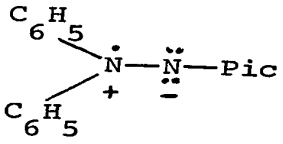
The reaction of the t-butoxyl radical with DPPH may give a similar product, although the bulky t-butyl group now attached to the oxygen may hinder this method of attack. However, the possible products arising from these reactions were not considered by Dulog and Baum.

Radical capture by DPPH at the p-position of one of the phenyl rings has been excluded for the radicals studied in this work. Some further support for the absence of this method of capture can be obtained from theoretical considerations. The usual structural formula for DPPH is 22. The unpaired electron is alloted to the nitrogen adjacent to the picryl ring, but it is clear that in order for the radical to be stable, the unpaired electron must be considerably delocalized over both sets of ring systems. Electron spin resonance studies (106) have also indicated large spin densities on both the central nitrogen atoms of DPPH. The only plausible way in which the unpaired electron can migrate on to the phenyl rings and on to the other nitrogen, is to assume that an ionic structure contributes to the molecular wave function. The more important contributors

to the structure of DPPH may be represented by the resonance structures 63 and 64.



(63)

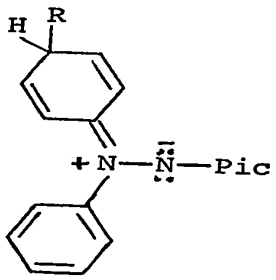


(64)

Calculations based on esr studies (107) have shown that 63 contributes about 62% and 64 about 26% to the structure of DPPH. The remaining 10% was divided between resonance structures derived from 63 and 64 that delocalized the odd electron into the ring system. It is obvious therefore that the charge separated species 64 is the least favorable.

This conclusion may now be applied to the initial products from radical capture by DPPH at either the phenyl ring or the picryl ring. If the radical R• is captured at the p-position of the phenyl ring, a charge separated species 65 is obtained as in eq. [61].

[61] DPPH + R• ⟶



(65)

Because of the charge separation 65 would be expected to be less stable than the species 53 obtained in eq. [52] from radical capture at the para-position of the picryl ring.

Theoretical calculations (108), assuming that there is an equal contribution from structures 63 and 64 to the ground state of DPPH, show that the electron density, ρ, is greater at the para-position in the picryl ring (ρ = 0.190) than at the para-position of the phenyl ring (ρ = 0.122), consistent with the route in eq. [52].

The products of the decompositions of 32 and 55 in the presence of DPPH are consistent with the theoretical calculations presented above and confirm that the electron density must be greatest in the para-position of the picryl ring.

So far, evidence has been presented that indicates that radical capture by DPPH takes place exclusively at the para-position of the picryl ring and in doing so substitutes for the nitro group. In only one case, the decomposition of t-butyl hydroperoxide, is there evidence that radical capture takes place at another position, namely the radical nitrogen (77). However, the reaction of DPPH and NO_2 yields 26 and 28, both substituted in the para-position of the phenyl ring (59,69). Similarly the

reaction of DPPH with bromine in chloroform (109) gives a mixture of 2-(4-bromophenyl)-2-phenyl- and 2,2-di-(4-bromophenyl)-1-picrylhydrazines which are separable by chromatography. The same products were obtained when DPPH was treated with hydrobromic acid and when DPPH-H was treated with bromine in the presence of a trace of hydrobromic acid. Similar reactions were observed with chlorine and hydrochloric acid although the products were not characterized. With iodine in the presence of hydriodic acid, no reaction was observed. The authors propose that the reaction of halogens with DPPH-H is a normal electrophilic substitution reaction but offer no comment on the reaction of bromine with DPPH. However, it is likely that this is still a normal electrophilic substitution reaction and it would be expected to substitute in the <u>para</u>-position of the phenyl ring. Aromatic amines undergo halogenation in the absence of a catalyst; treatment of triphenylamine with bromine in chloroform yields tri-(<u>p</u>-bromophenyl)-amine.

The reaction of nitrogen dioxide may proceed by an electrophilic substitution reaction, if first a charge transfer takes place to give NO_2^+ eq. [62].

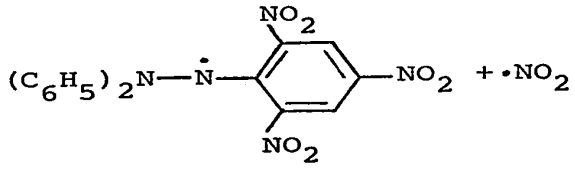
[62] $(C_6H_5)_2N—\dot{N}—Pic + \cdot NO_2 \longrightarrow (C_6H_5)_2N—\ddot{\underline{N}}—Pic + NO_2^+$

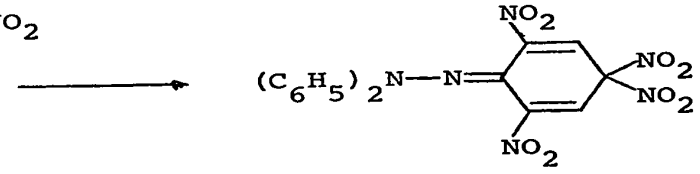
Once the nitronium ion is produced it will react at the para-position of the phenyl ring of DPPH to give the observed product. The NO_2 ion should also react with the benzene solvent, although this may be slow compared to the reaction with the DPPH. However, it appears that the reaction in eq. [62] is thermodynamically unfavorable from consideration of the half wave potentials of the reactants and products, eqs. [63] and [64].

[63] $DPPH + e^{\ominus} \longrightarrow DPPH^{\ominus}$ $E_{1/2} = 0.22v$ (110)

[64] $NO_2 - e^{\ominus} \longrightarrow NO_2^{\oplus}$ $E_{1/2} = 1.64v$ (111)

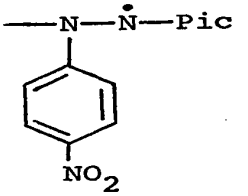
Nitrogen dioxide may still be undergoing a radical reaction with capture at the picryl ring eq. [65].

[65] 



(66)

The intermediate 66 may now transfer a nitro group to a second DPPH molecule in an analagous reaction to eq. [54].

[66] (66) + DPPH $\longrightarrow$ $\longrightarrow$ DPPH + 

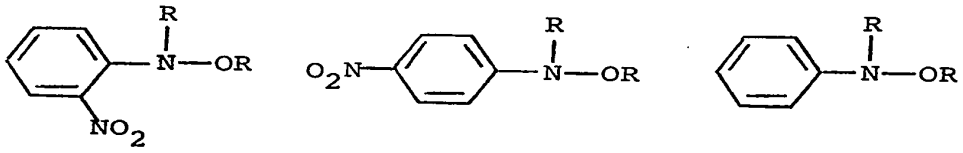
(27)

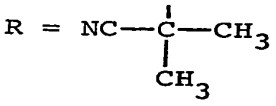
However, the mechanism here cannot be verified because of the similar groups. The mechanism of the reaction of DPPH with NO_2 thus remains unsolved.

Further evidence to support or rationalize the observed reaction could not be found in the literature. The study of radical reactions with neutral nitro compounds has been shown to occur by two reaction pathways. Fieser (112) has isolated nuclear substitution products from the reaction of aromatic compounds with lead tetraacetate. This reaction presumably proceeds to produce highly reactive methyl radicals (113) although the methylating action of this reagent also has been considered as due to the formation of carbonium ions (114). Mono-, di- and trinitrobenzenes could be methylated on the ring once and sometimes twice. Substitution was made at carbons bearing hydrogen only and not at carbons bearing a nitro group. Similarly, phenylation of nitrobenzene has been accomplished with lead tetrabenzoate (115). Other examples of nuclear substitution by radicals in nitrobenzene have been carried out with hydroxyl radicals (116), aryl radicals (117) and peroxides (118).

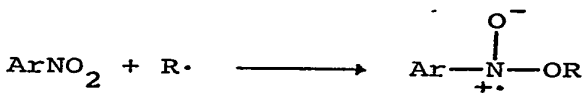
Norris (119) has studied the reaction of some polynitrobenzenes with the 2-cyano-2-propyl radical formed from the thermal decomposition of azo-bis-isobutyronitrile.

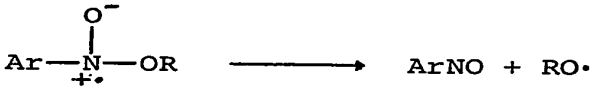
This work confirmed the earlier results of Inamota and Simamura (120). Both groups isolated nitro compounds of the structures:





They postulate an initial attack at the oxygen of the nitro group followed by the formation of an aromatic nitroso compound, eqs. [67] and [68].

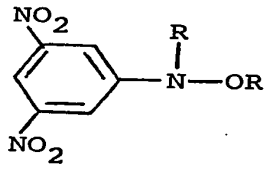
[67] 

[68] 

The nitroso compound may then react with more radicals to give the product, eq. [69].

[69] 

Other workers (121,122) have postulated initial attack of the radical at the oxygen atom of the nitro group to explain the retarding action of nitro compounds in polymerization reactions. It should be noted that in the case of trinitrobenzene, Norris could only isolate 2% of product corresponding to the structures above, i.e.



The remainder of the product was a highly colored material which was not identified. This suggests an alternative route may be operating for trinitroaromatic compounds.

There must be no attack of a radical at the oxygen of the nitro groups in DPPH in this work, since a 100% product balance was obtained for DPPH in the decomposition of 35. Although a complete product balance was not obtained in the decomposition of 32, the isolation of the same type of radical - DPPH adducts as for 35 is evidence that radical attack at oxygen is also absent here.

Further evidence for the formation of 1

The isolation of 50 from the DPPH inhibited thermal

polymerization of styrene is convincing evidence for the production of the 4-phenyl-1-tetralyl radical, 2. It is highly improbable that 50 is formed by some other route than by capture of 2 by DPPH. The formation of 50 is also evidence for the inhibiting mechanism proposed in eqs. [3], [12] and [14], where DPPH abstracts a hydrogen from the Diels-Alder adduct 1 to give the radical 2, followed by a reaction of 2 with DPPH to give 50. This sequence of reactions then supports the proposal that 1 is formed as a necessary precursor for the formation of radicals in the thermal polymerization of styrene.

EXPERIMENTAL

Preparation of azo compounds

1,1'-Diphenylazoethane (32)

Acetophenone azine (10 g, 0.042 mole) dissolved in 150 ml ethyl acetate was hydrogenated over 400 mg of 5% palladium on charcoal until there was no further uptake in hydrogen (15 hours). The resulting solution of 1,2-bis-(1-phenylethyl)-hydrazine was filtered, the solvent removed by evaporation, the almost colorless residue taken up in ether (50 ml) and oxygenated by stirring in an oxygen atmosphere at 5 psi pressure. The pale yellow ethereal solution was washed four times with water (100 ml) and dried over anhydrous sodium carbonate. Removal of the solvent by evaporation gave a white residue which was recrystallized from methanol to give 4.7 g (48%) of white needles mp 71-72°; lit. mp 72.3-72.9° (81). The infrared spectrum (CCl_4) showed an absence of N-H absorption. The nmr spectrum (CCl_4) showed peaks at τ2.80 (s), τ5.46 (q, J = 7 cps), τ8.50 (d, J = 7 cps), in the ratio 5.1 : 1 : 3.1, required 5 : 1 : 3. The ultra-violet spectrum (EtOH) showed λ_{max} = 335 mμ; lit. λ_{max} = 335 mμ (81).

4-Phenyl-1-tetralone Ketazine (33)

To 2.5 g (0.011 mole) 4-phenyl-1-tetralone in 25 ml

98% ethanol was added 0.32 g (0.011 mole) of an 85% solution of hydrazine hydrate and one drop of glacial acetic acid. The mixture was heated under reflux for three and one half hours during which time the ketazine precipitated from solution as a yellow solid. The product was filtered at the pump and washed with a little cold ethanol to yield 2.35 g (84%) of fine yellow powder mp 207-210°. The infrared spectrum ($CHCl_3$) showed an absorption at 1690 cm^{-1} (C=N). The nmr spectrum ($CDCl_3$) showed peaks at τ1.80 (m), τ2.90 (m), τ5.87 (t), τ7.25 and τ7.80 (broad triplets), in the ratio 1 : 8 : 1 : 4, required 1 : 8 : 1 : 4.

Analysis for $C_{32}H_{28}N_2$. Calculated: C, 87.24; H, 6.41; N, 6.36. Found: C, 87.06; H, 6.49; N, 6.54.

4,4'-Diphenylazo-1-tetralin (35)

To 1.7 g of 33 dissolved in 300 ml of dry benzene was added 500 mg of 5% palladium on charcoal and the compound was hydrogenated for 48 hours at atmospheric pressure, until no more uptake of hydrogen. The catalyst was removed from the colorless solution by filtration on a Celite pad and the solvent removed by evaporation under reduced pressure to give a white sticky solid. This was immediately dissolved in 125 ml ether contained in a flask

fitted with a serum cap and syringe needle, and oxidized by bubbling oxygen through the solution. The oxygen pressure was maintained at 5 psi and the solution stirred constantly. After 24 hours a white solid had settled out and was filtered at the pump. Cooling of the ether filtrate yielded more white powder giving a total of 0.785 g (46%) mp 121-124° with decomposition. The infrared spectrum ($CHCl_3$) showed an absence of N-H and C=N absorptions. The nmr spectrum ($CDCl_3$) showed peaks at τ2.87 (m), τ5.32 (m), τ5.82 (m), τ7.80 (m), in the ratio 9.1 : 2 : 4, required 9 : 2 : 4. The ultra-violet spectrum (2.26×10^{-3} M in ether) showed λ_{max} 362 mμ (ε 110). Addition of one drop concentrated hydrochloric acid to the solution gave a new maximum after 24 hours for the hydrazone λ_{max} 286 mμ (ε 11,000). No azo compound could be observed.

Analysis: Calculated for $C_{32}H_{30}N_2$: C, 86.84; H, 6.83; N, 6.33: Found C, 86.79; H, 6.50: N, 6.09.

Preparation of authentic DPPH-radical products

1-(4-Methoxyphenyl)-1-phenylethylene (37)

To 14.6 g (0.61 moles) magnesium turnings in a three-necked one litre flask equipped with mechanical stirrer, dropping funnel and reflux condenser, was added

14.2 g bromobenzene in 30 ml anhydrous ether. The reaction started spontaneously and a solution of 80 g bromobenzene in 250 ml anhydrous ether was added so as to keep the solution under a gentle reflux. At the end of the addition, the solution was stirred for a further 30 minutes. To the Grignard, in situ, was added 88 g (0.59 moles) 4-methoxyacetophenone dissolved in 250 ml anhydrous ether. The reaction mixture was heated for a further 30 minutes at the end of the addition to effect completion. The complex was decomposed by the addition of a saturated aqueous ammonium chloride and the clear ether layer decanted. The residual salts were washed with two 100 ml portions of anhydrous ether and the washings combined. After drying over anhydrous magnesium sulfate the ether was removed by rotary evaporation to give a pale yellow liquid. The crude alcohol was dehydrated by heating for one hour at 210°, distilling off the water and any unreacted bromobenzene. The resulting clear solution set to a mass of pale yellow crystals on cooling and was recrystallized from pentane to give 83 g (74%) giant white prisms mp 73-74°; lit. mp 75° (92). The infrared spectrum (CCl_4) showed an absence of O-H absorption. The nmr spectrum (CCl_4) showed peaks at τ2.72 (s), A_2B_2 system centered at τ3.02, τ4.68 (doublet of doublets), τ6.30 (s), in the ratio 5 : 4 : 2 : 3, required 5 : 4 : 2 : 3.

1-(4-Methoxyphenyl)-1-phenylethane (38)

To 83 g (0.39 moles) 37 dissolved in 250 ml ethyl acetate was carefully added 100 mg platinum oxide and the compound was hydrogenated at two atmospheres until no more uptake of hydrogen occurred. The catalyst was removed by filtration and the solvent removed under vacuum to yield a pale colorless liquid. Distillation under reduced pressure gave 82 g (99%) of a colorless liquid bp 121° (1.5 mm), n_D^{26} = 1.5680; lit. bp 183 (17 mm), n_D^{26} = 1.5680 (93). The nmr spectrum (CCl_4) showed peaks at τ2.88 (s), A_2B_2 system centered at τ3.12, τ5.95 (q, J = 7 cps), τ6.38 (s), τ8.40 (d, J = 7 cps), in a ratio 9 : 1.0 : 3.0 : 3.0, required 9 : 1 : 3 : 3.

1-(4-Hydroxyphenyl)-1-phenylethane (39)

1-(4-Methoxyphenyl)-1-phenylethane was cleaved to the phenol according to the method of Curphey, Hoffman and McDonald (94). In a three-necked 500 ml flask, fitted with a thermometer and magnetic stirrer was placed 80 ml commercial pyridine and 84 ml cencentrated hydrochloric acid added rapidly with efficient stirring. The flask was fitted for distillation and the contents distilled until the internal temperature rose to 210°. The flask was cooled to 140° and 39.5 g (0.186 mole) 38 added. The

distillation apparatus was replaced with a reflux condenser fitted with a T-joint connected to a dry nitrogen supply and a mercury bubbler. A nitrogen atmosphere was obtained and the contents heated under reflux for three hours and cooled. To the warm solution was added 80 ml water and the contents poured into 600 ml water. The aqueous solution was extracted with three 300 ml portions of ether. The combined ether extracts were washed with distilled water and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a viscous straw-colored liquid which on distillation under reduced pressure afforded 33 g (91%) of a colorless viscous liquid bp 133-134° (0.5 mm). On cooling in ice water, the liquid set to a white crystalline solid mp 54-56°; lit. bp 185-190° (10 mm) (95); mp 64° (97). The infrared spectrum (CCl_4) showed a band at 3350 cm^{-1}. The nmr spectrum (CCl_4) showed peaks at τ2.92 (s), A_2B_2 centered at τ3.26, τ3.95 (broad singlet), τ6.05 (q, $\underline{J}$ = 7 cps), τ8.50 (d, $\underline{J}$ = 7 cps), in the ratio 9 : 1 : 1 : 3, required 9 : 1 : 1 : 3. The peak at τ3.95 disappeared on D_2O exchange.

Analysis: Calculated for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found C, 84.88; H, 6.90.

Potassium 2,6-dinitro-4-(1-phenylethyl)-phenoxide (40)

1-(4-Hydroxyphenyl)-1-phenylethane was nitrated according to the method of Gasparic (98). To 9.75 g (0.045 mole) 39 dissolved in 1000 ml of buffer solution (800 ml glacial acetic acid, 150 ml 10% aqueous potassium hydroxide, 50 ml distilled water) was added 125 ml concentrated sulfuric acid. The solution was stirred well and heated to 60° when 125 g sodium nitrite in 400 ml water was added slowly during 80 minutes. After the addition, stirring was continued for a further one hour at 60°, the solution cooled and 2500 ml water added. The aqueous mixture was extracted with three 300 ml portions of benzene. The combined benzene extracts were washed with two 400 ml portions of water and finally extracted with two 50 ml portions of 10% potassium hydroxide. The potassium salt was insoluble in the aqueous layer and was recovered by filtration, to give 7.8 g (50%) of orange-red needles. Recrystallization from boiling water gave 7.6 g of long orange-red needles.

2,6-Dinitro-4-(1-phenylethyl)-phenyl p-touenesulfonate (41)

To 1.0 g (0.005 moles) of p-toluenesulfonyl chloride dissolved in 15 cc acetone was added 1.6 g (0.005 moles) of 40 and the slurry stirred at reflux temperature for

four hours. The dark red solution gradually lost its color and at the end of the heating period was a light yellow. The precipitated potassium chloride was filtered and the solvent removed to give a buff colored solid. Recrystallization from methanol, after decolorizing with Norit A, afforded white needles 1.8 g (81%) mp 114-115°. The nmr spectrum ($CDCl_3$) showed peaks at τ2.0 (s), A_2B_2 system centered at τ2.43, τ2.70 (s), τ5.70 (q, $\underline{J}$ = 7 cps), τ7.55 (s), τ8.30 (d, $\underline{J}$ = 7.3 cps), in the ratio 2 : 9.1 : 1 : 2.9 : 3, required 2 : 9 : 1 : 3 : 3.

Analysis: Calculated for $C_{21}H_{18}N_2O_7S$: C, 57.01; H, 4.10; N, 6.33; S, 7.25: Found C, 57.20; H, 4.11; N, 6.05; S, 7.33.

2,6-Dinitro-4-(1-phenylethyl)-amine (42)

In a 50 ml three-necked flask fitted with reflux condenser and serum cap, was placed 1.8 g (0.004 moles) of 41 in 20 cc diglyme. The solution was heated to 160° and anhydrous ammonia bubbled through the solution by inserting a hypodermic needle in the serum cap which reached below the liquid level. At the end of three hours the solution had turned a dark red color and a precipitate of fine white needles had settled out. The precipitate was filtered at the pump (ammonium salt of

p-toluenesulfonic acid) and the solvent removed from the filtrate to give a dark orange solid. Recrystallization from methanol gave bright orange prisms 940 mg (81%) mp 115°. The infrared spectrum ($CHCl_3$) showed absorptions at 3485 cm^{-1} 3370 cm^{-1} (NH stretch) and 1647 cm^{-1} (NH bend). The nmr spectrum ($CDCl_3$) showed peaks at τ1.58 (broad singlet), τ2.70 (s), τ5.89 (q, $\underline{J}$ = 7.5 cps), τ8.33 (d, $\underline{J}$ = 7.5 cps), in the ratio 4 : 5 : 1 : 3, required 4 : 5 : 1 : 3.

Analysis: Calculated for $C_{14}H_{13}N_3O_4$: C, 58.53; H, 4.56; N, 14.63. Found C, 58.40; H, 4.75; N, 14.50. The mass spectrum gave peaks at m/e 287 (P), 272 (P-15) 180 (P-107), 152 (P-135).

1,1-Diphenylhydrazine hydrochloride

Two solutions, one containing 5 g of recrystallized diphenylamine (technical grade) in 40 ml of warm ethanol and the other containing 2.5 g sodium nitrite in 5 ml water, were cooled in an ice bath until the temperature fell to 5°. To the diphenylamine solution was added 40 ml concentrated hydrochloric acid steadily with stirring and then without delay the sodium nitrite solution was poured into the well stirred mixture. The diphenylnitrosamine rapidly crystallized out and the solution was allowed to stand in ice-water for a further 20 minutes. The light yellow

crystals were filtered at the pump, drained thoroughly, washed with water to remove any sodium chloride and air dried to give 5 g (85%) of pale yellow crystals. The crude nitrosamine (5 g) was suspended in 20 cc ethanol and 7.5 g zinc dust added. To the rapidly stirred suspension, cooled in an ice bath, was added 10 g acetic acid over a period of half an hour. At the end of the addition the solution was boiled on a water bath and filtered hot to remove the zinc sludge, and the residue was washed with a little acetic acid. The filtrate was diluted with water, neutralized with 6N sodium hydroxide and extracted with ether (2 x 100 ml). Addition of concentrated hydrochloric acid to the ether extracts gave a crystalline white precipitate of 1,1-diphenylhydrazine hydrochloride which was filtered at the pump and air dried to give 4.1 g (65% based on diphenylamine) mp 144-150° with decomposition. The salt was used directly without any further purification.

1,1-Diphenyl-2-(2,6-dinitro-4-(1-phenylethyl)-phenyl)-hydrazine (43)

To 0.5 g of 1,1-diphenylhydrazine hydrochloride (0.0023 mole) in 10 ml ethanol was added 0.50 g (0.006 moles) anhydrous sodium bicarbonate and when the evolution

of carbon dioxide had ceased, 1.0 g (0.0023 moles) of 41 was added and the mixture boiled gently under reflux for two and a half hours. The mixture was cooled, filtered to remove the precipitated sodium tosylate and the intensely dark red solution evaporated under vacuum to give a dark red oil. Recrystallization from $CHCl_3$/EtOH mixture (1 : 1 by volume) gave only a gel. Recrystallization from 98% ethanol yielded 720 mg brick-red prisms mp 133° (charred at 131°). The infrared spectrum ($CHCl_3$) showed an absorption at 3310 cm^{-1} (N-H stretch). The nmr spectrum ($CDCl_3$) showed peaks at τ0.52 (s), τ2.18 (s), τ2.80 (m), τ5.93 (q, $\underline{J}$ = 7 cps), τ8.42 (d, $\underline{J}$ = 7 cps) in the ratio 1 : 2 : 17 : 1 : 3 required, 1 : 2 : 17 : 1 : 3. The peak at τ0.52 disappeared after prolonged shaking with D_2O. The same spectrum was obtained in acetone-$\underline{d}_6$ solvent except the peaks were now at τ0.30 (s), τ1.99 (s), τ2.76 (m), τ5.75 (q, $\underline{J}$ = 7 cps), τ8.50 (d, $\underline{J}$ = 7 cps) in the same ratio as before.

Analysis: Calculated for $C_{26}H_{22}N_4O_4$: C, 68.71; H, 4.88; N, 12.11: Found C, 68.81; H, 4.83; N, 12.11

1-Phenyl-4-(4-methoxyphenyl)-1,2-dihydronaphthalene (45)

To 2.4 g (0.1 mole) of magnesium turnings in a dry three-necked flask fitted with a mechanical stirrer, reflux condenser and dropping funnel, was added 50 ml dry ether and a few drops of ethylene dibromide. The reaction started immediately and 18.7 g (0.1 mole) of 4-bromoanisole in 30 ml dry ether was added dropwise over one hour to the stirred magnesium. The contents were heated under gentle reflux for a further two hours, cooled, and a solution of 16, 6.2 g (0.028 mole) in 100 ml ether, was added dropwise over one hour. The contents were heated under gentle reflux for a further 3 hours and hydrolyzed by the addition of a saturated solution of ammonium chloride. The clear yellow ethereal layer was decanted from the residual salts, washed with 100 ml of water and dried over anhydrous magnesium sulfate. The ether was removed under vacuum to yield a viscous straw-colored oil which was heated at 210° and 60 mm pressure for 30 min This procedure effected dehydration of the crude alcohol 44 and distilled any anisole and unreacted 4-bromoanisole from the product. The residual viscous oil, 8.5 g (89%), could not be purified by recrystallization from common solvents, but was only recovered as an oil. The infrared

spectrum showed an absence of -O-H and C=O absorptions due to the intermediate and starting materials, respectively. The nmr spectrum (CCl_4) showed peaks at τ2.80 (s) overlapping an A_2B_2 system centered at τ3.05 and a multiplet at τ2.85, τ4.10 (t, $\underline{J}$ = 4.5 cps) τ5.90 (t, $\underline{J}$ = 8.5 cps, τ6.26 (s), τ7.35 (doublet of doublets, $\underline{J}$ = 4.5 cps, $\underline{J}$ = 8.5 cps) in the ratio 13.0 : 1.0 : 1.0 : 3.0 : 2.0, required 13.0 : 1.0 : 1.0 : 3.0 : 2.0.

An analysis of a thin film gave the following results: Calculated for $C_{23}H_{20}O$: C, 88.43; H, 6.45. Found: (i) C, 86.30; H, 6.27; (ii) C, 84.95; H, 6.31; (iii) C, 85.24; H, 6.55. The compound was used without further purification in the next step.

1-Phenyl-4-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalene (46)

To 7.5 g (0.024 mole) 45 dissolved in 50 ml ethylacetate was added 50 mg platinum oxide and the mixture hydrogenated at two atmospheres until there was no more uptake of hydrogen. The catalyst was removed by filtration through a Celite pad and the solvent removed under vacuum to yield 7.5 g (100%) of a viscous straw-colored oil. The nmr spectrum (CCl_4) showed peaks at τ3.0 (broad

multiplet), τ5.90 (broad multiplet), τ6.28 (s), τ8.0 (m) in the ratio 13.1 : 2 : 3 : 4, required 13 : 2 : 3 : 4. Attempts to recrystallize the compound only gave an oil which set to a glass. The compound was used directly in the next step.

1-Phenyl-4-(4-hydroxyphenyl)-1,2,3,4-tetrahydronaphthalene (47)

46 was cleaved to 47 according to the method of Curphey, Hoffman and McDonald (94). In a three-necked 100 ml flask was placed 10 ml commercial pyridine and 10.5 ml concentrated hydrochloric acid was added rapidly with stirring. The flask was equipped for distillation and the contents distilled until the internal temperature rose to 210°. The contents were cooled and 7.5 g of 46 was added. The distillation condenser was replaced by a reflux condenser and an atmosphere of nitrogen was maintained. The contents were heated under gentle reflux for two hours, cooled and poured into 300 ml water. The aqueous solution was extracted with two 100 ml portions of ether. The combined ether portions were washed with distilled water and finally dried over anhydrous magnesium sulfate. Removal of the solvent yielded 6.2 g (86%) of a straw-colored oil. The infrared spectrum (CCl_4) showed an

absorption at 3350 cm^{-1} (-O-H stretch). The nmr spectrum (CCl_4) showed peaks at τ3.0 (broad multiplet), τ5.90 (broad multiplet) τ6.70 (s), τ8.0 (m), in the ratio 13.2 : 2 : 1 : 4, required 13 : 2 : 1 : 4. The compound was used directly in the next step.

1,1-Diphenyl-2-(2,6-dinitro-4-(4-phenyl-1-tetralyl)-phenyl)-hydrazine (50)

The conversion of 47 to the potassium salt of the dinitrophenol 48 was carried out by the same procedure as described for the conversion of 39 to 40. To 3.05 g (0.01 mole) of (47) dissolved in 200 ml buffer solution (160 ml acetic acid; 30 ml 10% potassium hydroxide; 10 ml water) was added 25 ml of concentrated sulfuric acid. To the stirred solution was added 25 g sodium nitrite in 80 ml water over a period of half an hour maintaining the temperature of the solution at 60°. Stirring was continued for a further half hour at this temperature. The solution was cooled, poured into 500 ml water, and extracted with two 100 ml portions of benzene. The benzene layer was washed with 100 ml water and extracted with two 25 ml portions of 10% potassium hydroxide. The sticky insoluble red salt was filtered at the pump and air-dried to yield 0.8 g (18%) of a sticky red solid. The compound could not be recrystal-

lized from water. The crude potassium salt, 48, was dissolved in 10 ml of acetone containing 0.4 g (0.002 mole) p-toluenesulfonyl chloride, and the solution was heated under reflux until the disappearance of the dark-red color. The precipitate of potassium chloride was removed by filtration and the acetone was removed from the amber filtrate to yield a sticky fawn colored solid. This solid could not be recrystallized and was added directly to 10 ml ethanol, containing 0.45 g (0.002 moles) 1,1-diphenylhydrazine hydrochloride and 0.45 g sodium carbonate. The solution was heated gently under reflux for two and one half hours, cooled, filtered and the solvent removed. The residue was chromatographed on a 20 x 20 cm preparative tlc plate coated with 2 mm of silica gel (PF-254, E. Merck and Co.) acetone-petroleum ether, 1 : 8 by volume, was used as the eluent. After six developments of the plate, there was obtained a well separated red-brown band which was removed and extracted with benzene, using a Sohxlet apparatus. The benzene was removed from the extract to yield 73 mg, (13% based on crude 48) of an orange-red brittle solid. The infrared spectrum (CCl_4) showed an absorption at 3310 cm^{-1} (N-H stretching). The nmr spectrum was consistent with the structure of the material and has been discussed in the results section of this Chapter. The compound

melted over a range 69-72° and appeared to char at approximately 60°.

The analysis of the compound gave for $C_{34}H_{28}N_4O_4$: Calculated: C, 73.37; H, 5.07; N, 10.07. Found: C, 68.43; H, 5.01; N, 8.01.

1-Phenyl-1-(4-nitrophenyl)-2-picrylhydrazine (26)

The procedure was due to Poirier and Bevington (55). Dry nitrogen dioxide gas was bubbled through a solution of 2 g DPPH in 25 ml dry benzene at room temperature. After 20 minutes a red-brown precipitate had formed and the solution had changed in color from a deep violet to a red-brown. Concentration of the benzene solution to 15 ml yielded more of the precipitate which was removed by filtration. The filtrate was evaporated to dryness to yield a brick-red powder which was recrystallized from ethyl acetate-chloroform 1 : 2 by volume. There was obtained 260 mg of brown-red prisms mp 146-148°; lit. mp 152-153° (55). The infrared spectrum (KBr disc) showed a singlet at 3310 cm^{-1} (-N-H stretch). The nmr spectrum (acetone-d_6) matched that reported for 26 (65,88) and showed peaks at τ-1.00 (s), τ1.05 (s), τ2.53 (s), A_2B_2 system centered at τ2.24 (J = 9 cps) in the ratio 1.0 : 2.0 : 5.0 : 4.0, required 1.0 : 2.0 : 5.0 : 4.0.

Isolation of 50 from the DPPH-Inhibited Polymerization of Styrene.

This has been reported in Chapter I of this thesis and in the results section of this Chapter.

N-(1-Phenylethyl)-2,4,6-trinitroaniline (51)

To 2.0 g (0.008 moles) of picryl chloride in 50 ml of chloroform was added 1.0 g (0.008 moles) 1-phenylethylamine and 1 g anhydrous sodium carbonate and the solution heated under reflux for 30 minutes. The dark-red solution was washed with water (2 x 50 ml), dried over anhydrous magnesium sulfate and the solvent removed to give a dark red solid. Recrystallization from 95% ethanol after decolorisation gave 2.45 g (89%) small bright yellow needles, mp 108-109°. The infrared spectrum ($CHCl_3$) showed an absorption at 3350 cm^{-1} (N-H). The nmr spectrum ($CDCl_3$) showed peaks at τ1.1 (s), τ2.75 (s), τ5.70 (q, J = 6.5 cps), τ7.25 (s) broad (loss on D_2O exchange), τ8.30 (d, J = 6.5 cps, in the ratio 2 : 5 : 1 : 1 : 3, required 2 : 5 : 1 : 1 : 3.

Analysis: Calculated for $C_{14}H_{12}N_4O_6$: C, 50.45; H, 3.64; N, 16.86. Found C, 50.47; H, 3.69; N, 17.02.

N-Phenyl-4-(1-phenylethyl)-aniline (52)

The method used was a modification of that described by Meldola (90). To 11.2 g (0.08 mole) of 1-phenylethyl-chloride was added 13.6 g (0.04 mole) of diphenylamine and 13.6 g zinc chloride. The mixture was heated for 80 minutes at 100° in an oil bath until no more hydrogen chloride gas was evolved. The dark brown residue was extracted with two 100 ml portions of boiling water to remove any unchanged zinc chloride and then taken up in ether. The ethereal solution was dried over anhydrous magnesium sulphate and the solvent removed to yield a dark brown viscous liquid. Distillation at 1 mm pressure afforded a small amount of unreacted diphenylamine which cooled to a crystalline white solid and a viscous yellow liquid. The liquid showed the presence of three components when analyzed by tlc on silica gel using acetone-petroleum ether 1 : 20 as eluent. A 1 g portion of the yellow liquid was chromatographed on 100 g silica gel (80-200 mesh) in a 3 x 30 cm column. The first fraction collected was analyzed by nmr spectroscopy after removal of the solvent. The nmr spectrum (CCl_4) showed peaks at τ2.90 (s) overlapping an A_2B_2 system centered at τ3.25 (J = 9 cps), τ5.05 (broad singlet), τ5.82 (q, J = 7 cps), τ8.40 (d, J = 7 cps) in the ratio 14.5 : 1.0 : 1.0 : 3.3, required 14.0 : 1.0 : 1.0 : 3.0.

Decomposition of Azo Compounds and Isolation of Decomposition Products

Decomposition of 32 (Run 1)

Into a 5 ml ampoule were placed 21 mg (0.9 mmole) 32 dissolved in 1.2668 g (2.0 ml) of purified benzene and 134 mg (3.4 mmole) of recrystallized DPPH. The solution was thoroughly degassed by four freeze-thaw cycles in dry-ice/acetone on a high-vacuum rack. The ampoule was sealed under vacuum and heated in a thermostated oven at 84° for 72 hours. This period of time corresponded to greater than ten half-lives for the decomposition of 32 at this temperature, thus ensuring complete decomposition. The ampoule was cooled and opened in preparation for analysis.

Glc Analysis of the Products of Decomposition of 32 (Run 1)

A sample of the benzene solution from the decomposition of 32 in the presence of DPPH was injected into the gas chromatograph. A 5 ft x 1/4 in column of 15% SF 96 fluid on 60/80 Chrom W was used with a column temperature of 220°, helium flow rate of 60 ml/min, an injector temperature of 275° and detector temperature of 285°. Four well resolved fractions were observed with retention times of 6.0 min; 14.4 min; 25.4 min and 43.5 min.

The retention time of the first fraction, 6.0 min, coincided with the retention times of diphenylamine and meso and dl-2,3-diphenylbutane. These compounds were separated using a 5 ft x 1/4 in column of 20% PDEAS on 60/80 Chrom W with a helium flow rate of 60 ml/min. The injector temperature was at 275° and the detector temperature at 285°. The column temperature was programmed from 90° to 225° over 20 minutes. The retention times of these products were meso and dl-2,3-diphenylbutane 17.2 min and 17.7 min; diphenylamine 36.0 min.

The second fraction, 14.4 min, was identified as 2,4,6-trinitroaniline by comparison of its retention time with an authentic sample. Preparative glc gave 37 mg of this product with a melting point of 187° which was not depressed when mixed with an authentic sample. The nmr spectrum ($CDCl_3$) showed a sharp singlet overlapping a broad singlet, both centered at τ1.02. The broad singlet disappeared on D_2O exchange and the integrated signal decreased exactly by one half. The ratio of peaks was 1 : 1, required 1 : 1. The nmr spectrum matched exactly that of the authentic material.

Fraction 3, 25.4 min, and fraction 4, 43.5 min, could not be collected by preparative glc techniques because of their long retention times and the relative

smallness of the proportions of these compounds of the total fractions. The gas chromatograph was coupled to an AEI MS-12 mass spectrometer and the mass spectra of the fractions 2, 3 and 4 were recorded. The mass spectrum of fraction 2 showed a parent peak at m/e 228 and peaks at m/e 198 (P - 30), m/e 166 (P - 62), m/e 136 (P - 92) and matched exactly the mass spectrum of authentic 2,4,6-trinitroaniline. The mass spectrum of fraction 3 showed a parent peak at m/e 214 and peaks at m/e 182 (P - 32) m/e 167 (P - 47) and matched exactly the mass spectrum of authentic 4-nitrodiphenylamine. The mass spectrum of fraction 4 showed a parent peak at m/e 287 and had peaks at m/e 272 (P - 15), m/e 228 (P - 59), m/e 180 (P - 107) and m/e 152 (P - 135) and matched exactly the spectrum of an authentic sample of 2,6-dinitro-4-(1-phenylethyl)-aniline.

Decomposition of 32 (Run 2)

The same procedure was used as for Run 1 except the quantities of materials used were increased by a factor of ten times, i.e:

207 mg azo compound 32
20 ml benzene
1.34 g DPPH

The period of heating was still for 72 hours at 84°C. The ampoule was broken and the contents analyzed by glc using the same column and conditions as in Run 1. An identical chromatogram was obtained showing that the results could be duplicated.

Isolation of Decomposition Products (Run 2)

The benzene solvent was then removed and 750-850 mg of the decomposition products were chromatographed on a 5 cm diameter x 38 cm column of microcrystalline cellulose (260 g) made up in heptane solvent. Heptane was used as the eluent and two large fractions of material were collected, the first coming off as a brown red band and the second as a violet band. The two bands overlapped rather badly. A total of 400 mg of material was collected after removal of the solvent. Tlc analysis, using silica gel and acetone-petroleum ether solvent, 1 : 10 by volume, showed the presence of 43 and DPPH. The total material was chromatographed on four preparative thin layer plates, 20 x 20 cm, coated with 2 mm silica gel PF-254 (E. Merck and Co.), using acetone-petroleum ether, 1 : 10 by volume, as the eluent. The compounds were eluted by repeated development with the solvent system at a temperature of 5°. After six developments there were two strong bands

and several very minor bands at longer retention times, all of which were highly colored. The two major bands were removed from the plates and extracted with chloroform in a Soxhlet apparatus.

Fraction 1, 178 mg of red-brown colored solid. The nmr spectrum (acetone-$\underline{d}_6$) showed only broad signals indicating the presence of free radicals. Addition of one drop of a solution of hydroquinone in acetone-$\underline{d}_6$ gave a well resolved spectrum that matched exactly the nmr spectrum of 43. (Figure X).

Fraction 2, 146 mg of violet colored solid. The nmr spectrum (acetone-$\underline{d}_6$), after the addition of a few drops of hydroquinone solution, matched exactly the nmr spectrum of DPPH-H. (Figure X). The original violet color indicated that most of the material was present as the hydrazyl.

The solvent for the column chromatography on cellulose was changed to heptane-benzene, 1 : 1 by volume. The eluent was collected in 12 fractions of 250 ml each and each fraction was analyzed by tlc on silica gel using acetone-petroleum ether, 1 : 4 by volume as eluent. The fractions containing the same compounds were combined. Once again two major fractions were obtained, the first a red-brown color and the second a violet color. As

before the fractions badly overlapped each other as they were collected from the column. A third fraction at a longer retention time was also observed, which was a deep indigo color, although this was only a minor portion. The first three fractions collected, 105 mg, were found to contain DPPH and 43 by comparison of their retention times on tlc. Fractions 4, 5 and 6, 77 mg, contained DPPH, an unknown compound, and the first of the major compounds observed from the column chromatography. Fractions 7 - 11, 285 mg, contained the major bands, the first being an orange-red and the second a violet color. A portion of the combined 7 - 11 fractions, 85 mg, was chromatographed on a preparative thin layer plate, (20 x 20 cm with 2 mm silica gel as before), using acetone-petroleum ether, 1 : 6 by volume, as the eluent. Six repeated developments of the plate gave a complete separation of the fractions. The first major band was extracted from the silica gel with chloroform using a Sohxlet apparatus to yield 48 mg of an orange-red solid. After addition of a few crystals of hydroquinone the nmr spectrum (acetone-$\underline{d}_6$), showed peaks at τ-1.05 (s), τ0.97 (s), an A_2B_2 system centered at τ2.24 ($\underline{J}$ = 9 cps) and τ2.53 (m), in the ratio 1 : 2 : 4 : 5, required 1 : 2 : 4 : 5. The

spectrum matched exactly that reported in the literature for 1-p-nitrophenyl-1-phenyl-2-picrylhydrazine (65,91). The violet band was extracted from the silica gel with chloroform to yield 33 mg of a dark purple solid. The nmr spectrum (acetone-d_6) after the addition of a few crystals of hydroquinone, matched that of the brown band exactly. The violet band was thus 2-phenyl-2-p-nitrophenyl-1-picrylhydrazyl.

Attempts to crystallize these compounds gave only sticky gels. Similar difficulty has been reported for these compounds in the literature (65).

The combined fractions 4 - 6, 77 mg, were chromatographed on a tlc preparative plate using acetone-petroleum ether, 1 : 8 by volume, as eluent. After six developments, there were three major bands, with the first two bands well separated from the third. The first two bands were only slightly apart, but were taken off the plate as separately as possible. After extraction from the silica gel with chloroform, the second band was analyzed by nmr. A total of 16 mg was collected, and its nmr spectrum (acetone-d_6) showed peaks at τ-1.00 (broad singlet), τ1.05 (s), τ1.82 (d), τ2.01 (s), τ2.53 (m), τ5.71 (q), τ8.40 (d). The nmr appeared to be a mixture of DPPH-H and 1-phenyl-1-(4-nitrophenyl)-2-(2,6-dinitro-

4-(1-phenylethyl)-phenyl)-hydrazine as the integration for the proton assignment of the substituted hydrazine was not correct in the aromatic region. Further attempts to characterize this material were not possible because of the small amount isolated.

Decomposition of 35

To 76.0 mg (1.7 mmole) of 35 dissolved in 3 ml benzene was added 134 mg (3.4 mmole) DPPH and the solution thoroughly degassed by four freeze-thaw cycles in dry-ice/acetone. The ampoule was sealed under vacuum and heated for 72 hours at 84°C. The half-life of 35 was assumed to be of the same order as for 32, since both compounds will decompose to secondary benzylic radicals. The ampoule was cooled, opened and the benzene solvent removed under vacuum to yield an almost black residue.

Isolation of Decomposition Products

The total sample was dissolved in a minimum of acetone and placed on three 20 x 20 cm preparative tlc plates coated with 2 mm silica gel PF-254 (E. Merck and Co.). Approximately equal amounts were applied to each plate. A total amount of 186 mg was chromatographed, a

small amount being left on the sides of the reaction ampoule. The plates were eluted with acetone-petroleum ether solvent, 1 : 8 by volume, using the multiple development technique. The chromatography was carried out at 5°C. Each plate showed four well defined colored bands as well as a colorless band that moved almost with the solvent front. There were also several very faint colored bands that were not collected. The respective bands on each plate were scraped off with a spatula, combined, and extracted from the silica gel with chloroform, using a Sohxlet extraction apparatus. The five fractions collected were analyzed as follows:

Fraction 1, 40 mg of colorless material was identified as hydrocarbon products from the glc analysis using 5 ft x 1/4 in column of 20% SF 96 on 60/80 Chromosorb P at 217° with a helium flow rate of 100 ml/min. The injector temperature was 260° and the detector temperature was 280°. The chromatogram indicated the presence of 1-phenyltetralin and 1-phenyl-1,2-dihydronaphthalene, identified by comparison of retention times with authentic materials and by mixed injections with authentic materials.

Fraction 2, 38 mg of orange-brown solid. The nmr spectrum (CCl_4) showed peaks at τ0.51 (s), τ2.38 (s),

τ2.92 (m), τ5.88 (m), τ8.10 (broad multiplet) in the ratio 1 : 2 : 20 : 2 : 4, required 1 : 2 : 19 : 2 : 4. It matched exactly the spectrum of authentic 50. (Figure XI). The infrared spectrum (CCl_4) showed an absorption at 3310 cm^{-1} (-N-H stretch) and matched exactly that of the authentic material. The chemical ionization mass spectrum (CH_5^+ as proton source), showed an M+1 peak at m/e 557 and showed significant peaks at m/e 509 (P - 46), m/e 390 (P - 167), m/e 312 (P - 245) m/e 229, m/e 223 and m/e 206. The mass spectrum (70 ev) showed no peaks above that at m/e 272. The use of normal mass spectroscopy for these materials is therefore not a suitable means of characterization.

Fraction 3, 47 mg of orange-red solid. The nmr spectrum (acetone-d_6) showed peaks at τ-0.07 (broad singlet), τ1.07 (broad singlet), τ2.71 (broad singlet) in the ratio 1 : 2 : 10.3, required 1 : 2 : 10 and matched exactly the nmr spectrum of authentic DPPH-H. (Figure XI). The infrared spectrum (CCl_4) showed an absorption at 3295 cm^{-1} (-N-H stretch) and was identical to that of an authentic sample. The mass spectrum showed a parent peak at m/e 395 and peaks at m/e 394, m/e 378, m/e 347, m/e 255, m/e 228, m/e 169, m/e 168 and m/e 167 and was identical to that of an authentic sample.

Fraction 4, 23 mg orange-red solid. The nmr spectrum (acetone-d_6) showed peaks at τ0.75 (s), τ1.90 (d, J = 9 cps), τ2.08 (s), τ2.80 (broad band of multiplets), τ5.75 (broad multiplet, τ8.05 (broad multiplet) in the ratio 1 : 2 : 2 : 16.8 : 2 : ? The last peak could not be integrated since the solvent peak (acetone-d_5) was overlapping. The spectrum can, however, be assigned to the compound 1-(p-nitrophenyl)-1-phenyl-2-(2,6-dinitro-4-(4-phenyl-1-tetralyl)-phenyl)-hydrazine which should integrate 1 : 2 : 2 : 16 : 2 : 4. All the peaks correspond to the expected τ values for this compound. The doublet at τ1.90 is one half of the A_2B_2 system expected for the p-nitrophenyl substituent. The infrared spectrum ($CHCl_3$) showed an absorption at 3305 cm^{-1} (-N-H stretch). The mass spectrum (70 ev) showed no peaks greater than m/e 314. The chemical ionization mass spectrum (CH_5^+ as proton source) showed peaks at m/e 556 (P - 46) m/e 415, m/e 390, m/e 386, m/e 360, m/e 206. No peak was observed for M+1 (602). However the assignment of (P - 46) to the peak at m/e 556 was made by assuming that the same loss occurred as for the mass spectrum of 50, giving the parent peak m/e 602. Further evidence for the assignment was the appearance of peaks at m/e 390 and m/e 206 as seen in the chemical ionization mass spectrum of 50.

Fraction 5, 40 mg of red-brown solid. The nmr spectrum (acetone-d_6) showed peaks at τ-1.05 (broad singlet), τ0.97 (s), an A_2B_2 system centered at τ2.24 (J = 9 cps), and τ2.53 (m) in the ratio 1 : 2 : 4 : 5, required 1 : 2 : 4 : 5. The spectrum matched exactly that reported in the literature for 1-*p*-nitrophenyl-1-phenyl-2-picrylhydrazine (65,91) and the nmr spectrum of 26 prepared in this work (Figure XI). The infrared spectrum ($CHCl_3$) showed an absorption at 3300 cm^{-1} (-N-H stretch) and matched that reported in the literature (55) and that of the authentic material prepared here.

Fraction 6, 8 mg was the residue that did not move from the base line and was not identified. The total material that was recovered, weighed 196 mg (105% of starting material) indicating a complete product recovery and product balance.

Thermal Decomposition of DPPH in Benzene Solution

A solution of 134 mg (3.4 mmole) DPPH in 3 ml purified benzene was carefully degassed by three freeze-thaw cycles in dry-ice/acetone and sealed under vacuum. The solution was heated for 72 hours at 84°C and the contents analyzed using preparative tlc plates as before for the decomposition products of 32 and 35. The contents

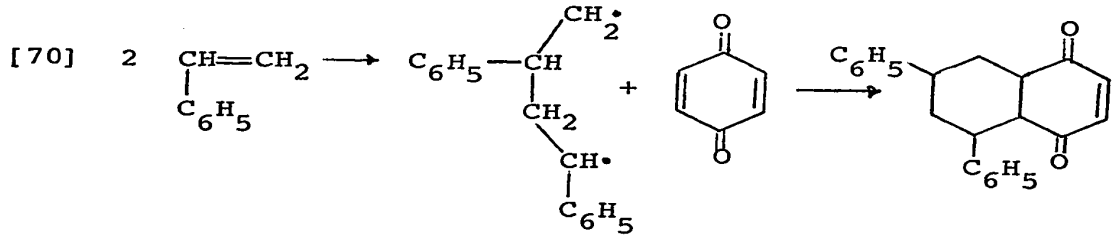
were applied to two 20 x 20 cm plates coated with 2 mm silica gel PF-254 (E. Merck and Co.) and eluted with acetone-petroleum ether, 1 : 10 by volume, using repeated developments. After six developments there were three well separated fractions. The first fraction, a deep violet band, was scraped from the plate, extracted from the silica gel with chloroform, using a Sohxlet extraction apparatus and the solvent removed to give 127 mg of DPPH identified from its melting point and its tlc retention time. The other two bands, one brown and the last a violet color were identified as 1-(p-nitrophenyl)-1-phenyl-2-picrylhydrazine and its hydrazyl from comparison of their tlc retention times with authentic samples.

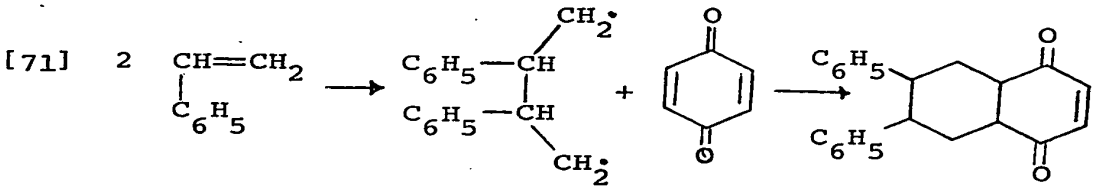
CHAPTER III

The Chemical Reaction Underlying the Inhibition of the Thermal Polymerization of Styrene by p-Benzoquinone

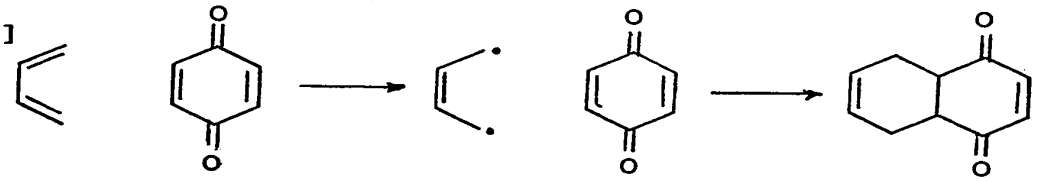
INTRODUCTION

The inhibition of the thermal polymerization of styrene by quinones has been extensively studied without any positive identification of the mechanism of the chemical reaction underlying this process. Breitenbach and Breitenbach (123) observed that in the thermal polymerization of styrene, in the presence of various quinones, low molecular weight products were formed. When using p-benzoquinone they found that hydroquinone was also formed. The nature of the low molecular weight products was investigated by Kern and Feuerstein (124) and later their work was repeated by Melville and Watson (125). In both cases the authors isolated a compound corresponding to an adduct of two molecules of styrene to one molecule of quinone. The structure and composition of the adduct was obtained only from its elemental analysis and a molecular weight determination. Both authors postulate a mechanism involving diradical formation from two molecules of styrene, followed by condensation with a molecule of p-benzoquinone, eqs. [70] and [71].

[70] 

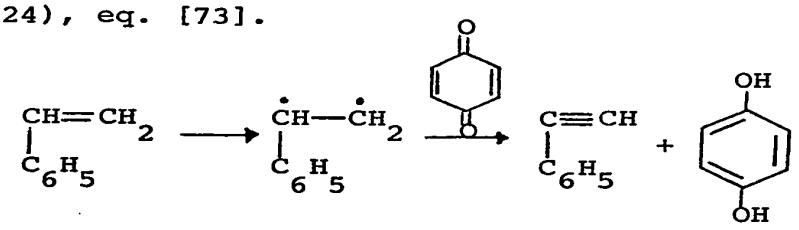
[71] 

The structures for the adduct were suggested assuming a bimolecular initiation step for the polymerization involving diradical formation. This formation of diradicals has since been shown to be incorrect (6,7,8,9). An analogy between the formation of the adducts in eqs. [70] and [71] and the Diels-Alder reaction, was made by Melville and Watson. However, they assume that the Diels-Alder reaction proceeds via an activated diene (diradical) (126) as in eq. [72].

[72] 

Corral (127) has investigated the reactions of styrene and its derivatives with substituted quinones and has isolated substituted 1,4-phenanthraquinones and dibenzanthraquinones as the products. These are formed by a normal Diels-Alder reaction between a styrene and a benzoquinone molecule, either in a 1:1 molecular ratio or a 1:2 molecular ratio. The adducts are dehydrogenated to the aromatic systems in the presence of the reacting quinone. He suggested that the adduct isolated by the above authors is either 1,2,5,6-dibenzanthraquinone or 1,2,7,8-dibenzanthraquinone, by analogy with the Diels-Alder products observed in his work. He also points out that the reported melting point of 1,2,5,6-dibenzanthraquinone (128) matches the melting point of the isolated adduct from the quinone inhibited thermal polymerization of styrene.

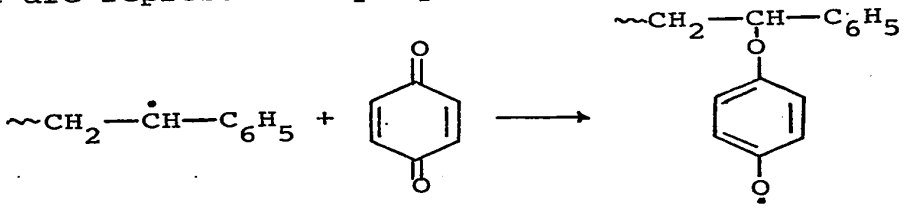
The absence of phenylacetylene in the products from the quinone inhibited polymerizations was taken as evidence against hydroquinone formation occurring by a direct abstraction of hydrogen atoms from an activated styrene molecule (123,124), eq. [73].

[73] 

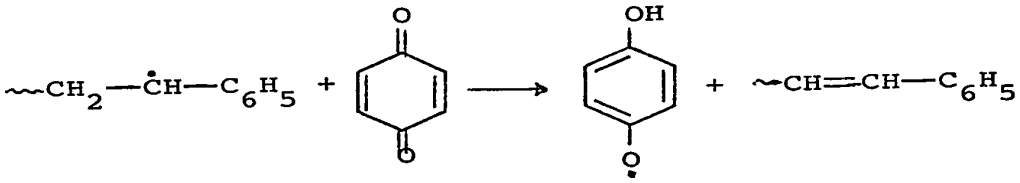
It was also shown (125) that hydroquinone has no retarding or inhibiting action during styrene polymerization.

The inhibition products derived from initiated polymerizations have also been extensively studied. Cohen (129, 130) observed induction periods in the styrene-benzoyl-peroxide-p-benzoquinone system. He concluded that p-benzoquinone inhibits mainly by stopping the growth of two chain radicals. Hydrogen abstraction from a polymer chain may also take place and a 1:1 stoichiometry was also argued. These are represented by eqs. [74] and [75].

[74]



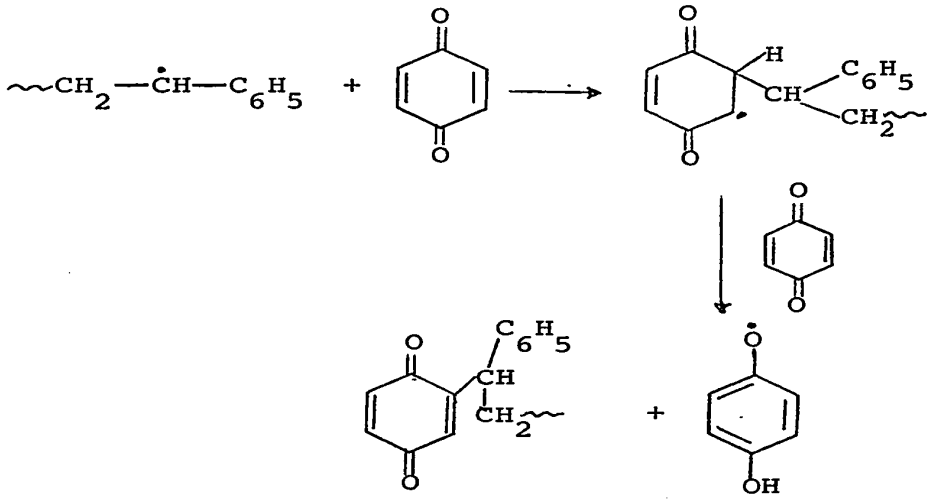
[75]



Price and Read (131,132), however, suggested an initial polymer radical attack on the aromatic nucleus, eq. [76]. This mechanism was prompted by the work of

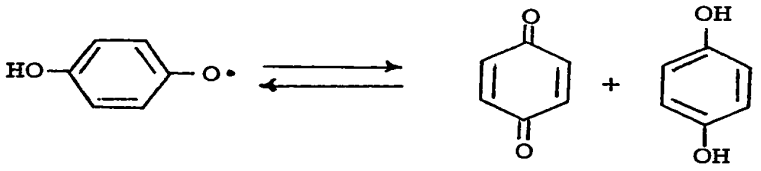
Fieser on alkylation of p-quinones with acyl peroxides (133).

[76]



Further disproportion between two hydroquinone radicals would give hydroquinone, eq. [77].

[77]



The precise radical/quinone stoichiometry is therefore dependant upon the further reaction of the inhibitor

radicals produced in eqs. [74], [75] and [76].

With the use of p-benzoquinone-^{14}C and AIBN-^{14}C in the polymerization of styrene at 60°C it has been confirmed (134) that about 90% of the quinone was incorporated into the polymer during the induction period. There was considerable polymer-radical-quinone interaction and only a small amount of direct reaction between the inhibitor and the primary cyanoisopropyl radicals. The loss of activity after treatment of the polymer formed from a styrene-p-benzoquinone-^{14}C-AIBN system with acetic acid/trifluoroacetic anhydride was taken as evidence for the existence of ether linkages of the type shown in eq. [74] and that the limited growth of the rather unreactive radicals produced occurred by addition of monomer or a polymer chain. On the average there were two molecules of quinone consumed per polymer molecule during the inhibition period, and the preferred termination mechanism is given in eq. [78].

[78] $$R{-}O{-}C_6H_4{-}O{-}R\bullet \;+\; \bullet O{-}C_6H_4{-}O{-}R \longrightarrow R{-}O{-}C_6H_4{-}O{-}ROC_6H_4O{-}R$$

R = polymer chain

The ratio of the rate of consumption of benzoquinone, R_{BZQ}, compared to the rate of formation of initiating radicals produced in the thermal polymerization of styrene, ($R_{i,th}$), has been found to be greater than unity. Mayo and Gregg (135) found that 16-17 molecules of p-benzoquinone were consumed per polymer chain radical produced at 100°, while Russell and Tobolsky (3) report a value of $R_{BZQ}/R_{i,th}$ = 21 at the same temperature. The former authors suggest that a considerable amount of copolymerization must be taking place between the styrene and quinone. However, Tudos (136) has shown that no copolymerization takes place between p-benzoquinone and styrene in the absence of initiator at 90 and 105°, but some does take place at higher temperatures. A more recent study (137) shows that styrene and benzoquinone initiated at 40° and 70° gives no evidence for copolymerization. Low yields of quinhydrone were, however, isolated. The p-benzoquinone must be being consumed in some other reaction than trapping radicals or radical chains. All of the mechanisms proposed for the inhibiting action of p-benzoquinone have dealt with the trapping of radical products. In the case of the thermal polymerization, a reinvestigation of the inhibition products in the light of the termolecular initiation sequence given by eqs. [3] and [4] of Chapter I, and the inhibiting mechanism of DPPH

proposed in Chapter II, might yield more information about the possible 2:1 adduct between styrene and quinone.

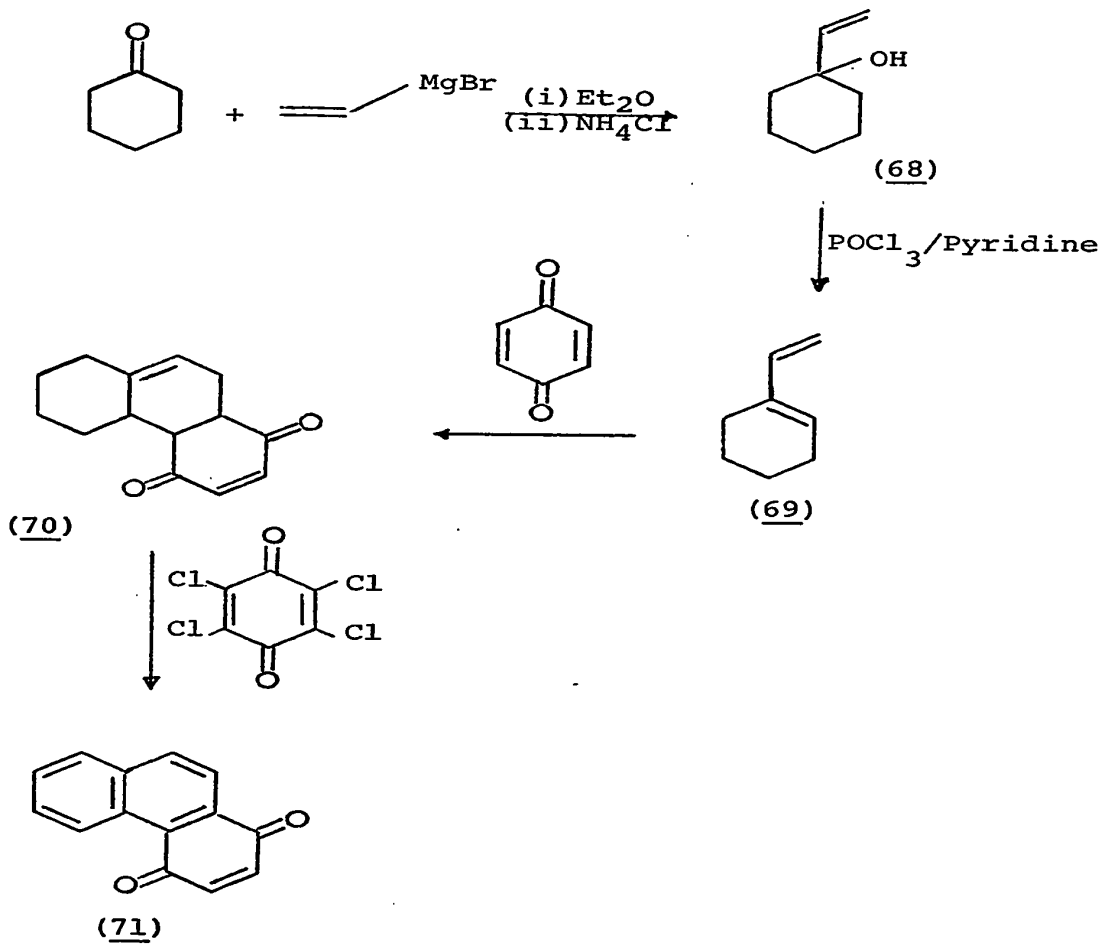
RESULTS

Preparation of authentic adducts expected from the reaction between styrene and p-benzoquinone

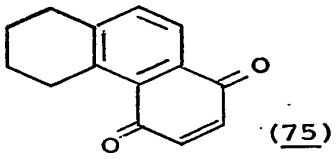
1,4-Phenanthraquinone 71

The preparation of 71 is outlined in Scheme 18. 1-Vinylcyclohexanol (68) was prepared by the Grignard reaction between vinylmagnesium chloride and cyclohexanone. After work up with saturated ammonium chloride there was obtained 68% of 68. The nmr and infrared spectra were consistent with the structure of the product. 68 was dehydrated to 69 in a 60% yield using phosphorous oxychloride in pyridine solution. The physical properties matched those reported in the literature. The Diels-Alder reaction between 69 and p-benzoquinone was carried out according to the method of Robins and Walker (140). 69 was used in excess so that only the monoadduct was obtained. The monoadduct 70 was obtained in an 81% yield based on p-benzoquinone. The nmr and infrared spectra were consistent with the structure of the compound and the melting point matched that reported in the literature. In the above procedure the p-benzoquinone is added in small portions over a period of 30 minutes to a methanolic

Scheme 18

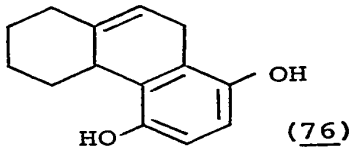


solution of 69. In an alternative procedure (145) attempted, equimolar proportions of p-benzoquinone and 69 were heated together in refluxing benzene for 48 hours. A mixture of 75 and 76,



(75)

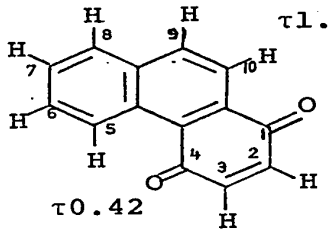
mp 115.5-116.5°



(76)

mp 178-179°

was obtained in approximately equal proportions. Identification was made on the basis of nmr and infrared spectra. The total yield of 75 and 76 was, however, only 15% and this procedure was abandoned. Dehydrogenation of 70 to 1,4-phenanthraquinone (71) was carried out using four equivalents of chloranil. (71) was obtained as brilliantly yellow needles from benzene-petroleum ether. The infrared spectrum showed a doublet for the carbonyl stretching at 1690 and 1680 cm^{-1}. The nmr spectrum ($CDCl_3$) showed peaks at τ0.42 (m), τ1.87 (s), τ2.75 (m), τ3.07 (s) in the ratio 1 : 2 : 3.1 : 2, required 1 : 2 : 3 : 2. The proton assignments are shown in the following structure of the compound.

τ2.25  τ1.87

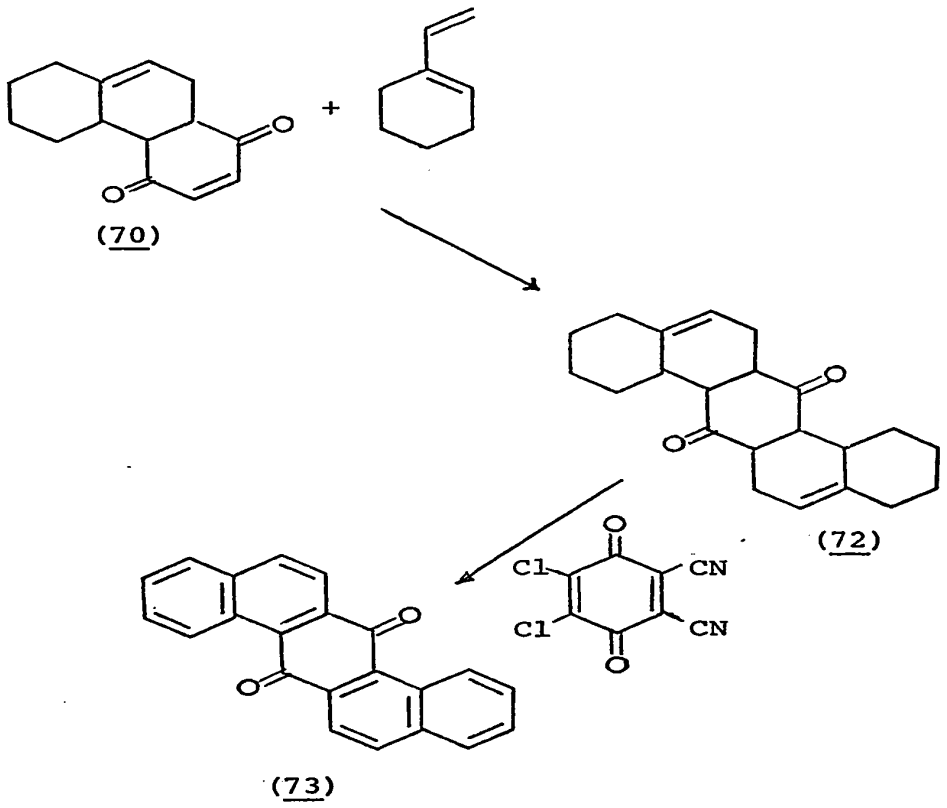
τ0.42 τ3.07 (71)

The chemical shifts of the protons at C_9 and C_{10} must be the same as they show up as a singlet at τ1.87. The proton at the C_5 position is subject to a deshielding effect by both the adjacent phenyl ring and the carbonyl group and appears at low field τ0.42.

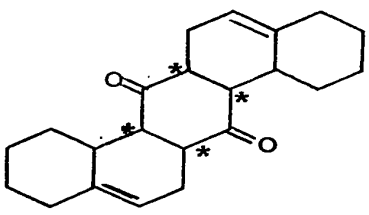
Dibenz-[a,h]-anthra-9,10-quinone 73

The preparation of 73 is outlined in Scheme 19. The Diels-Alder reaction between 69 and 70 was carried out in the same manner as described for the preparation of the monoadduct 70 except 69 now replaced p-benzoquinone. On standing for 48 hours at room temperature a crystalline solid had precipitated from solution and was filtered at the pump. This compound, 72, melted at 205-206° in agreement with the melting point reported in the literature for

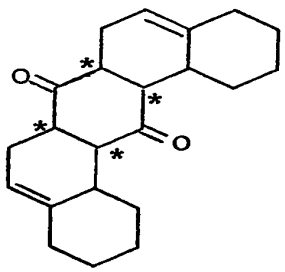
Scheme 19



1,2,5,6-bis(tetramethylene)-1,4,5,8,11,12,13,14-octahydro-9,10-anthraquinone (140). 72 was found to be insoluble in most common solvents and no nmr spectrum could be obtained. The infrared spectrum (KBr disc) showed absorptions at 795 cm^{-1} and 1630 cm^{-1} (>C=C-H, C-H bending and C=C stretching frequencies) and 1710 cm^{-1} (C=O stretching). Cooling of the filtrate yielded a second compound, 77, which formed white needles mp 162-164° after recrystallization from benzene. 77 was soluble in chloroform and benzene and the nmr spectrum ($CDCl_3$) showed a multiplet at τ4.62 and a broad band of multiplets at τ6.65 - τ9.21 in the ratio 1 : 13.1. The infrared spectrum (KBr disc) matched that of 72 almost exactly. From the nmr and infrared spectra 72 and 77 were concluded to be geometric isomers, represented by the "S" and "C" forms:



"S" 72



"C" 77

The ring system present in 72 has been established by hydrogenation of 72 with platinum black to yield dibenz-[a,h]-anthracene (128). Only the "S" isomer was used in further reactions. Models of these compounds show that the junctions * can only be cis-anti-cis in both isomers. In both cases the syn form is sterically hindered. Further evidence for these assignments may be found in the solubility characteristics of 72 and 77. It has been found for the dehydrogenated adducts dibenz[a,j]anthra-9,10-quinone and dibenz[a,h]anthra-9,10-quinone that the former compound, i.e., the "C" form, is the more soluble in common solvents. This same observation may be applied to the "S" and "C" forms of the partially saturated adducts 72 and 77.

Backer and Van der Bij (142) had previously prepared 72 from the Diels-Alder reaction between 69 and p-benzoquinone mixed in a 2:1 molecular ratio. However, they report no finding of the isomer 77. When their procedure was used 72 was isolated in only a 10% yield, although the authors report a figure of 20%.

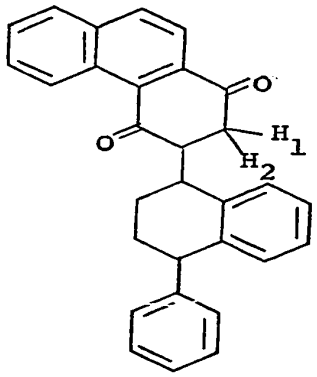
72 was dehydrogenated to 73 in a 65% yield using 2,3-dicyano-5,6-dichloro-p-benzoquinone. The mp 248.5-250° agreed with that reported in the literature (128). The compound was insoluble in almost all the common solvents and an nmr spectrum could not be obtained. The infrared

spectrum (KBr disc) showed a doublet carbonyl absorption at 1680 and 1690 cm^{-1}.

Inhibited polymerization by p-benzoquinone

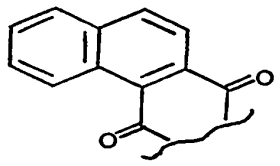
Freshly distilled styrene was heated under reflux at 140° in the presence of a 10% by weight amount of p-benzoquinone. On cooling the reaction mixture, there was obtained an orange colored filtrate and a red-orange residue. The filtrate and the residue were worked up by separate procedures.

The unreacted styrene was removed from the filtrate to yield a sticky red residue. A column chromatography of the residue showed that it consisted of a dimer fraction, containing cis- and trans-1,2-diphenylcyclobutanes, (3) and (4), 1-phenyltetralin (13), and 1-phenylnaphthalene (14), and fractions containing unreacted p-benzoquinone and the products from a Diels-Alder reaction between styrene and p-benzoquinone. The total yield of these materials was 1.08 g. The latter compounds were identified as 1,4-phenanthraquinone (71), 305 mg, and 1,2,5,6-dibenz-9,10-anthraquinone (73), 14 mg, from comparison of melting points, infrared spectra and in the case of (71), from its nmr spectrum. A compound with a nmr spectrum that seemed to correspond to the formula below was also isolated. This appeared as

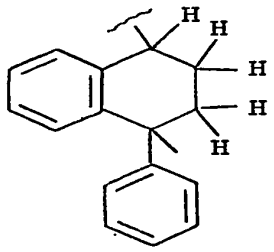


(74)

the first quinone adduct in the elution sequence from the chromatography. Attempts were made to purify the compound using preparative tlc techniques, but it remained as a sticky solid. The nmr spectrum showed peaks at τ0.50 (m), τ2.00 (m), τ2.35 (m), τ2.75 (m), τ5.35 broad multiplet, τ5.80 broad multiplet, τ7.90 broad multiplet, τ8.49 (d, $\underline{J}$ = 7 cps), in the approximate ratio 1 : 2 : 3 : 12 : 0.8 : 0.9 : 4 : 1.8. The peaks at τ0.50, τ2.00 and τ2.35 were characteristic of aromatic ring system in the 1,4-phenanthraquinone molecule



while the aromatic peak at τ2.75 and the peaks at τ5.35, τ5.80 and τ7.90 are characteristic of the 1-phenyltetralyl system.



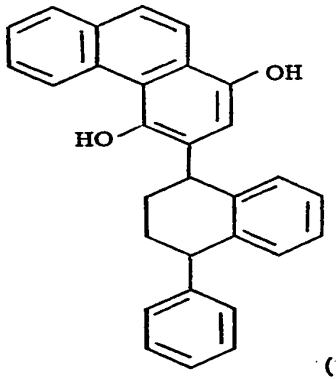
The presence of the doublet at τ8.45 could only be rationalized as a methylene doublet, possibly due to H_1 and H_2 in structure 74. However the unexpectedly high field position of these protons, since they are adjacent to a carbonyl group, cannot be explained. The mass spectrum showed a weak parent peak at m/e 414 and other peaks at m/e 312, 297 and 295. The parent peak is two units less than needed to correspond to the above structure and the cracking pattern does not fit the obvious sites of cleavage in the structure. We can therefore only speculate as to the possible types of structure for the adduct. An almost identical nmr spectrum was obtained for a similar fraction isolated from a column chromatography of a second inhibited polymerization.

The initial reaction residue was taken up in benzene, leaving 1.0 g of an insoluble material, identified as hydroquinone from a comparison of its melting point and spectral

characteristics with the authentic material. The benzene solution was diluted with twice its volume of methanol to give polystyrene, identified from its infrared and nmr spectra which matched those reported in the literature (144). Concentration of the benzene-methanol solution only gave more polymer, which must have incorporated a small amount of benzoquinone since the infrared spectrum showed a weak carbonyl absorption at 1710 cm^{-1}.

Several inhibited polymerizations were conducted using the same conditions as above, but using the work-up procedures reported by Kern and Feuerstein (124) and Melville and Watson (125). Both of these procedures failed to yield the unidentified 2:1 adduct of styrene and benzoquinone which they reported. However, using the procedure of Kern and Feuerstein, where the unreacted styrene was distilled from the reaction flask, the residue taken up in ether and extracted with 2N NaOH, yielded, after neutralization of the basic extracts followed by chromatography, a compound with an nmr spectrum similar to (74) isolated above. The notable differences in the nmr spectrum were the absence of the doublet at τ8.45 and the multiplet at τ0.42. There was also the addition of an -OH peak (loss on D_2O exchange) and a peak at τ3.35. The latter corresponds to the absorption of the aromatic protons observed for hydroquinone.

Treatment of 74 with base could give 78.



(78)

These however are only tentative assignments, made purely on the basis of nmr spectra and are not proof for the structures of these compounds.

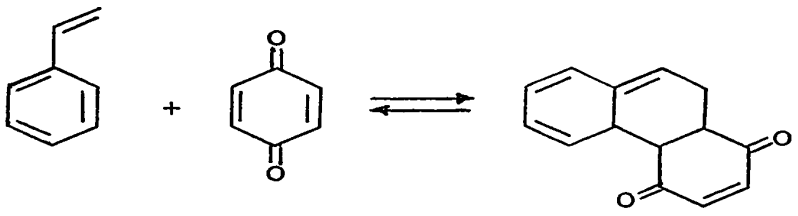
Glc analysis of the dimeric fraction made using a column containing 10% Apiezon L on 60/80 Firebrick, showed cis- and trans-1,2-diphenylcyclobutanes, (3) and (4), 1-phenyltetralin (13), and 1-phenylnaphthalene (14). The compounds were identified from their retention times and by mixed injections with authentic samples. No 1-phenyl-1,2-dihydronaphthalene could be observed under the conditions used. The composition of the dimer fraction, measured from the respective peak areas is given below.

Compound	% composition	
3	22.0	
4	61.9	3/4 = 2.81
13	7.0	
14	9.1	

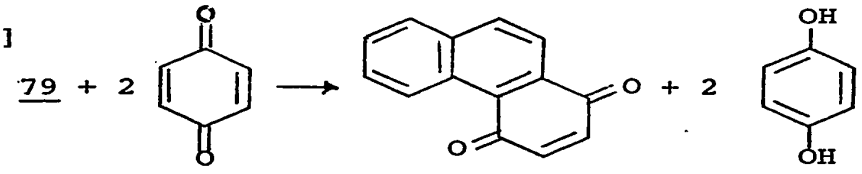
DISCUSSION

Formation of styrene-benzoquinone adducts

The formation of 71 and 73, isolated from the p-benzoquinone inhibited thermal polymerization of styrene, can only be rationalized as occurring by way of a Diels-Alder reaction between styrene and p-benzoquinone eqs. [79] to [82].

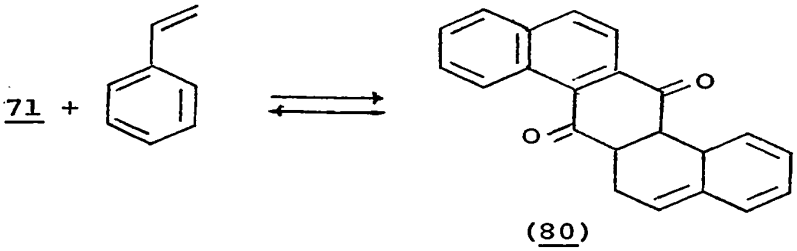
[79] 

(79)

[80] 

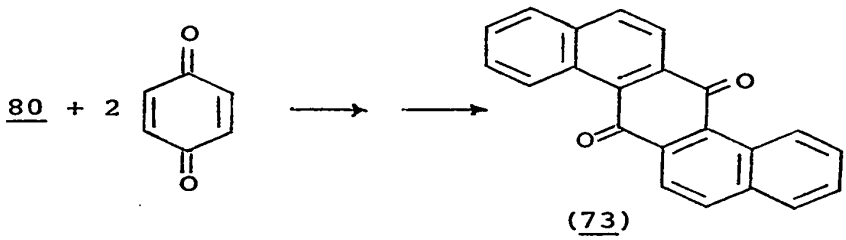
(71)

[81]



(80)

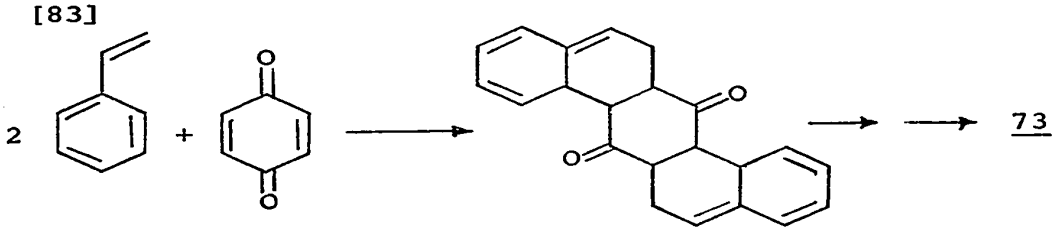
[82]



(73)

The mechanism for formation of 71 from 79, eq. [80], is only represented as a series of hydrogen abstraction reactions by p-benzoquinone and may or may not give rise to intermediate products which will undergo further chemical reactions. This same postulate applies to eq.[82]. An alternative route to 73 could be the direct formation of a 2:1 adduct of styrene and p-benzoquinone followed by dehydrogenation, eq. [83]. The formation of 71 and 73 from the initial Diels-Alder adducts may therefore be

[83]



(81)

much more complicated than presented here.

The adduct 73 must correspond to the 2:1 adduct observed by Kern and Feuerstein, and Melville and Watson, as the melting points are exactly the same. It would be highly fortuitous if the compound isolated here was different from that isolated by the above workers, and yet have exactly the same melting point.

Melville and Watson have commented upon the apparently high yield of 73 isolated by Kern and Feuerstein from their polymerization reaction. Although no figures are given for the yield of 73 by Kern and Feuerstein, they conduct a subsequent degradation study employing 7.5 g of their adduct. Melville and Watson report no yield for the adduct they isolated but say that it is very small. This work

confirms the findings of Melville and Watson. Only 14 mg of 73 was isolated using the techniques described here, although the polymerization conditions were copied from those of Kern and Feuerstein. Experimental observations indicate that the yield of 73 would not be expected to be greater than the yield of monoadduct 71. In the reaction of p-benzoquinone with 1-vinylcyclohexene the monoadduct was formed in 81% yield. In contrast, the reaction between two equivalents of 1-vinylcyclohexene and one equivalent of p-benzoquinone gave the diadduct in only a 16% yield. A similar yield has been obtained by other workers (142). The proportions of mono and diadduct observed in the products of the inhibition of the thermal polymerization of styrene by p-benzoquinone are in agreement with the above experiments.

An estimate of the amount of p-benzoquinone consumed in the adduct formation can be obtained from the amount of 71, 73 and 74 isolated. The diadduct 73 will contain 5 mg and the monoadduct 150 mg of p-benzoquinone. In addition, the monoadduct requires two equivalents of p-benzoquinone to dehydrogenate it to the isolated quinone 71, and the diadduct will require four equivalents of p-benzoquinone to give 73. This will account for a further 320 mg of p-benzoquinone. The unknown fraction 2 may be estimated

as containing a further 15 mg and requires 30 mg of p-benzoquinone for dehydrogenation, giving a total of 45 mg. The amount of unreacted p-benzoquinone recovered was 419 mg. Since 5.4 g of p-benzoquinone was added, we can estimate that of the 5.0 g that reacted, 10% of the quinone is consumed in Diels-Alder reactions and dehydrogenation reactions of the Diels-Alder adducts. The amount of hydroquinone formed (1.0 g) is in excess of that required from the dehydrogenation reaction of the Diels-Alder adducts, although other dehydrogenation reactions must be taking place. These may include dehydrogenation of polymer chains and dehydrogenation of any saturated dimeric adducts that are formed from the thermal initiation sequence of styrene. Evidence for dehydrogenation of part of the dimer fraction is given later.

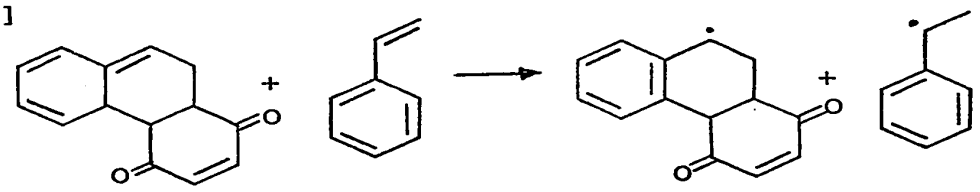
Possible Inhibiting Mechanism

The competing reactions, i.e., a Diels-Alder reaction between styrene and p-benzoquinone and the inhibiting action of p-benzoquinone, both consume p-benzoquinone. Russell and Tobolsky (3) and Mayo and Gregg (135) both found that the rate of disappearance of p-benzoquinone was many times greater than the calculated rate of formation of radicals in the absence of this inhibitor. The inhibiting action of

p-benzoquinone, as measured by its rate of disappearance, must be more complex than simple radical capture. This postulate is supported by the isolation from the inhibited polymerization of styrene of 71 and 73 which can only be formed by a Diels-Alder reaction between styrene and p-benzoquinone followed by dehydrogenation.

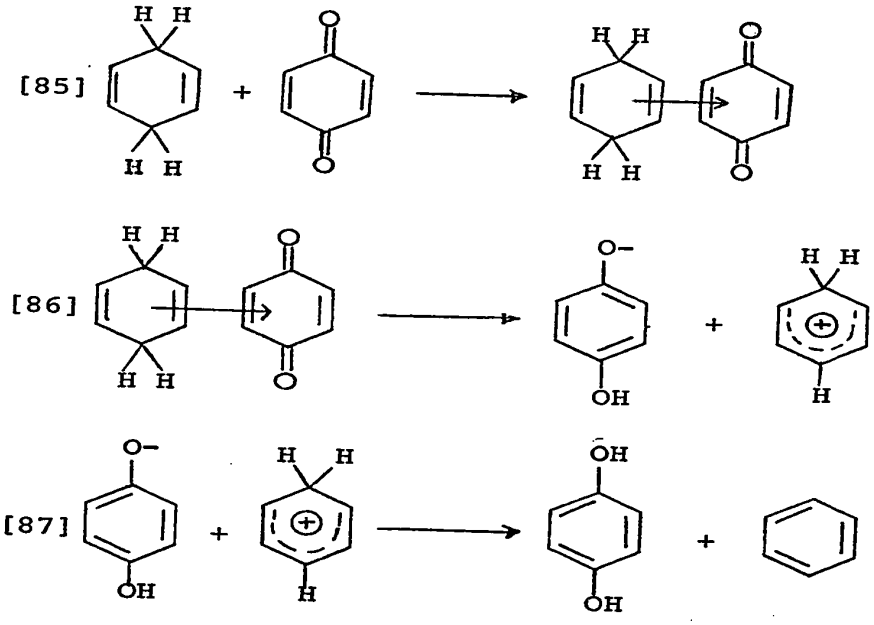
The initiating sequence for the thermal polymerization of styrene is given in eqs. [3] and [4]. In the presence of p-benzoquinone, a much more reactive dienophile than styrene, it might be expected that it will take the place of a styrene molecule in eq. [3]. This is given by eq. [79] as part of the pathway to formation of 1,4-phenanthraquinone (71). The initial adduct 79 is then analagous to the adduct 1 proposed for the pure thermal polymerization of styrene, eq. [3]. 79 must now react with p-benzoquinone in a series of dehydrogenation reactions to form the isolated quinone 71. An alternative reaction, involving hydrogen transfer to a second molecule of styrene, eq. [84],

[84]

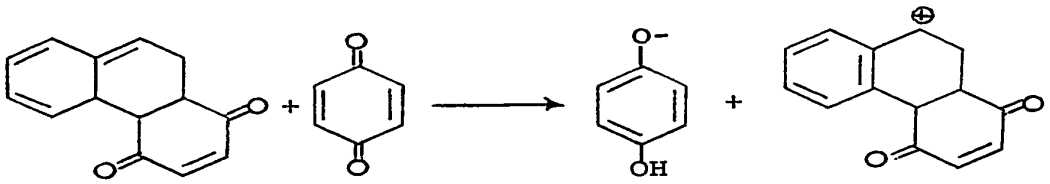


would produce a pair of initiating radicals similar to those in the thermal initiation sequence for styrene, eq. [4]. However, no evidence was found for this kind of reaction.

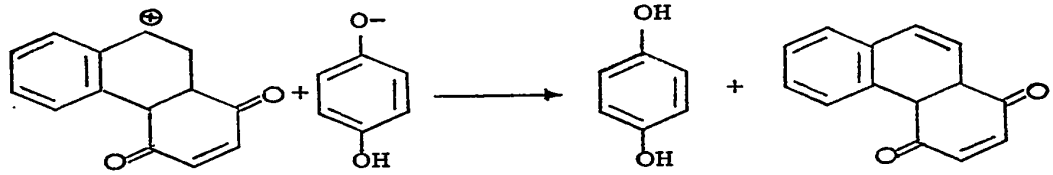
It is generally agreed that the mechanism of hydrogen abstraction by quinones proceeds by an ionic pathway (146). An example of the reaction mechanism is outlined in eqs. [85] to [87] for 1,4-hexadiene.

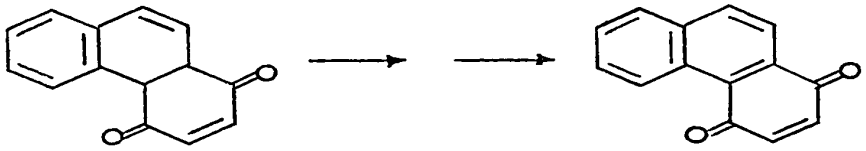


A similar pathway may be proposed for the conversion of 79 to 71, eqs. [88] to [90].

[88] 

(79)

[89] 

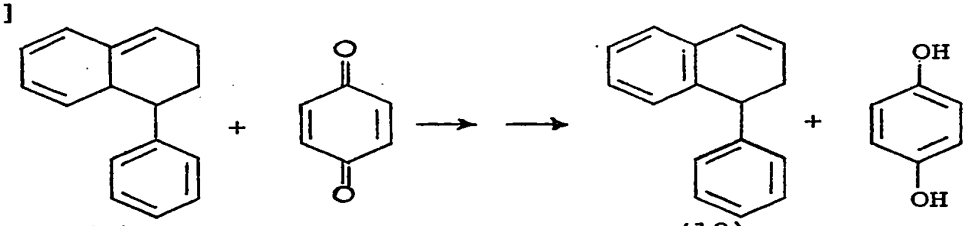
[90] 

(71)

This mechanism rules out any radical formation between the reaction of 79 and p-benzoquinone. The pair of ions formed in eq. [88] would be expected to further react as in eq. [89] rather than act as initiators for any ionic polymerization. Ionic polymerizations are characterized by very fast rates at low temperatures and rapid polymerization is not observed in the present system.

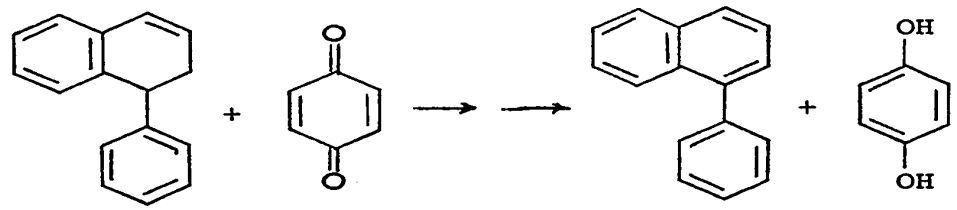
This same mechanism may be taking place with any adduct 1 that is formed yielding 1-phenylnaphthalene as the final product, eqs.[91] and [92].

[91]



(1) (18)

[92]

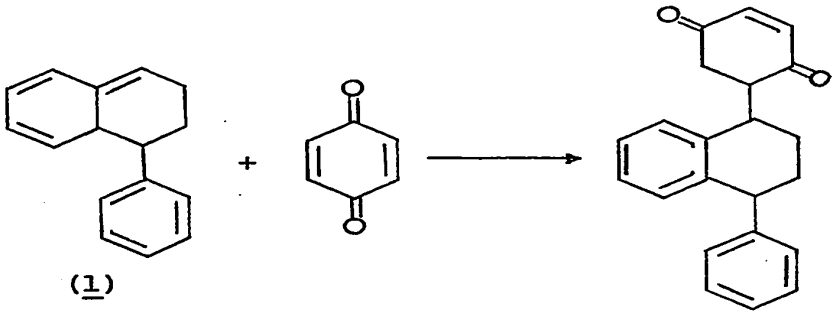


(18) (14)

The absence of (18) in the dimer fraction is not surprising since it will be dehydrogenated in the presence of the excess p-benzoquinone to yield (14) and hydroquinone.

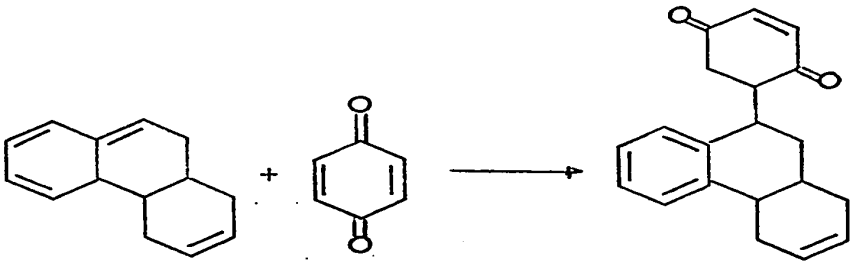
An alternative reaction of 79 or 1 with p-benzoquinone involves an "ene" addition as in eqs. [93] and [94].

[93]



(1)

[94]

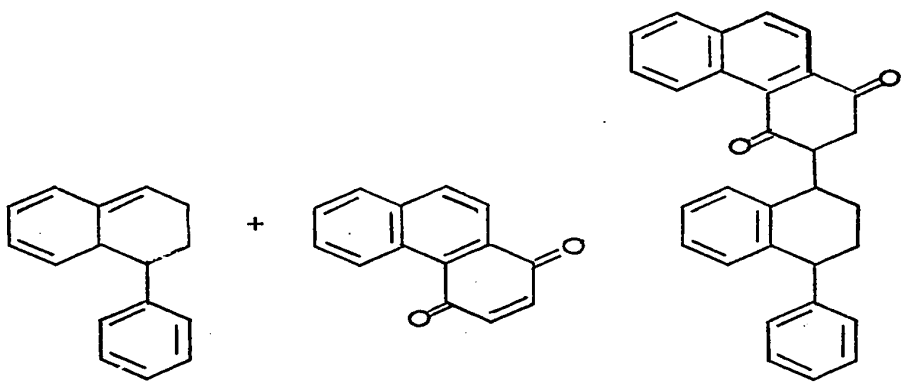


(79)

An "ene" addition of styrene to 1 has been propcsed by Kirchner and Bucholz (16) to explain the formation of trimeric products in the thermal polymerization of styrene.

Although no products corresponding to these structures were isolated, a compound tentatively identified as 74 from its nmr spectrum, could have been formed by an "ene" addition between 1 and 71, eq. [95].

[95]



(1) (71) (74)

The order of elution by chloroform from silica gel, was found to be 73, 71 and p-benzoquinone, i.e., in order of decreasing substitution of the double bonds. The adduct 74 would therefore be eluted before 73, as observed experimentally.

The formation of considerable amounts of polymer in the presence of unreacted p-benzoquinone indicates that p-benzoquinone is not an efficient inhibitor at elevated temperatures. A weak carbonyl absorption in the infrared spectrum of the polymer possibly indicates some incorporation of p-benzoquinone which must be linked at a carbon, and not at the carbonyl oxygen. The nature of the p-benzoquinone incorporation was not studied any further.

Analysis of the dimer fraction

The analysis of the dimer fraction shows that the ratio of cis-3 to trans-4 is 2.8:1, in agreement with the value reported in Chapter II for ratio in the absence of inhibitors and the proposal that they are formed by a separate mechanism (Scheme 2, Chapter I). Thus the relative proportions of 3 and 4 isolated in the thermal polymerization of styrene are not affected by the addition of p-benzoquinone, as previously reported by Kirchner and Bucholz (16). The presence of 1-phenyltetralin may be a result of an isomerization of 1 by benzoquinone or hydroquinone. Alternatively, it could arise from a radical disproportion reaction between the two initiating radicals from the purely thermal initiation sequence, eq. [31].

Although the above reactions, eqs. [88] to [95] represent a possible mechanism for inhibition of the initiation sequence by benzoquinone in styrene, since they remove (1) as inactive products, the total inhibiting action of p-benzoquinone seems to be highly complex and requires further investigation.

EXPERIMENTAL

1-Vinylcyclohexanol (68)

To 375 ml (1.0 moles) of vinyl magnesium chloride solution (Alfa Inorganics, 2.65 M in tetrahydrofuran) contained in a two-litre round-bottomed flask was added 84.0 g (0.85 mole) cyclohexanone in 200 ml dry tetrahydrofuran. The addition was carried out at a rate that kept the contents at reflux temperature. At the end of the addition the flask was heated for a further one hour to ensure completion of the reaction. The flask and its contents were cooled and worked up by the addition of 200 ml saturated ammonium chloride solution. The clear yellow organic layer was decanted and the salts washed with two 50 ml portions of tetrahydrofuran. The combined organic portions were evaporated at reduced pressure to yield 103 g of viscous orange liquid. Distillation at reduced pressure gave 68 g (68%) of a colorless liquid bp 68-69° (14.5 mm), $n_D^{25} = 1.4746$; lit. bp 61° (13 mm), $n_D^{16} = 1.4801$ (138). The infrared spectrum (neat) showed an absence of C=O absorption and a strong OH band at 3400 cm^{-1}. The nmr spectrum (CCl_4) showed absorptions at τ4.05 (doublet of doublets, J = 11 cps, J = 18 cps), τ4.32 (broad singlet), τ5.12 (doublet of doublets, J = 18 cps, J = 11 cps), τ7.90 (m) and τ8.35 (m), ratio

1 : 1 : 2 : 8.5, required 1 : 1 : 2 : 8.

1-Vinylcyclohexene (69)

To a solution of 10 g (0.08 moles) 68 in 15 ml dry pyridine was added 5.5 ml phosphorous oxychloride in 5.5 ml dry pyridine. Addition was made at such a rate that kept the contents at reflux temperature. After the addition was complete the solution was heated on a steam bath for one hour, cooled, poured on to 150 g crushed ice and extracted with two 100 ml portions of pentane. The pentane extracts were dried over anhydrous magnesium sulfate and the solvent removed by evaporation. The pale yellow liquid was distilled to yield 4.8 g (60%) of a colorless liquid bp 142° (704 mm), n_D^{28} = 1.4937; lit. bp 145-146° at 760 mm, n_D^{16} = 1.5013 (139). The infrared spectrum (neat) showed an absence of OH band. The nmr spectrum (CCl_4) showed peaks at τ3.73 (doublet of doublets, $\underline{J}$ = 10.5 cps, $\underline{J}$ = 17.5 cps), τ4.35 (broad singlet), τ5.05 (doublet of doublets, $\underline{J}$ = 17.5 cps, $\underline{J}$ = 2 cps), overlapping τ5.21 (doublet of doublets, $\underline{J}$ = 10.5 cps, $\underline{J}$ = 2 cps), τ7.90 and τ8.35 overlapping multiplets, ratio 1 : 1 : 2 : 9, required 1 : 1 : 2 : 9.

$\Delta^{2,9(14)}$Decahydro-1,4-diketophenanthrene (70)

The method employed was due to Robins and Walker (140).

p-Benzoquinone, 3 g, (0.03 mole) was added in small portions during 30 minutes to a well stirred solution of 5 g, (0.05 mole) 69 in 25 ml methanol, each portion being allowed to dissolve before another was added. After a further 30 minutes stirring, the reaction mixture was left at room temperature for four hours, during which time a crystalline solid began to separate. The solution was diluted with 5 ml of water and cooled to -5°C overnight. Filtration afforded large prisms of the product, 5.0 g (81% based on p-benzoquinone). Recrystallization from petroleum ether yielded 4.4 g of large white needles mp 84-85°; lit. mp 87-88° (140). The infrared spectrum (CCl_4) showed a C=O absorption at 1670 cm^{-1}. The nmr spectrum (CCl_4) showed peaks at τ3.37 (s), τ4.67 (m) τ6.55 - τ9.25 (broad band of multiplets) in the ratio 2 : 1 : 13.2, required 2 : 1 : 13.

1,4-Phenanthraquinone (71)

To 1.5 g of 70 dissolved in 60 ml of chlorobenzene, was added 14.8 g of chloranil (four equivalents) and the mixture heated under reflux for 72 hours. On cooling, the total mixture set to a crystalline solid absorbing all the solvent. The solvent was removed under vacuum and the residue taken up in 250 ml boiling ligroine. The insoluble 1,4-dihydroxy-2,3,5,6-tetrachlorobenzene was removed by

filtration and the filtrate cooled to give 0.70 g (50%) yellow crystals mp 146-149°. Recrystallization from benzene-petroleum ether, (1:4) after decolorizing with Norit, yielded 0.560 g small brilliantly yellow needles mp 152-153°; lit. mp 153° (141). The infrared spectrum ($CHCl_3$) showed absorption at 3040 cm^{-1} (aromatic C-H), 1690 and 1680 cm^{-1} C=O. The nmr spectrum ($CDCl_3$) showed peaks at τ0.42 (m), τ1.87 (s), τ2.25 (m), τ3.07 (s) in the ratio 1 : 2 : 3.1 : 2, required 1 : 2 : 3 : 2.

1,2,5,6-bis-Tetramethylene-1,4,5,8,11,12,13,14-octahydro-9,10-anthraquinone (72)

To 5.0 g (0.023 mole) 69 dissolved in 25 ml methanol was added 1.9 g (0.018 mole) 70 in small portions, allowing each portion to dissolve before adding another. After 48 hours at room temperature a white crystalline precipitate had formed and was filtered at the pump. The product (0.35 g, 16.5% based on 70) had a mp 204-206°. Recrystallization from benzene-methanol, (1:1), gave fine white needles mp 205-206°; lit. mp 202-204° (142). The compound was insoluble in all the common nmr solvents. The infrared spectrum (KBr disc) showed C=O, 1710 cm^{-1} and C=C 1630 cm^{-1}, 795 cm^{-1}. Cooling of the filtrate from the reaction mixture gave more white crystals mp 153-158°. Recrystallization from benzene

gave large white needles mp 162-164°. These were soluble in chloroform and the nmr spectrum ($CDCl_3$) showed peaks at τ4.62 (m), τ6.65 - τ9.21 (broad band of multiplets) in the ratio 1 : 13.1, required 1 : 13. The compound was not characterized any further. The two compounds were assumed to be geometric isomers.

Dibenz-[a,h]-anthra-9,10-quinone (73)

To 200 mg of 72 in 15 ml chlorobenzene was added 1.22 g (four equivalents) of 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ) and the total mixture heated under reflux for 36 hours. The mixture was cooled and the solvent removed under vacuum. The residue was taken up in 50 ml boiling benzene and filtered hot to remove the grey residue of 2,3-dicyano-5,6-dichloro-1,4-dihydroxy-benzene. The filtrate was concentrated to 25 ml and passed through a 8" x 1/2" column of alumina, using 200 ml benzene as the eluting agent. Evaporation of the benzene yielded 130 mg (65%) of a bright yellow solid mp 247-250°. Recrystallization from benzene gave beautiful yellow-orange needles mp 248.5-250°; lit. mp 248-249° (128). The infrared spectrum (KBr disc) showed a carbonyl doublet absorption at 1680 and 1690 cm^{-1}.

Inhibited Polymerizations

The styrene used in the polymerizations was purified as described in the experimental of Chapter I. Benzoquinone (Aldrich Chemical Co. Inc.) was used directly without purification. The procedure followed was that due to Kern and Feuerstein (124). Into a three-necked flask, fitted with a nitrogen inlet tube extending below the surface of the added liquid, was weighed 50.2 g (0.50 mole) styrene. Nitrogen was bubbled through the styrene for three hours to displace as much oxygen as possible. At the end of this time the flask was fitted with a reflux condenser and 5.4 g (0.05 mole) p-benzoquinone was carefully added. The solution turned a deep red-brown color and was heated under reflux at 145° in an atmosphere of dry nitrogen for nine hours. Cooling overnight yielded a dark-red residue which settled on the sides and bottom of the flask and a pale orange solution. The solution and the residue were worked up by separate procedures.

The orange solution was decanted and distilled at reduced pressure on a steam bath to yield 30.5 g (63%) of unreacted styrene and a brown-red residue. The residue was dissolved in chloroform and chromatographed on a 3 cm x 6 cm column packed with 160 g silica gel using chloroform as the eluent. The eluent was collected in 20 ml portions, analyzed

by tlc, using silica gel plates with chloroform as the eluent, and the fractions containing the same product were combined. Five combined fractions were obtained and were analyzed to contain:

Fraction 1. (226 mg) cis- and trans-1,2-diphenylcyclobutanes, (3) and (4), 1-phenyltetralin (13) and 1-phenylnaphthalene (14). The compounds were analyzed by glc on a 10' x 1/8" column of Apiezon L on 60/80 Firebrick. The column temperature was 202° with a helium flow rate of 75 ml/min; the injector temperature was 250° and the detector temperature was 275°. The retention times of the compounds under these conditions were: 3, 23.5 min; 4, 31.7 min; 13, 35.1 min; 14, 54.2 min. The compounds were identified by a comparison of their retention times with those of authentic samples and by mixed injections with authentic samples. The relative proportions of the components of the dimer fraction as measured from their respective peak areas were: 3, 22%; 4, 61.9%; 13, 7.0%; 14, 9.1%.

Fraction 2. (105 mg) 1,2,5,6-dibenz-9,10-anthraquinone (73) and an unknown compound (74). The mixture was separated on preparative tlc plates, 2 mm silica gel on 20 cm x 20 cm glass plates (E. Merck and Co. Ltd.), by repeated development using acetone-petroleum ether solvent

(1:6 by volume). 73, 14 mg, was identified from its infrared spectrum (KBr disc) by comparison with an authentic sample and from its melting point, 248-250°, which was not depressed when mixed with an authentic sample of 73.

The unknown compound 74 (58 mg) showed a weak carbonyl absorption at 1680 cm^{-1}. The nmr spectrum ($CDCl_3$) showed peaks at τ0.50 (m), τ2.00 (m), τ2.35 (m), τ2.75 (m), τ5.35 (broad multiplet), τ5.80 (broad multiplet) τ7.90 (broad multiplet), τ8.49 (d, J = 7 cps).

Fraction 3. (330 mg) 1,4-phenanthraquinone. The nmr spectrum matched exactly that of the authentic material, but showed a small amount of impurity. The total amount was chromatographed again on a 1 cm x 20 cm column of neutral alumina with chloroform as the eluent. There was obtained 305 mg of a bright yellow powder mp 151-152°. There was no depression of melting point when it was mixed with an authentic sample of 71.

Fraction 4. (419 mg) p-benzoquinone. The nmr spectrum was identical with that of authentic p-benzoquinone. The melting point matched that of the authentic material and was not lowered when a mixed melting point was taken.

Fraction 5. The remaining material, 500 mg, was assumed to be polymeric and was not identified.

The dark-red residue (19.0 g) from the initial reaction mixture was taken up in benzene to give an orange colored solution and a crystalline white residue. The residue was filtered at the pump and washed with 25 ml benzene to give 1.0 g of white crystals identified as hydroquinone mp 168-170°; lit. mp 170° (143). This was not lowered when mixed with an authentic sample of hydroquinone. The nmr spectrum (acetone-$\underline{d}_6$) showed peaks at τ2.49 (s), τ3.35 (s) in the ratio 1 : 2, required 1 : 2. The peak at τ2.49 disappeared on D_2O exchange.

The orange colored filtrate was diluted with twice its volume of methanol to yield a sticky yellow polymeric residue. The residue was leached several times with fresh methanol until it became powdery. The powder was filtered at the pump to give 16.1 g of pale yellow solid. The nmr spectrum ($CDCl_3$) showed broad bands at τ2.90, τ3.40 and τ8.50, characteristic of polystyrene (144). The infrared spectrum ($CHCl_3$) matched exactly that of a polystyrene film used in calibration of the spectrophotometer. Further concentration of the benzene-methanol filtrate gave a floculent pale yellow sticky precipitate. The infrared spectrum again matched the spectrum of polystyrene except for the presence of a weak carbonyl band at 1710 cm^{-1}. No other material than these polymeric residues could be identified.

APPENDIX

Calculation of ΔH for the Thermal Initiation Sequence in the Thermal Polymerization of Styrene

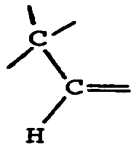
The calculations given below are based on the additivity of group properties as proposed by Benson (147,148,149). The values used for the calculations can be found in the references cited above except in the few cases noted.

According to the concept the thermodynamic property of a compound is treated as being composed of contributions due to groups. A group is defined as a polyvalent atom (ligancy ≥ 2), in a molecule together with all of its ligands. The nomenclature used by Benson can be illustrated by a few examples:

$[C-(H)_3(C)]$ represents a C atom connected to three H atoms and another C atom, i.e., a primary methyl group.

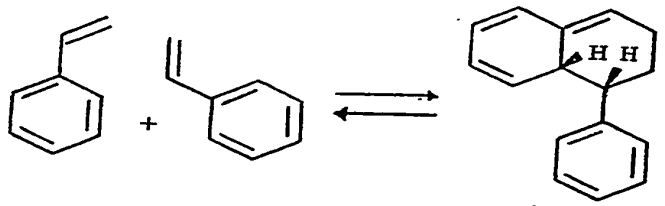
$[C_B-(H)]$ represents a benzene carbon carrying a H substituent.

$[C_d-(H)(C)]$ represents a double bond carbon connected to a carbon and a hydrogen, i.e.



The thermal initiation sequence for styrene polymerization is proposed to proceed by a fast reversible Diels-Alder reaction between two molecules of styrene, eq. [3], followed by a slow rate-determining step involving hydrogen atom transfer between the Diels-Alder adduct and a third molecule of styrene, eq. [4]. These two steps will be treated separately.

The first step is given by eq. [3].

[3] 

(1)

If the normal rule of the Diels-Alder reaction applies here, i.e., addition taking place in such a manner that there is a maximum overlap of double bonds in the transition state, then the hydrogens at the bridgehead and benzylic carbon atoms shown in (1) will be in a cis configuration to each other.

The enthalpy of formation of styrene, $\Delta H°_f = 35.22$ kcal/mole (149).

Compound (1) may be represented by the following

groups:

$5[C_B—(H)]$, $[C_B—(C)]$, $[C—(H)(C_B)(C)_2]$, $[C—(H)_2(C)_2]$,
$5[C_d—(H)(C)]$, $[C_d—(C)_2]$, $[C—(C)_3(H)]$

In addition to these group contributions, corrections must be added for non-group interactions such as ring strain, and cis relations of ring subtituents that are larger than a hydrogen atom. The ring strain in (1) has been assumed to be equal to the sum of the ring strains in the 1,3-cyclohexadiene and cyclohexene rings. This additivity of ring strains can however be misleading in some cases (149), but the error introduced is only of the order of 1-2 kcal/mole. A correction for the gauche interaction between the phenyl group on C, and the bridgehead ring methylene group C_B and for the cis configuration of the hydrogen atoms is also to be added.

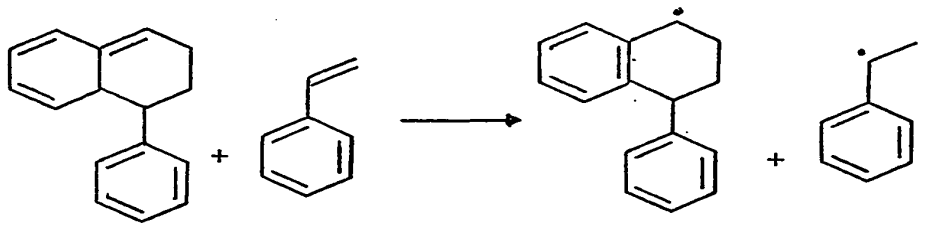
This will give:

$$\Delta H°_f = 5(3.30) + 5.51 - 0.98 - 2(4.95) + 5(8.59) + 10.34 - 1.90 + 6.2 \text{ (ring strain)} + 2.2 \text{ (gauche and cis corrections)} = 70.92 \text{ kcal/mole.}$$

The enthalpy change in the Diels-Alder reaction of styrene is then given by:

$$\Delta H°_{298}\ \text{(reaction)} = \Delta H°_f\ \text{(products)} - \Delta H°_f\ \text{(reactants)}$$
$$= 70.92 - 70.44$$
$$= 0.48\ \text{kcal/mole.}$$

A similar calculation can now be made for the second step, eq. [4].

[4] 

(1) (2)

$\Delta H°_f$ (reactants) = 70.92 + 35.22 = 106.14 kcal/mole.
For the radical (2) the group contributions are: $9[C_B—(H)]$, $[C_B—(C\cdot)]$, $2[C_B—(C)]$, $[C\cdot—(H)(C_B)(C)]$, $[C—(H)_2(C\cdot)(C)]$, $[C—(H)_2(C)_2]$, $[C—(H)(C_B)_2(C)]$*
The ring strain for this system is taken to be equal to the ring strain for the tetralin system (149), i.e., 1.9 kcal/mole. A gauche correction must also be added for the phenyl ring at C_4, 0.8 kcal/mole.

$$\Delta H°_f\ (1) = 9(3.30) + 5.51 + 2(5.51) + 24.7 - 4.95$$
$$- 4.95 + 0.36 + 1.9 + 0.8$$
$$= 64.09\ \text{kcal/mole.}$$

For the 1-phenylethyl radical, the groups are :

$5[C_B—(H)]$, $[C_B—(C\cdot)]$, $[\cdot C—(H)(C_B)(C)]$, $[C—(H)_3(C\cdot)]$

$\Delta H°_f = 5(3.30) + 5.51 + 24.7 - 10.08$

$= 36.63$ kcal/mole.

The enthalpy change in eq. [4] is

$\Delta H°_{298}$ (eq. [4]) $= \Delta H°_f$ (products) $- \Delta H°_f$ (reactants)

$= 100.72 - 106.14$

$= -5.42$ kcal/mole

*The value for the group $[C—(C_B)_2(C)(H)]$ was estimated from the following known group values:

$[C—C_B)_2(C)(H)] = 2[C—(C_B)(C)(H)_2] - [C—(C)(H)_3]$

$= 2[—4.86] - [—10.08]$

$= 0.36$

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