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THE UNIVERSITY OF ALBERTA

I. THE REPLACEMENT OF THE NITRO GROUP BY HYDROGEN USING TRI-n-BUTYLTIN HYDRIDE, A VARIATION OF THE KORNBLUM REACTION.

II. ON THE MECHANISM OF REDUCTION OF KETONES BY ORGANOTIN HYDRIDES.

BY

(C) GILBERTO E. DIAZ MONTELLANOS

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled SOME REDUCTIONS INVOLVING ORGANOTIN HYDRIDES submitted by GILBERTO E. DIAZ MONTELLANOS in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

Dennis D. Tanner
Supervisor

Karl S. Kopecky

External Examiner

Date April 21, 1983

A mi querida Anita.

A mi familia.

ABSTRACT

Reduction to the corresponding hydrocarbons of a number of structurally different tertiary nitro compounds has been achieved by the use of the initiated reaction with tri-n-butyltin hydride in solvent benzene. The mechanism of the reaction was shown to proceed via a free-radical chain process, one of the propagation steps consisting of an electron transfer from the stannyl radical to [redacted] organic nitro compound to form a transient radical anion. The radical generated from the decomposition of the radical anion intermediate is rapidly converted to the hydrocarbon, by reaction with the tin hydride regenerating a stannyl radical. The facility of the hydrogen transfer step precluded the occurrence of undesirable radical-radical or radical-substrate reactions. Although the emphasis was placed on an understanding of the mechanism, the reaction was also shown to be synthetically useful since the products were formed in high yield and were easily separable from their accompanying tin residues.

PART II

The reduction of a number of aromatic ketones by triphenyl- and tri-n-butyltin hydride was studied in solvents benzene, acetonitrile and methanol. The reductions occurred with some ketones in the absence of an

initiator. Evidence is presented that in benzene these reductions proceed by a molecule-induced homolytic process while in the more polar solvents acetonitrile and methanol both induced homolytic and heterolytic pathways are followed.

It is suggested that the induced homolytic reductions proceed by an electron transfer process, the tin hydride being the donating species. Under initiating conditions (AIBN) the reactions were shown to proceed by a free-radical chain process. The absence of a solvent effect upon the yield obtained from the reduction of four of the ketones under study suggested that the propagation sequence involves the addition of the stannyl radical to the carbonyl oxygen followed by hydrogen atom transfer from the tin hydride, the final product being the alkoxystannane. With the more electronegatively substituted ketones, α,α,α-trifluoroacetophenone and ω-fluoroacetophenone, the propagation of the chain involves electron transfer from the stannyl radical to the carbonyl substrate.

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TABLE OF CONTENTS

LIST OF TABLES

PART I

INTRODUCTION

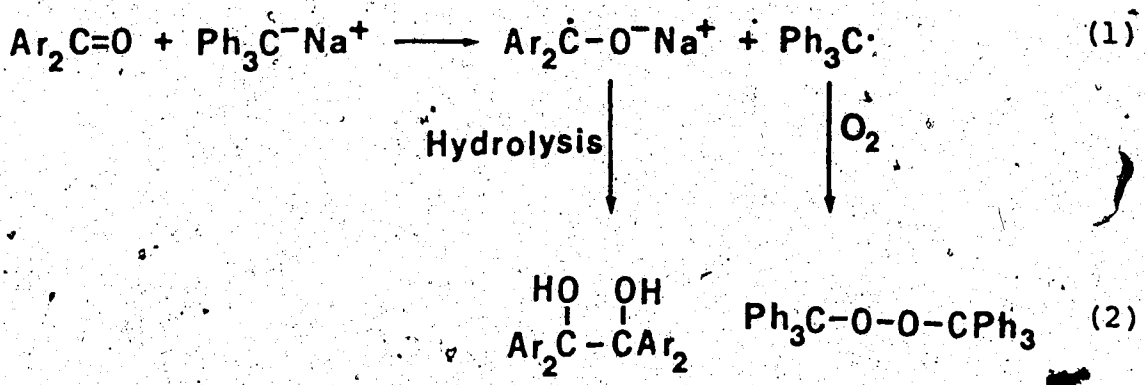
Organic reaction processes involving the transfer of an electron from one reactant to another to give radical-ion intermediates have been known for almost a century.

One of the earliest reports of this type of reaction occurred in 1891 by Beckman and Paul.[1] They apparently first recognized that metallic sodium reacts with benzophenone and other diaryl ketones. The intense blue coloration observed in the absence of oxygen and the nature of the products were attributed to the formation of the radical-anion of the ketones. The free-radical nature of these metal ketyls has been confirmed by numerous subsequent investigations.[2-9]

Later, in 1916 Schlenk[10-11] found that triphenylmethyl sodium reduces a number of aromatic ketones. The reduction was proposed to proceed through the formation of sodium ketyl and triphenylmethyl radical. Their presence was indicated by the color of the solution which upon hydrolysis and atmospheric oxidation yielded the corresponding pinacol and triphenylmethyl peroxide (Scheme 1).

In the early 1930's the intermediacy of ketyl and trityl radicals was also proposed to explain the conversion of aryl ketones into pinacols by triphenylmethyl

SCHEME 1



magnesium bromide.[12-13] Here, electron transfer was indicated to occur from the incipient carbanion of the Grignard reagent to the ketone.

The reduction of diazonium salts by hypophosphorous acid was studied by Kornblum[14] in 1950. He found that the reaction was accelerated by catalytic amounts of oxidizing agents such as cupric sulphate, sodium nitrite, etc., and inhibited by small amounts of quinones. He proposed a free-radical chain mechanism, whose propagation sequence contains a single-electron transfer to the diazonium ion as shown in Scheme 2.

Nevertheless, prior to 1950 most of the oxidation-reduction processes involving only organic species were generally believed to occur by pathways in which electrons could only be transferred in pairs. In the period 1955-1962 the number of exceptions to this

SCHEME 2

Initiation:

$$Ar-N\equiv N-X \longrightarrow Ar\cdot + N_2 + X\cdot \quad (3)$$

Propagation:

$$Ar\cdot + H_3PO_2 \longrightarrow ArH + H_2PO_2^{\cdot} \quad (4)$$

$$Ar-\overset{+}{N}\equiv N + H_2PO_2^{\cdot} \longrightarrow Ar\cdot + N_2 + H_2PO_2^{+} \quad (5)$$

accepted theory became more numerous. A variety of organic substrates were reported to be involved in single-electron transfer processes. Those include donors such as anions of ketones,[15] mercaptans,[16] and hydrocarbons,[17-21] organometallics[22] and amines;[23-25] and acceptors such as iodonium salts[15], nitroaromatics,[16-17] alkyl halides,[18-22] and activated olefins.[23-25]

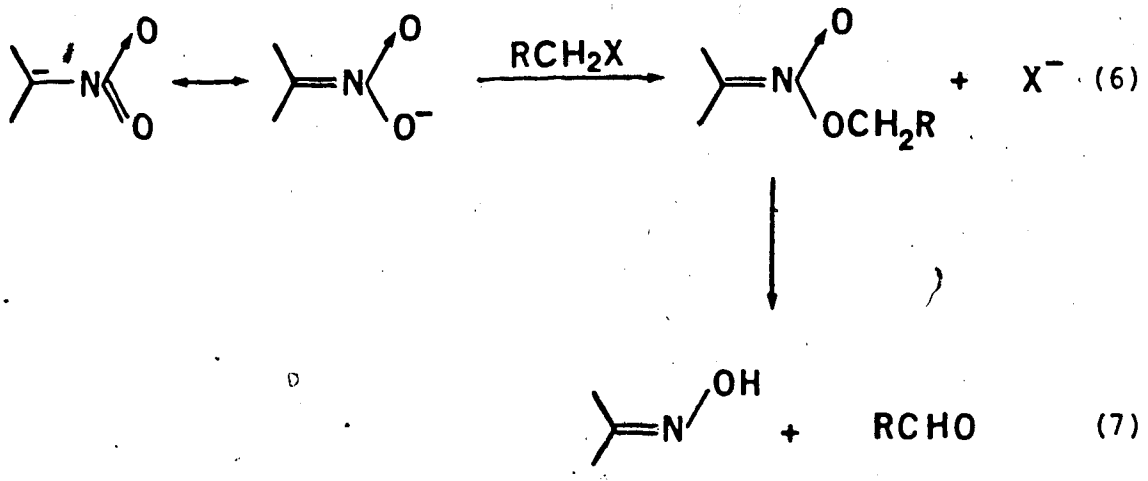
In 1964 Russell[26] expanded the scope of this type of reaction. He observed the existence of electron transfer for a variety of donor-acceptor systems by monitoring the concentration of radical-anions formed by e.s.r. spectroscopy. The donors used in this work were anions and organometallics. The acceptors were unsaturated systems like azo compounds, olefins, ketones, and nitroaromatics.

Despite this large body of evidence the role of single-electron transfer processes was only adequately

recognized among organic chemists when Kornblum and Russell proposed a mechanism for the carbon alkylation of nitroparaffin salts using p-nitrobenzyl halides.

The usual mode of reaction of the salts of nitro compounds with aliphatic, allylic, and benzylic halides is oxygen alkylation. This results simply from nucleophilic displacement of halogen to produce intermediate nitronic esters and eventually carbonyl compounds (see Scheme 3). This method serves as a useful means of preparing aldehydes and ketones.

SCHEME 3



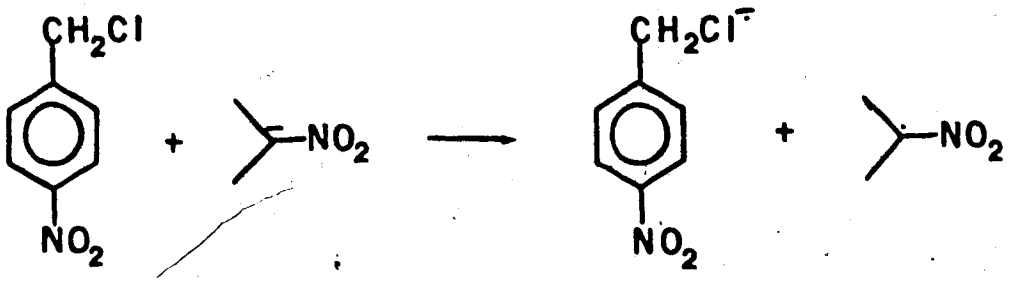
During the reactions of a series of p-nitrobenzyl halides, and specifically with p-nitrobenzyl chloride, a second reaction pathway has a chance to compete and it is this second process which results in carbon alkylation, as shown in equation 8.

(8)

On the basis of rate studies, e.s.r. detection of intermediate species, and the observation of inhibition by m-dinitrobenzene Kornblum[27] proposed that carbon alkylation, in contrast to oxygen alkylation, is a radical-anion process. The final product emerges from a selective coupling of 2-nitro-2-propyl and p-nitrobenzyl radicals. Later, Russell[28] and Kornblum[29] concluded that this reaction is a chain process involving as a key step the attack of the p-nitrobenzyl radical upon the 2-nitro-2-propyl anion. The radical-anion adduct acts as an electron transfer reagent, which rapidly transfers an electron to the p-nitrobenzyl halide (see Scheme 4).

Subsequently Bunnett[30] recognized this reaction as providing a mechanism for radical mediated nucleophilic aromatic substitution and proposed the name $S_{RN}1$. This mechanism is unimolecular in the same sense as S_N1, except that unimolecular bond fission occurs in a radical anion instead of in a neutral molecule. However, it should be pointed out that in the S_N1 mechanism, the departure of the leaving group is the rate determining step, whereas in the $S_{RN}1$ mechanism this may not be the

SCHEME 4



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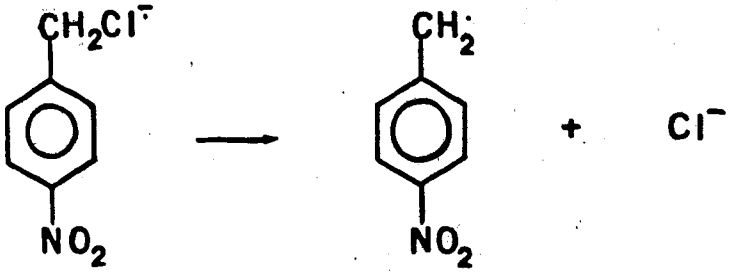

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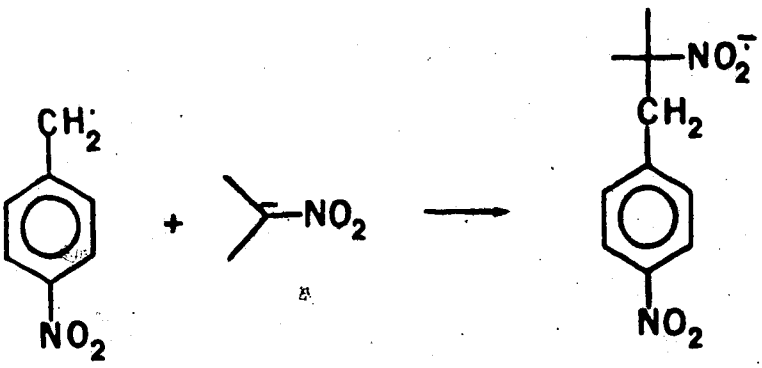

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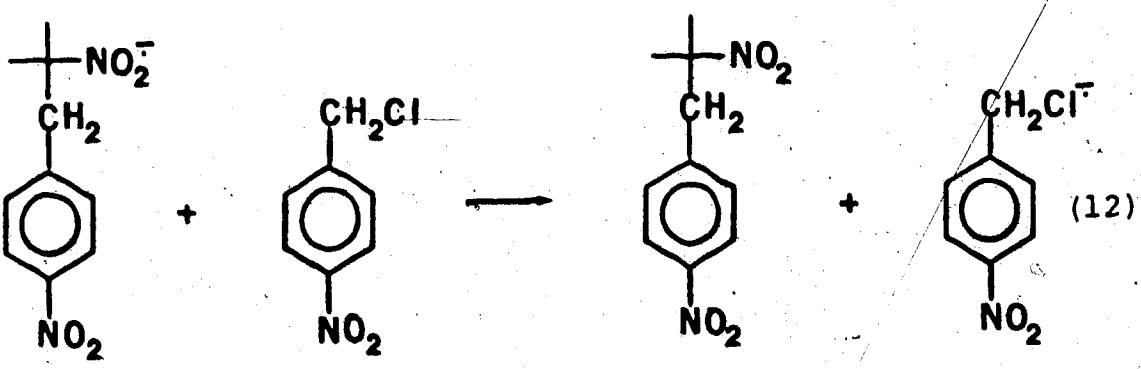


(12)

case in all the reported examples. The relevant mechanistic steps are outlined as Scheme 5.

SCHEME 5

$$ArI + \text{electron donor} \longrightarrow ArI^{\cdot-} + \text{residue} \quad (13)$$

$$ArI^{\cdot-} \longrightarrow Ar\cdot + I^- \quad (14)$$

$$Ar\cdot + NH_2^- \longrightarrow Ar\text{-}NH_2^{\cdot-} \quad (15)$$

$$Ar\text{-}NH_2^{\cdot-} + ArI \longrightarrow Ar\text{-}NH_2 + ArI^{\cdot-} \quad (16)$$

Today, single-electron transfer is perhaps the most important mechanism under study. A large body of evidence now exists in support of the view that these processes occur more frequently than was previously realized. A wide variety of chemical species are known to act as donors in electron transfer reactions. For example metals,[31-41] organometallic reagents and carbanions,[42-55] anions,[56-64] metals in their lower oxidation states,[65-72] Lewis bases,[73-79] and alkyl radicals[72,80-83] are recognized being able to transfer an electron to appropriate substrates. Conversely, when energy requirements are satisfactorily met carbonium ions,[84-86] metal ions in their higher oxidation

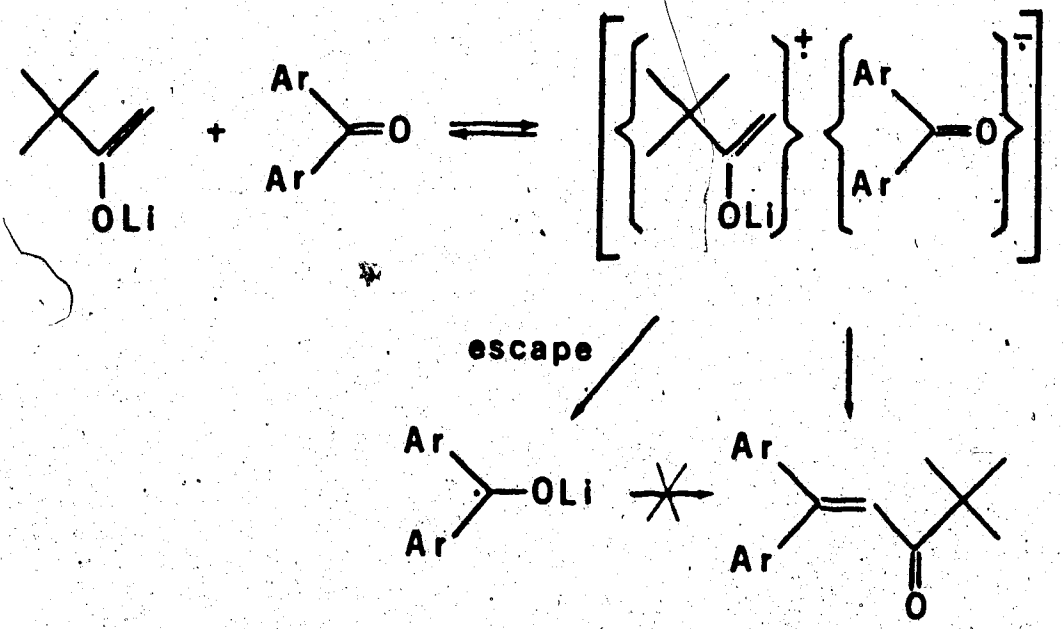
states,[67,87-90] aromatic hydrocarbons,[91-97] molecules with electronegative substituents,[89-99] and radicals[100-101] accept electrons to produce the corresponding ions, radicals, or radical-anions.

Many reactions have been reinvestigated and their mechanisms reinterpreted. The condensation of an aldehyde or ketone in the presence of a base (Aldol condensation) is an important synthetic reaction, the mechanism of which is considered to be polar in nature. Nevertheless, the ability of enolate anions to transfer a single electron to various organic substrates is well documented.

The possibility that a radical-chain mechanism may be operating in these condensations was investigated by Ashby.[102] From rate studies in solvents of different dielectric constants and from e.s.r. spectroscopic results, it was concluded that typical enolate anions of aliphatic ketones may react with aromatic ketones by an electron transfer process to produce paramagnetic intermediates. The kinetic analysis showed that some paramagnetic intermediates disappear at the same rate that the condensation products form. Large amounts of free ketyl are observed when the pathway to condensation product is blocked by steric hindrance. These observations are consistent with the mechanism outlined

in Scheme. 6.

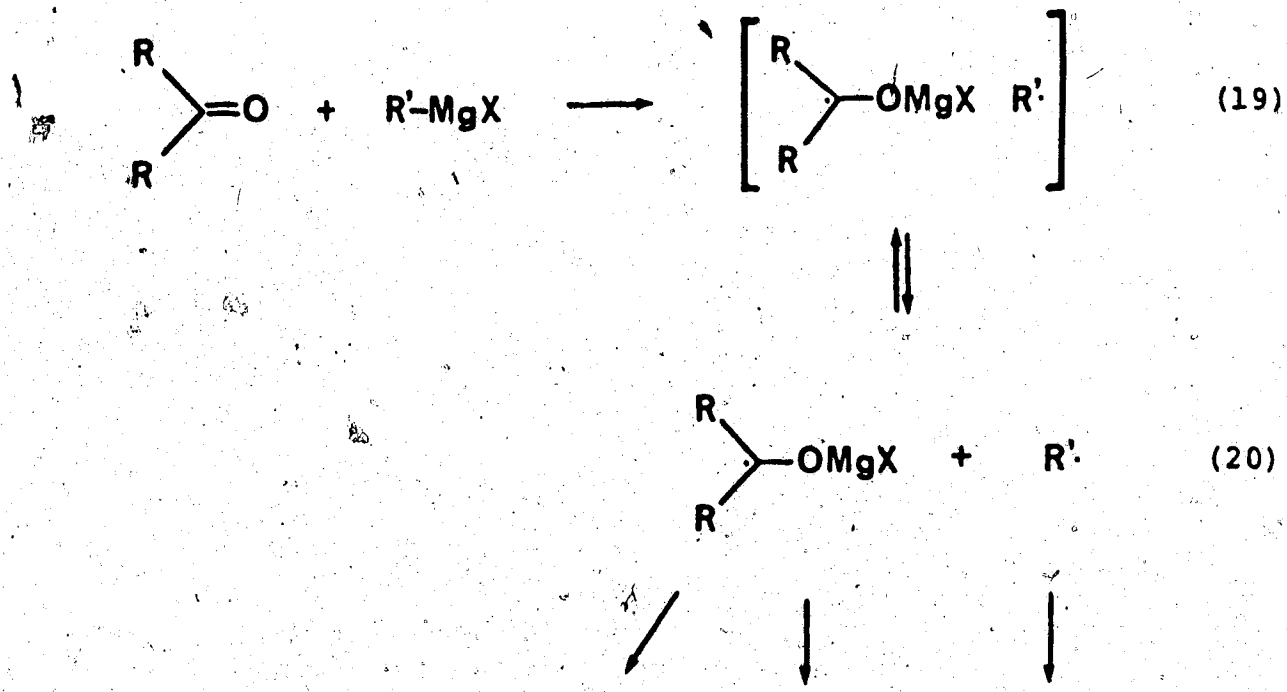
SCHEME 6



The study of the Grignard reaction with ketones has also been a subject for investigation. For many years the reaction was proposed to occur by a polar route which involves an attack of an anionic carbon upon the carbonyl group. Since 1964, however, positive advances have been made towards the understanding of the single electron transfer route. Convincing evidence has been presented for its occurrence in some Grignard reactions. This evidence includes the formation of anomalous products which cannot be explained by applying the polar mechanism: pinacols, hydrocarbons, other products arising from coupling of the ketyl[103-109] (Scheme 7).

Another body of evidence arises from the observation of radical species by physical and chemical techniques.[103,110-112] The single-electron transfer route has been openly demonstrated and proposed in a few articles.[42,104,113-114]

SCHEME 7



The reduction of alkyl and aryl halides with sodium borohydride is well known and has been proposed to proceed, depending upon the structure of the halide, via an S_N1 process,[115] and an S_N2 process, or nucleophilic attack on halogen.[116]

In 1973 Baltrop[117] studied the reaction of halo-

genated aromatic hydrocarbons with sodium borohydride in aqueous acetonitrile. The reactions were carried out under irradiation at 254 nm. The sole organic product in the case of halobenzenes was benzene formed in quantitative yield and with quantum yields considerably in excess of unity.

The radical chain nature of these processes was confirmed by using acrylonitrile, an efficient trap for phenyl radicals. Photoreductions were totally inhibited by small amounts of acrylonitrile. Quantitative photoreduction and inhibition were also observed for 2-bromonaphthalene and 9-bromophenanthrene. A mechanism consistent with these findings involves a free-radical chain process, whose propagation sequence contains an electron transfer from the borane radical-anion to the halides as shown in Scheme 8.

SCHEME 8

Initiation:

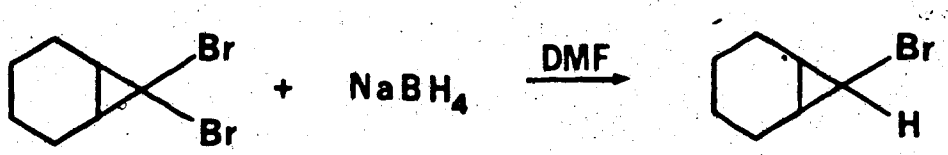
$$PhX \xrightarrow{h\nu} [PhX]^{\cdot} \longrightarrow Ph\cdot + X\cdot \qquad (21)$$

Propagation:

$$Ph\cdot + BH_4^- \longrightarrow PhH + BH_3^- \qquad (22)$$

$$PhX + BH_3^- \longrightarrow Ph\cdot + X^- + BH_3 \qquad (23)$$

A similar mechanistic pathway was proposed by Groves[118] for the conversion of gem-dibromocyclopropanes to the corresponding monobromides in DMF.

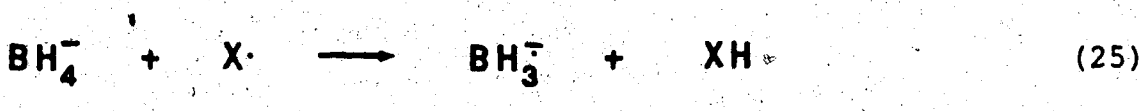


(24)

Although the initiation step is not clearly defined the results of the study are in accord with the mechanistic scheme proposed by Baltrop.[117]

SCHEME 9

Initiation:



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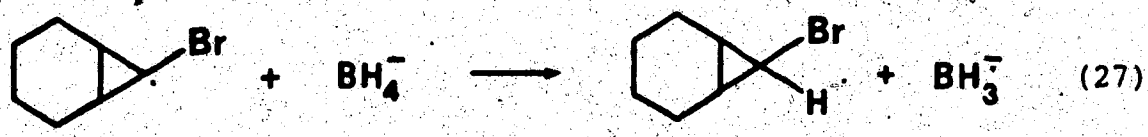
Propagation:

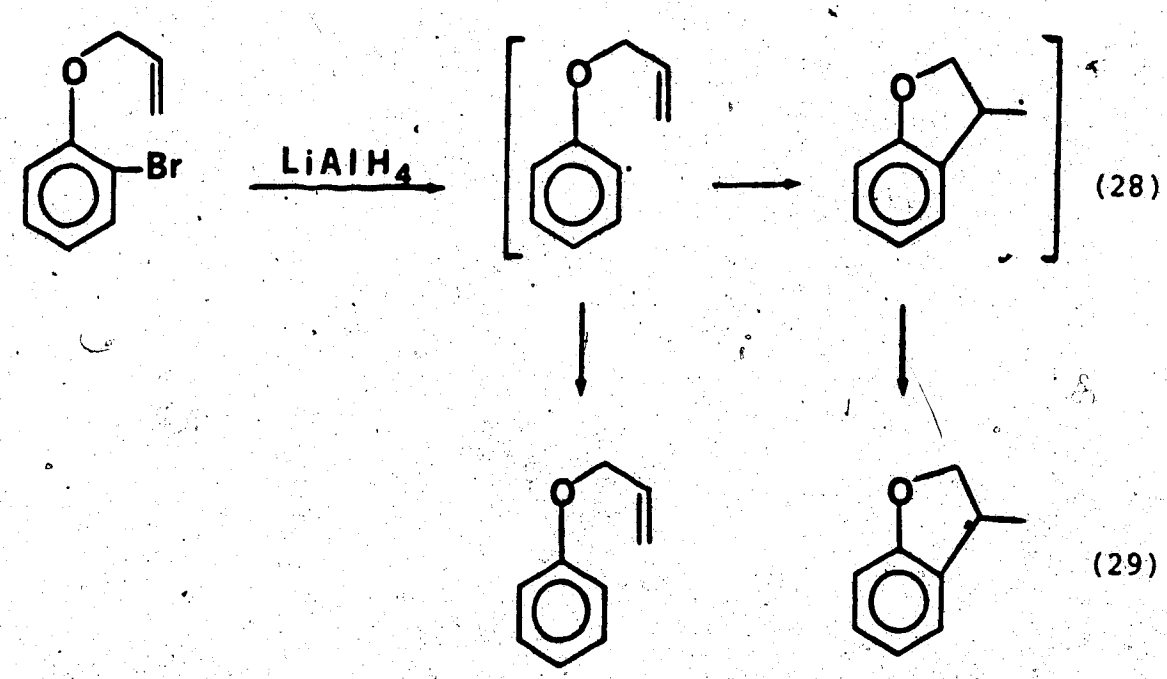
(26)



(27)

Electron transfer involving lithium aluminium hydride has also been reported.[119-121] o-Bromophenyl allyl ether produces phenylallyl ether and 3-methyl-2,3-dihydrobenzofuran. Lithium aluminium hydride acts not only as a source of electrons but also hydrogen atoms as illustrated in Scheme 10.

SCHEME 10



(28)

(29)

Recent studies on chemistry of organometallics have brought some interesting new insights into the understanding of electron transfer reactions. Interest in this field stems largely from the wide variety of reactions in which they are used, either as reactants or as intermediates, in synthetic procedures. In the donor-

acceptor interaction, which precedes electron transfer, organometallic substrates prefer the role of donors, but can also play that of an acceptor. The very important role of electron transfer mechanisms in organometallic chemistry has been reviewed by Kochi.[122-123]

Organotin hydrides are a class of organometallics of particular interest and their value is now widely recognized among organic chemists. In 1959 Noltes and van der Kerk[124-126] discovered that triphenyltin hydride reacts with allyl bromide to give propene and triphenyltin bromide in quantitative yield under mild conditions (room temperature). These original reports were followed by a number of other papers concerning the scope and mechanism of the reduction of alkyl and aryl halides with different organotin hydrides.

Kuivila[127-132] made a significant contribution to the understanding of the reaction and proposed a radical-chain mechanism for it, based upon several observations (Scheme 11). Kuivila found that reactions show catalysis by AIBN and light, and inhibition by small amounts of hydroquinone. Additional evidence of a carbon-centered free radical intermediate can be adduced from the fact that optically active α-phenylethyl chloride on treatment with triphenyltin deuteride yields racemic α-deuterioethyl-

SCHEME II

$$In\cdot + HSnR_3 \longrightarrow InH + \cdot SnR_3 \quad (30)$$

$$R'X + \cdot SnR_3 \longrightarrow R'\cdot + XSnR_3 \quad (31)$$

$$R'\cdot + HSnR_3 \longrightarrow R'H + \cdot SnR_3 \quad (32)$$

$$2\,R_3Sn\cdot \longrightarrow R_3Sn\text{-}SnR_3 \quad (33)$$

$$2\,R'\cdot \longrightarrow R'\text{-}R' \quad (34)$$

benzene. Similarly, α- and γ-methylallyl chlorides each lead to the formation of mixtures of 1-butene, and cis- and trans-2-butenes. Thirdly, the reduction of propargyl bromide leads to the formation of both propyne (85%) and allene (15%).

The most significant feature in this mechanistic scheme is the proposal that the halogen atom is abstracted in a direct manner by the trialkyltin radical.

$$R'X + \cdot SnR_3 \longrightarrow \left[R'\cdots X\cdots SnR_3\right]^{\ddagger} \longrightarrow R'\cdot + XSnR_3 \quad (35)$$

This radical-chain mechanism involving a halogen abstraction in the propagation sequence was later confirmed by the work of Carlson and Ingold.[133] They came to the conclusion that in the process, depending upon structural variations, either the X· abstraction (alkyl chlorides) or the H abstraction (alkyl bromides, methyl iodide) can be the rate controlling step.

Coates and Tedder[134] also accommodated their results in this scheme. They studied the reduction of alkyl halides by trimethyltin hydride in the gas phase and concluded that different halogens are abstracted by Me_3Sn· from similar sites in the order Br > Cl > F.

Tanner[135] examined the conversion of benzyl halides into toluenes by tri-n-butyltin hydride. He found that the relative rates of reduction determined by competitive reactions agreed well with the order previously reported for the relative rates in alkyl halides:[128] $ArCH_2I$ > $ArCH_2Br$ > $ArCH_2Cl$. α-Fluorotoluene and other alkyl fluorides were completely unreactive under the conditions employed in this study (90°C, solvent benzene, initiation by benzoyl peroxide).

Three mechanisms may be considered to explain the lack of reactivity of the fluorides:

a. A direct halogen transfer from the benzyl halide to the stannyl radical, as proposed by Kuivila.[128]

$$ArCH_2X + \cdot SnR_3 \rightleftharpoons [ArCH_2 \cdots X \cdots SnR_3]^{\ddagger} \rightleftharpoons ArCH_2\cdot + XSnR_3 \quad (36)$$

A high activation energy for the abstraction step would account for this non-reactivity.

b. A two step abstraction, which involves a reversible stannyl radical addition to the halogen, to form an intermediate with an expanded octet.

$$ArCH_2X + \cdot SnR_3 \rightleftharpoons [ArCH_2X^{\delta-} \cdots Sn^{\delta+}R_3]^{\ddagger} \rightleftharpoons ArCH_2-\dot{X}-SnR_3$$

$$\rightleftharpoons [ArCH_2^{\delta-} \cdots X^{\delta+}SnR_3]^{\ddagger} \rightarrow ArCH_2\cdot + XSnR_3 \quad (37)$$

This mechanism was originally proposed by Sakurai[136] in 1972 while investigating the reduction of benzyl chlorides by triethylgermanium hydride under almost similar conditions to those employed to study the reduction using tri-n-butyltin hydride (90°C, benzene, benzoyl peroxide). Fluorine, a first-row element, is energeti-

cally incapable of expanding its octet, and would not undergo reduction by this mechanism.

c. A radical-chain process which includes transfer of a single electron from the tin radical to the halide, in the propagation sequence as shown in Scheme 12.

SCHEME 12

$$ArCH_2X + \cdot SnR_3 \longrightarrow ArCH_2X^{\cdot -} + {}^{+}SnR_3 \quad (38)$$

$$ArCH_2X^{\cdot -} \longrightarrow ArCH_2^{\cdot} + X^- \quad (39)$$

$$ArCH_2^{\cdot} + HSnR_3 \longrightarrow ArCH_3 + \cdot SnR_3 \quad (40)$$

This mechanism would also suffer from the same limitation. A high activation energy would be required for electron transfer to the electronegative fluoride.

Tanner[135] calculated the enthalpies of reactions for reduction of halides proceeding by eq. 36, and then, using these data he determined the corresponding activation energies by the application of either the empirical Hirschfelder rules[137] or the empirical method suggested by Semenov.[138] He came to the conclusion that all of the benzyl halides are capable of undergoing a favorable direct abstraction process.

The total absence of reactivity of the fluorides

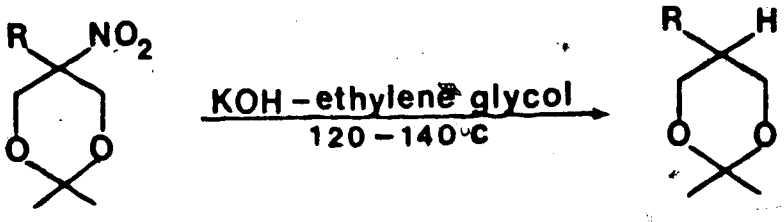
towards the tin hydride suggests that either the mechanism incorporating an intermediate with an expanded octet (37) or a mechanism involving electron transfer (Scheme 12) may be operating in these reductions. Some insight into this dilemma was obtained by analyzing the relative magnitude of the ρ values obtained for the reduction of a series of benzyl chlorides, bromides and iodides. Both of the mechanisms, if subject to polar substituent effects, would be predicted to show Hammett equation correlations which follow σ^- substituent constants. If only one mechanism were involved, then the relative magnitude of the ρ values should be the inverse of the relative rates since reactions which occur more readily should be less susceptible to substituent effects. The iodide series was expected to have the smallest ρ value. The series of benzyl bromides showed a lower ρ value than the chlorides ($\rho = 0.17$ vs $\rho = 0.34$) as expected. However, the ρ value for the iodide series was abnormally high ($\rho = 0.81$). This relative ordering of the magnitude of the ρ values is inconsistent with the operation of one mechanism for the reduction of the halides with tri-n-butyltin hydride. It was suggested that the iodides are reduced by a different mechanism than the bromides and chlorides.

The high ρ value observed for the series of benzyl

iodides was considered to be indicative of a greater charge separation which would be the case of the electron transfer process. Consistent with this hypothesis was the large solvent effect observed when the reductions of the iodides were carried out in acetonitrile. The ρ value became more negative. On the basis of these observations Tanner proposed an electron transfer radical-chain mechanism for the reduction of benzyl iodides.

In the last five years aliphatic nitro compounds have been widely used as substrates in electron transfer reactions. Aliphatic and alicyclic sec-nitro compounds are synthetically useful in carbon-carbon bond formation processes under mild conditions. The resulting product in these processes is a tert-nitro compound in which other functional groups may be present. The utility of these methods now appears greater because of the feasibilty of replacing the tert-nitro group by hydrogen.

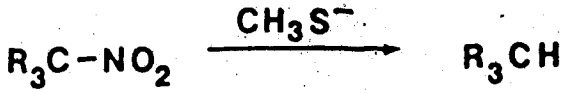
Four methods so far exist for this purpose. In 1979, Krasuska[139] reported the reductive elimination of tert-nitro group in 5-nitro-1,3-dioxanes. An ethylene glycol solution of potassium hydroxide was used as the reducing agent. The radical nature of the process was inferred by carrying out the reaction in the probe of an ESR spectrometer which gave signals of an unpaired



(41)

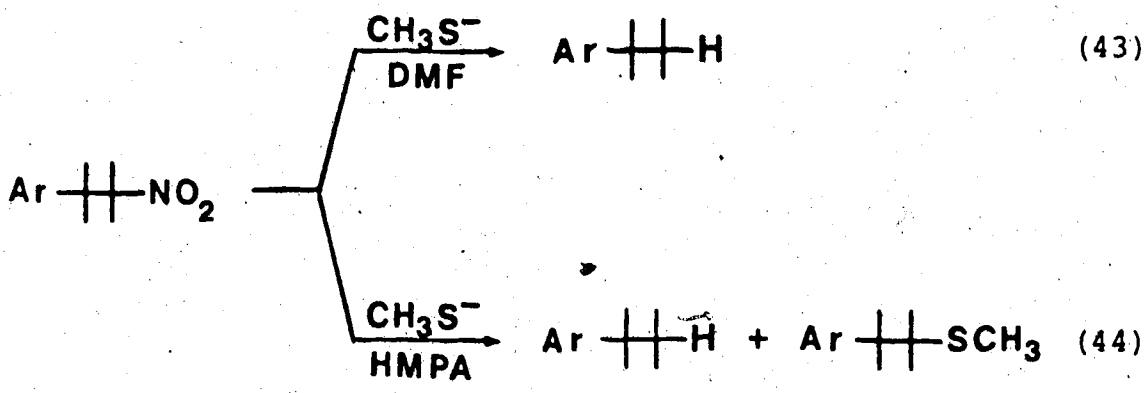
electron localized on the nitro group of the 5-nitro-1,3-dioxanes. Experiments using deuterated potassium hydroxide, o-deuterated, and perdeuterated ethylene glycol led to the conclusion that hydrogen abstraction takes place from the $-CH_2-$ of the glycol.

Kornblum[140] replaced the nitro group by the hydrogen in a wide variety of tert-nitro compounds using the sodium salt of methyl mercaptan. The substrates utilized in this work were empirically classified into three different categories on the basis of the influence of the solvent on the course of their reaction with the thiolate anion. The first group comprises aliphatic or alicyclic systems. The reduction of these substrates cleanly proceeds to afford the hydrogenated compound as the unique product regardless of the solvent employed (DMSO, DMF, HMPA).

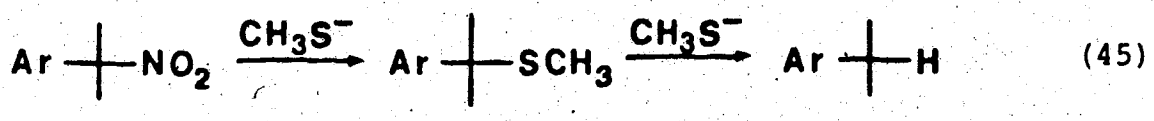


(42)

The second group is formed by β-arylated nitroparaffins. Here, a competitive process takes place depending upon the solvent. When reactions are conducted in DMF, the sole result is the replacement of the nitro group by hydrogen, whereas, in HMPA replacement by hydrogen and thiomethyl both occur.



An important feature in the reduction of the β-arylated nitroparaffins is that hydrogenated products do not arise from further reaction of the thioethers. The last group of substrates involves a variety of α-nitrocumenes. In this series, regardless of the solvent, the methyl thioether is formed first and then it is converted to the cumene.



The second process, replacement of the thiomethyl group by hydrogen, occurs at rates comparatively slower than the formation of the methyl thioether. For all of the three groups of nitroparaffins the solvent has a large influence on rates. Reactions are much faster in HMPA than in DMF or DMSO.

A number of additional observations led Kornblum to propose a radical-anion—free-radical chain mechanism for the replacement of the nitro group by hydrogen. All processes show inhibition by di-tert-butylnitroxide and m-dinitrobenzene. Most of the reactions take place in the dark at a measurable rate, but they are unambiguously accelerated by light. These observations are readily accounted for by the sequence of steps described by equations 46-49 in Scheme 13.

SCHEME 13

$$R\text{-}NO_2 + CH_3S^- \longrightarrow R\text{-}NO_2^{\cdot-} + CH_3S\cdot \quad (46)$$

$$R\text{-}NO_2^{\cdot-} \longrightarrow R\cdot + NO_2^- \quad (47)$$

$$R\cdot + CH_3S^- \longrightarrow RH + \dot{C}H_2S^- \quad (48)$$

$$R\text{-}NO_2 + \dot{C}H_2S^- \longrightarrow R\text{-}NO_2^{\cdot-} + CH_2S \quad (49)$$

A simplistic interpretation for thioether formation

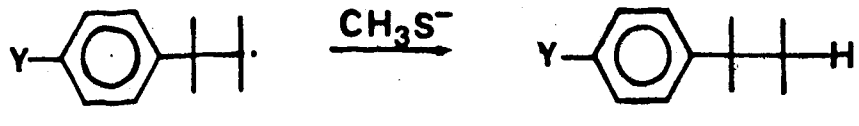
can be envisioned from an alternate encounter of the radical generated in equation 47 with the methylmercaptide ion to give a radical-anion followed by electron transfer to the starting nitro compound.

$$R\cdot + CH_3S^- \longrightarrow R\text{-}\dot{\bar{S}}CH_3 \quad (50)$$

$$R\text{-}NO_2 + R\text{-}\dot{\bar{S}}CH_3 \longrightarrow R\text{-}NO_2^- + R\text{-}SCH_3 \quad (51)$$

However, this assumption does not provide a satisfactory explanation for the fact that regardless of the solvent used aliphatic and alicyclic nitro compounds abstract only hydrogen from methylmercaptide ion, while β-arylated nitroparaffins also form thioethers when the reactions are carried out in HMPA.

Kornblum[140] proposes that β-aryl radicals differ from the other radicals in that they can cyclize to spiranes. A nucleophilic displacement by the methyl mercaptide ion on one of the carbons of the spirane ring leads to the formation of a relatively stable radical-anion. This species transfers one electron to the starting nitro compound with the overall result of a nitro group replaced by thiomethyl. The hydrogenated product arises from hydrogen abstraction by the open-chain radical.



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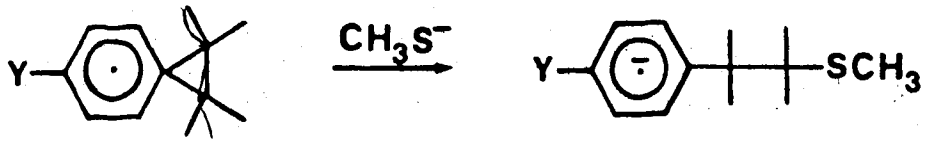
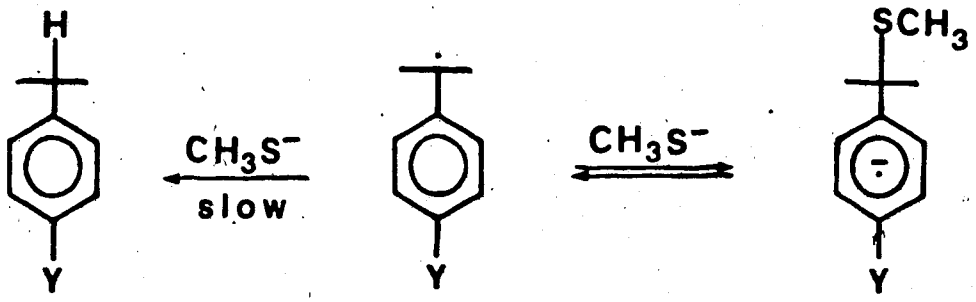


(52)

In HMPA the nucleophilic attack competes with the hydrogen abstraction process, whereas in DMF only the last process occurs. Radicals from aliphatic and alicyclic nitro compounds are unable to form the spirane and no thioether can be observed.

The pattern observed in the series of α-nitrocumenes, initial formation of methyl thioether followed by slow conversion to the cumene, is rationalized by Kornblum in terms of a kinetically controlled process. Cumyl radicals are well stabilized and consequently they are less reactive than a simple alkyl radical, because the odd electron is delocalized in the phenyl moiety of the system. These radicals can abstract a hydrogen atom from the methyl mercaptide ion in a slow, but irreversible process. As a consequence of this, relatively low energy radical anions are formed by collapse of cumyl radicals and mercaptide ions in a rapid, but reversible reaction.



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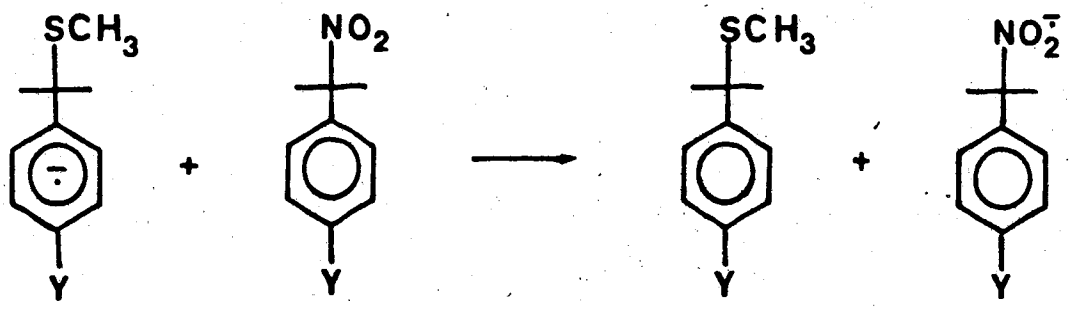
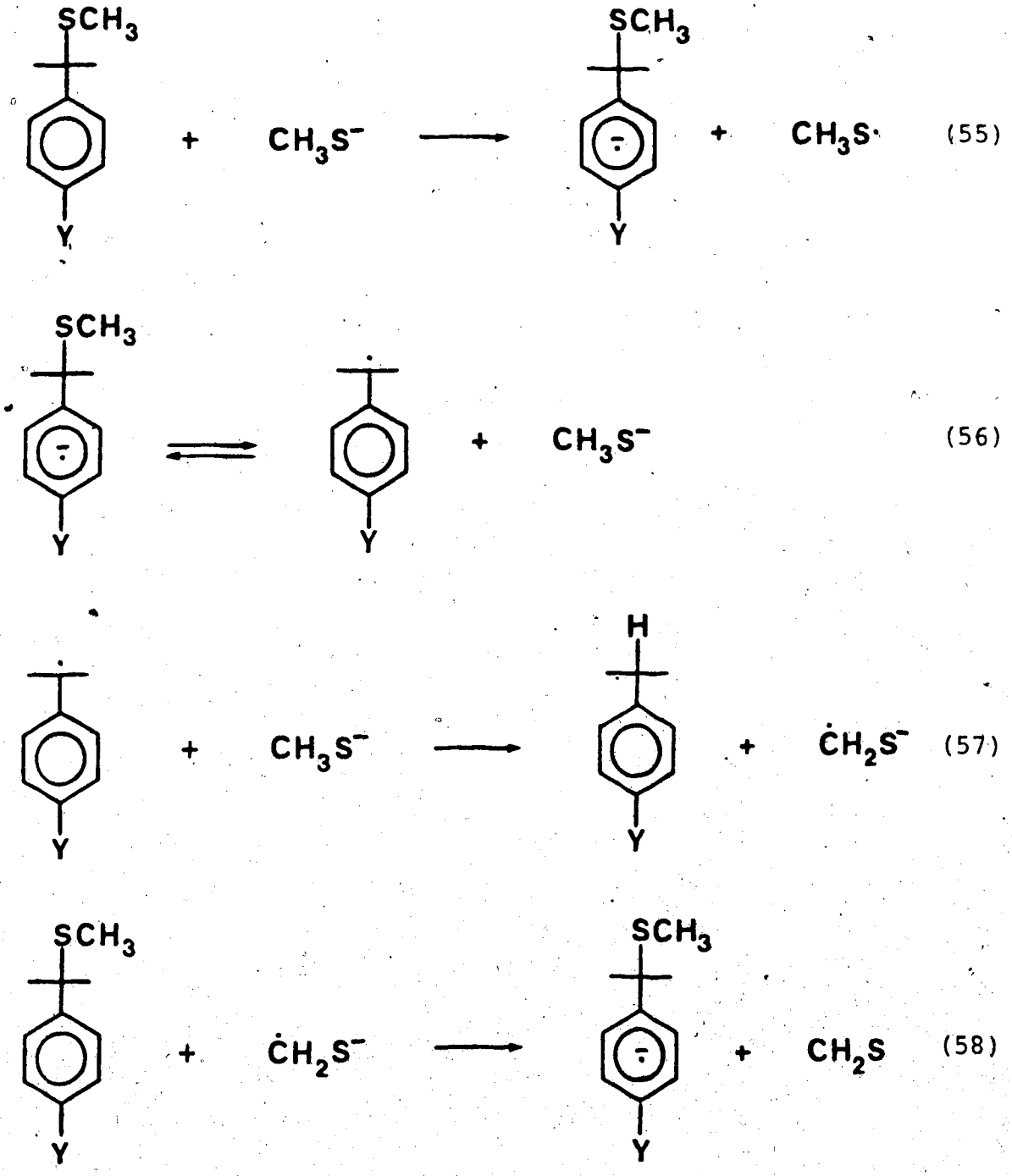
The formation of methyl thioether derives from an electron transfer process, which also generates the chain carrying radical anion of the nitro compound.



(54)

These cumyl thioethers are reduced to cumenes by the continued action of the sodium salt of methyl mercaptan. These transformations are easily understood on the basis of equations 55 to 58 in Scheme 14.

SCHEME 14

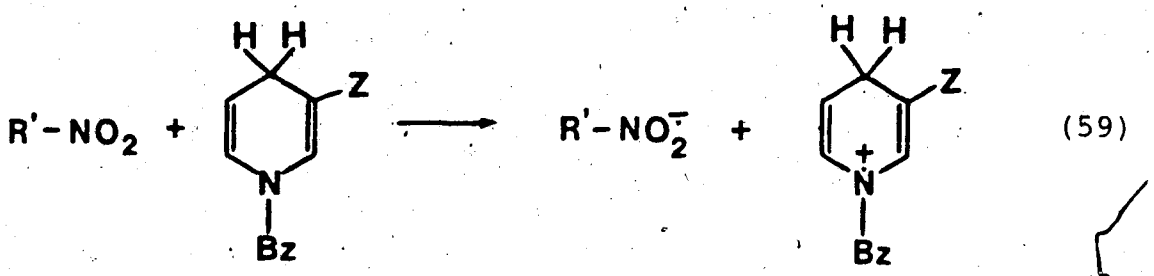

SCH3
Y
+ CH3S⁻
SCH3
Y
+ CH3S·
(55)
SCH3
Y
Y
+ CH3S⁻
(56)
Y
+ CH3S⁻
H
Y
+ ĊH2S⁻
(57)
SCH3
Y
+ ĊH2S⁻
SCH3
Y
+ CH2S
(58)

The pattern followed by α-nitrocumenes can be considered as a variation of the mechanism used to rationalize the chemistry of the first two groups of tert-nitro compounds.

In 1980, Ono[141] reported the replacement of the nitro group by hydrogen in a series of secondary and tertiary aliphatic nitro compounds using 1-benzyl-1,4-dihydronicotinamide as the reducing agent in solvents benzene, DMF and HMPA. The substrates utilized in this work were highly activated compounds of the type $(R_1)(R_2)(Y)C\text{-}NO_2$, where Y is the cyano, carboalkoxy or keto group. The reaction does not occur in the dark, but shows initiation by light and catalytic amounts of AIBN, di-tert-butylperoxyoxalate, and sodium dithionite. The reaction is inhibited by m-dinitrobenzene or di-tert-butyl nitroxide. Ono suggests that the reduction takes place [illegible] electron transfer radical chain reaction (Scheme [illegible]).

The fourth method of replacement of the nitro group by hydrogen in tert-nitroparaffins is the subject of the first part of this thesis. We have examined the reduction of a variety of tert-nitro compounds with tri-n-butyltin hydride in benzene as a solvent. The substrates used for this purpose were 2-(nitrocyclohexyl)isobutyronitrile (I), p-cyano-α-nitrocumene (II), and 2,3-dimethyl-2-(p-

SCHEME 15



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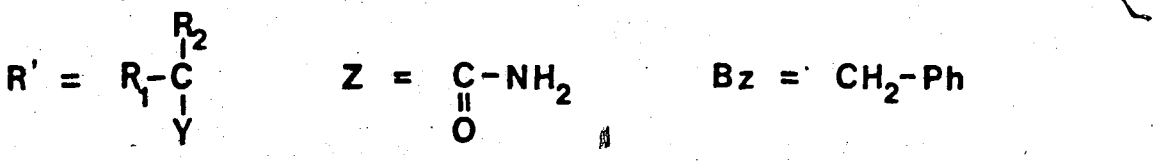

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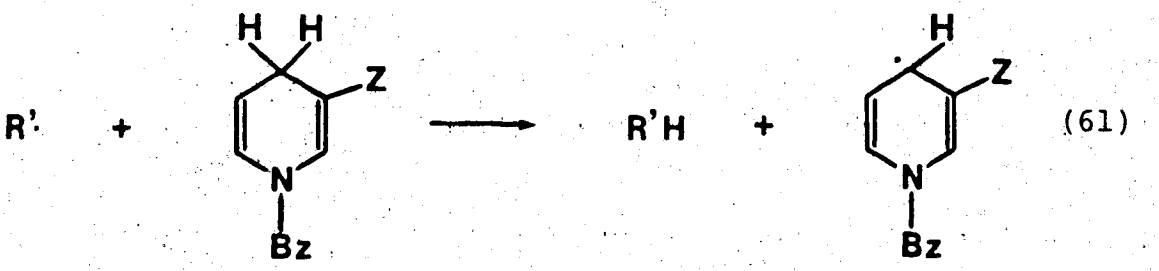
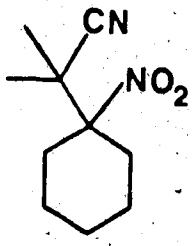


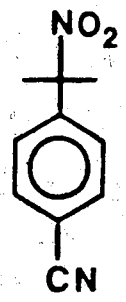
(61)

(62)

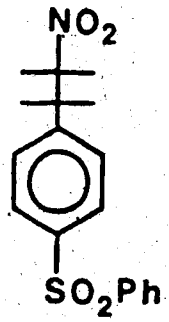
benzenesulfonylphenyl)-3-nitrobutane (III), which correspond to typical examples of each of the three groups of tert-nitro compounds empirically established by Kornblum.[140] In addition, α-nitrocumene (IV) was also included. This substrate was the least successful example of the synthetically useful reductions carried out by Kornblum with sodium thiomethoxide since it yielded a mixture of products in which only 29% corresponded to cumene.



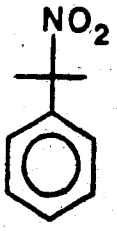
I



II



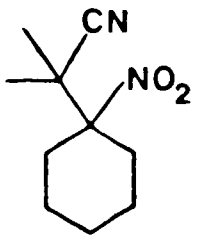
III



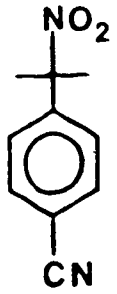
IV

RESULTS

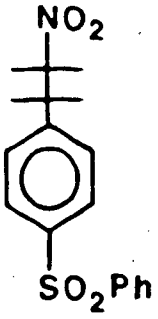
The four tertiary nitro compounds (I-IV) used in this work were synthesized by methods previously described by Kornblum (see Experimental Section).



I



II



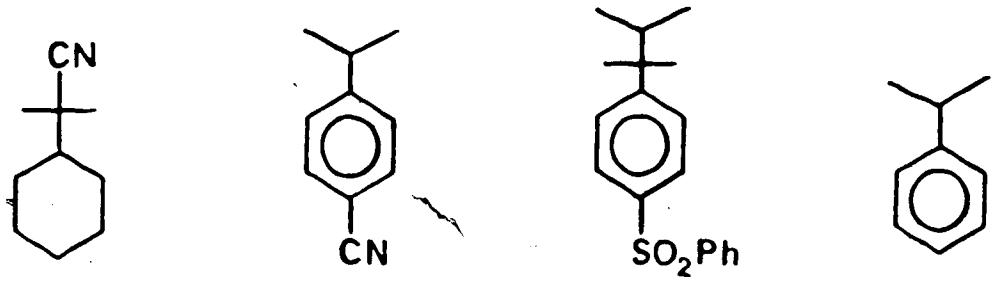
III

IV

Under satisfactory reaction conditions, treatment of these substrates with tri-n-butyltin hydride cleanly led to the replacement of the nitro-group by hydrogen. The products resulting from these reductions were 2-cyclohexyl-2-cyanopropane (Ia), p-cyanocumene (IIa), 2,3-dimethyl-2-(p-benzenesulfonylphenyl)butane (IIIa), and cumene (IVa).

A typical primary (1-nitropropane) and several secondary (2-nitropropane and nitrocyclohexane) nitro compounds were inert to this procedure.

The reduction mechanism of tertiary nitroparaffins was shown to proceed by a free-radical chain process by a



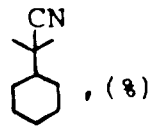
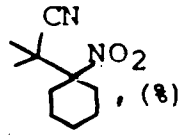
Ia IIa IIIa IVa

comparison of the yield of products obtained from thermal reactions of the reactants under a set of standard conditions (solvent benzene, at 38°C or 90°C, 18 h in the absence of light or oxygen) with those arising from reactions carried out under conditions to test initiation by light and benzoyl peroxide and inhibition by m-dinitrobenzene. Additional information in regard to the mechanism was obtained from reactions conducted in the presence of hexa-n-butyldistannane and oxygen. The yield of products was determined either by glpc or hplc (see Experimental Section). The results of these comparative reactions are listed in Tables I-III.

Mixtures of nitro compounds I, II, and IV were relatively unreactive (1-7%) at 38°C in the dark in absence of additives (Table I, reaction 5; Table II, reaction 4; Table III, reaction 5) When the thermal reactions were carried out at 90°C, the observed reactivities were relatively higher to afford the reduction products in

TABLE I

Reduction of 2-(Nitrocyclohexyl)isobutyronitrile (I) with Tri-n-butyltin Hydride in Benzene

Reaction[a]	RNO_2/Bu_3SnH mole ratio	Conditions	 , (%)	 , (%)
1	1:1	Bz_2O_2 (4%), 90°C	57 ± 1.0	42 ± 0.8
2	1:2	Bz_2O_2 (4%), 90°C	67 ± 0.5	30 ± 0.5
3	1:3	Bz_2O_2 (4%), 90°C	75 ± 0.4	20 ± 1.0
4	1:3	38°C, light[c]	96 ± 0.5	4 ± 0.3
5	1:3	38°C	7 ± 0.6	80 ± 0.3
6	1:3	Bz_2O_2 (4%), 90°C, m-DNB (10%)	30 ± 0.1	54 ± 0.3
7	1:3	Bz_2O_2 (4%), 90°C, m-DNB (25%)	9 ± 0.5	78 ± 1.5
8	1:1	90°C	12 ± 3.0	85 ± 2.3
9	1:3	90°C	36 ± 6.0	46 ± 3.0
10	1:3.5	Bz_2O_2 (12%), 90°C	95 ± 1.0	5 ± 0.0
11[b]	1:3	38°C, m-DNB (25%)	0	100
12[b]	1:3	90°C, m-DNB (25%)	0.5	100

continued.....

Table I (continued)

13[b]	1:3	38°C, $(Bu_3Sn)_2$[d]	5	93
14	1:3	90°C, $(Bu_3Sn)_2$[d]	37 ± 0.0	45 ± 1.0
15[b]	-	r.t., $(Bu_3Sn)_2$[e]	0	100
16[b]	-	38°C, $(Bu_3Sn)_2$[e]	0	100
17[b]	-	90°C, $(Bu_3Sn)_2$[e]	0	100
18	1:3	90°C, O_2[f]	42 ± 0.5	48 ± 0.3
19	1:3	Bz_2O_2 (12%), 90°C, O_2[f]	88 ± 1.0	8 ± 1.0

See Footnotes Page 37.

TABLE II

Reduction of p-Cyano-α-nitrocumene (II) and 2,3-Dimethyl-2-(p-benzenesulfonylphenyl)-3-nitrobutane (III) with Tri-n-butyltin hydride in Benzene.

Reaction[a]	Compd.	RNO_2/Bu_3SnH mole ratio	Conditions	Products	Yield, %	RNO_2, %
1	II	1:3	Bz_2O_2 (4%), 90°C	IIa	77 ± 0.4	0
2	II	1:3	Bz_2O_2 (8%), 90°C	IIa	90 ± 0.5	0
3	II	1:3	90°C	IIa	43 ± 0.3	24
4	II	1:3	38°C	IIa	traces	100
5[h]	III	1:3	Bz_2O_2 (4%), 90°C	IIIa	64 ± 0.5	33 ± 0.5
6[h]	III	1:3	Bz_2O_2 (12%), 90°C	IIIa	85 ± 0.8	11 ± 2.0
7[h]	III	1:3	90°C	IIIa	41 ± 1.0	55 ± 1.0

See Footnotes Page 37.

TABLE III

Reduction of α-Nitrocumene (IV) with Tri-n-butyltin hydride in Benzene

Reaction[a]	RNO_2/Bu_3SnH mole ratio	Conditions	 , %	 , %
1	1:1	Bz_2O_2 (4%), 90°C	39 ± 0.5	52 ± 1.0
2	1:3	Bz_2O_2 (4%), 90°C	64 ± 0.9	18 ± 1.7
3	1:3	90°C	33 ± 0.7	53 ± 1.2
4	1:3	38°C, light[c]	7 ± 0.5[g]	8 ± 1.0
5	1:3	38°C	1 ± 0.0	90 ± 1.4
6	1:3	Bz_2O_2 (4%), 90°C, m-DNB (10%)	20 ± 0.8	65 ± 0.7
7[h]	1:3	Bz_2O_2 (12%), 90°C	79 ± 1.0	6 ± 2.0

See Footnotes Page 37.

Footnotes

a. Average of three individual experiments, except when indicated.

b. Average of two individual experiments.

c. A Rayonet reactor fitted with a merry-go-round and 3500 A° BL lamps was used, while the other reactions were conducted in the dark.

d. Equal molar amounts of distannane and hydride were used.

e. No hydride, but a mole ratio 1:3 of $R-NO_2$ and distannane was used.

f. Reactions in the presence of oxygen were conducted in nondegassed ampules.

g. α-Methylstyrene (42%) and α-nitrosocumene (14%) are the major products in this reaction. Bicumyl (5%) was also detected.

h. Yield of products was determined by hplc using a 10 cm Radial PAK-A cartridge (reverse phase permanently bonded octadecylsilane) and 1:1 water-acetonitrile solvent system.

about 40% yield (Table I, reaction 9; Table II, reactions 3 and 7; Table III, reaction 3).

Nitro compound I showed enhanced reactivity with tri-n-butyltin hydride under exposure to light at 38°C. The reduction could be initiated by irradiation of the reaction mixture at a wavelength where the substrate showed tail absorption (3500 Å). Ia was produced in 96% yield (Table I, reactions 4 and 5). However, under identical conditions of irradiation compound IV yielded only 7% of IVa and a number of other products resulting from the photolysis of the substrate: α-methylstyrene (42%), and α-nitrosocumene (14%). Bicumyl was also produced in 5% yield. On the basis of these results no further use of photoinitiation was attempted since it appeared that, in some cases, the photodecomposition of the nitro compound was competitive with its chain reduction.

When the thermal reactions at 90°C of all of the nitro compounds were carried out in the presence of catalytic amounts of benzoyl peroxide (4%), the yield of the corresponding reduction products were considerably higher than those detected in the reaction without initiator (Table I, reactions 1 and 8, 3 and 9; Table II, reactions 1 and 3, 5 and 7; Table III, reactions 2 and 3). The effect of added benzoyl peroxide was more noticeable when larger amounts of initiator were used.

Addition of 8% or 12% of initiator caused a pronounced increase of the degree of reaction and led to the formation of reduction products in synthetically useful yields (Table I, reaction 10; Table II, reactions 2 and 6; Table III, reaction 7).

Both the benzoyl peroxide induced reactions and the dark thermally initiated reactions were inhibited by the addition of m-dinitrobenzene which presumably acts as an electron trap and interferes with the chain (Table I, reactions 3 and 6 or 7, 5 and 11, 9 and 12; Table III, reactions 1 and 6).

It was conceivable that the uninitiated reactions were initiated thermally by the homolysis of a small amount of hexa-n-butyldistannane, which appears to be always present in the starting tri-n-butyltin hydride. However, addition of this distannane to the reaction mixtures at 38°C and 90°C did not appear to affect the yield of the uninitiated reduction reactions (Table I, reactions 5 and 13, 9 and 14). Furthermore, nitro compound I was not affected by hexa-n-butyldistannane in the absence of tri-n-butyltin hydride. When mixtures of I and the distannane in a mole ratio 1:3 were subjected to reaction at room temperature, 38°C, and 90°C no Ia nor nonchain products (coupling or disproportionation) were detected, and the substrate was recovered unchanged

(Table I, reactions 15, 16, and 17).

It is widely recognized that molecular oxygen interferes with radical processes acting either as initiator or inhibitor. Although the free-radical reduction was not noticeably affected by the oxygen present in the undegassed reaction ampules (Table I, reactions 9 and 18, 10 and 19), the mixtures were routinely degassed prior to reaction only as part of the standard procedure.

On the basis of yield of products, the tin hydride reduction of tertiary nitro compounds compares favorably with Kornblum's method[140] (see Table IV). However, it should be pointed out that the yields reported in this work were determined by glpc or hplc analysis, whereas the yields reported by Kornblum for compounds I, II, and III correspond to isolated products.

Apart from the intrinsic interest from the mechanistic point of view, this reaction was also shown to be noteworthy for its potential value in synthesis. The reduction of p-cyano-α-nitrocumene (II) to p-cyanocumeme (IIa) was carried out as illustration of a synthetically useful reaction. A benzene solution of nitro compound, tri-n-butyltin hydride and benzoyl peroxide was heated to reflux under an atmosphere of nitrogen. Tin compounds were separated from the reaction mixture by filtration

TABLE IV

Comparative Yields for the Reduction of Compounds I-IV Using Thiolate vs Stannyl Radical Reduction[a]

Compound	Conditions	Product	Yield %	Ref.
I	90°C, benzene, 18 h.	Ia	95	This work
I	25°C, DMSO, 3 h.	Ia	95	140
II	90°C, benzene, 18 h.	IIa	90	This work
II	25°C, HMPA, 16 h.	IIa	82	140
III	90°C, benzene, 18 h.	IIIa	85	This work
III	25°C, DMF, 8 h.	IIIa	83	140
IV	90°C, benzene, 18 h.	IIa	79	This work
IV	25°C, HMPA, 30 h.	IIa	29	140

a. Benzoyl peroxide was used as initiator.

after trea[illegible]nt with iodine followed by precipitation with pota[illegible]oride. The impure material was purified [illegible]ography to afford a colorless oil (75% yiel[illegible] who[illegible]d nmr spectrum corresponded to p-cyan[illegible]ene[illegible]e Experimental Section).

DISCUSSION

The reduction of tertiary nitro compounds to hydrocarbons with tri-n-butyltin hydride takes place in a mechanistically predictable manner, free from experimental complications. The dark uninitiated reactions of these reactants at 38°C and 90°C could be accelerated by irradiation at 3500 Å and by the addition of small amounts of benzoyl peroxide or inhibited by m-dinitrobenzene. The results of these comparative reactions clearly established the reduction as one proceeding by a radical chain mechanism. The initiating step in both the photo and chemically induced reactions leads to the formation of stannyl radicals.

Photoinitiation:

$$R\text{-}NO_2 \xrightarrow{h\nu} R\text{-}NO_2^* \qquad (63)$$

$$R\text{-}NO_2^* + HSnBu_3 \longrightarrow R\text{-}NO_2H + \cdot SnBu_3 \qquad (64)$$

Chemical Initiation:

$$In_2 \xrightarrow{\Delta} 2\ In\cdot \qquad (65)$$

$$In\cdot + HSnBu_3 \longrightarrow InH + \cdot SnBu_3 \qquad (66)$$

Radicals of organometals, particularly those with alkyl groups as ligands are predicted to be good electron donors. Consequently, the efficiency of an electron transfer process under a set of satisfactory reaction conditions would depend upon the capability of the substrate to act as electron acceptor. The ability of tertiary nitro compounds to accept a single electron from a variety of donors has been demonstrated in a number of works. These include the already mentioned examples reported by Krasuska,[139] Kornblum,[140] and Ono,[141] where the nitro group is replaced by hydrogen. Many other reactions of these substrates with the anion of thiophenol, phenol, 2-carboethoxycumaran-3-one,[142] and 2-nitropropane[53] have also been rationalized in terms of radical-chain mechanisms which involve the transfer of an electron from the anion to the nitro compound:

$$R\text{-}NO_2 + A^- \longrightarrow R\text{-}NO_2^{\cdot-} + \text{residue} \qquad (67)$$

By analogy, the stannyl radical once generated from the starting tin hydride would be predicted to perform this electron transfer with even more facility. The chain mechanism of equations 68-70 provides a simple basis for understanding the foregoing facts and is consistent with what is known about related processes.[135,140]

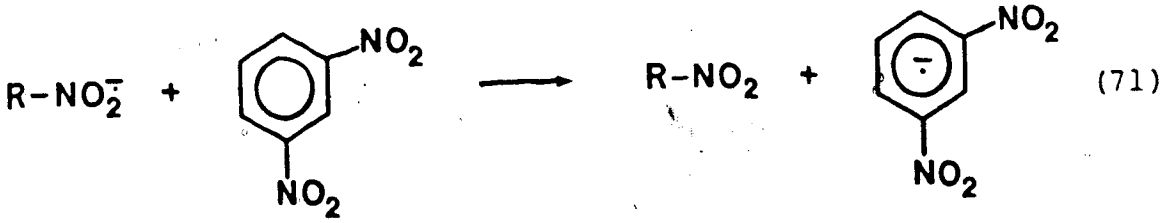
SCHEME 16

$$R\text{-}NO_2 + \cdot SnBu_3 \longrightarrow R\text{-}NO_2^{\cdot -} + {}^{+}SnBu_3 \quad (68)$$

$$R\text{-}NO_2^{\cdot -} \longrightarrow R\cdot + NO_2^- \quad (69)$$

$$R\cdot + HSnBu_3 \longrightarrow RH + \cdot SnBu_3 \quad (70)$$

The key step in this mechanism is the reaction of the nitro compound with the stannyl radical, which generates a transient radical anion. The radical formed from the decomposition of this transient intermediate is rapidly converted to the hydrocarbon. An additional observation supports this mechanistic sequence. Both the dark uninitiated and the benzoyl peroxide initiated reactions were inhibited by the addition of m-dinitrobenzene which is recognized as a diagnostic for radicals and/or radical-anions.[143] The nitroarene intercepts the chain probably by taking an electron away from the transient radical-anion before the loss of the nitrite takes place,[52] or by scavenging radicals

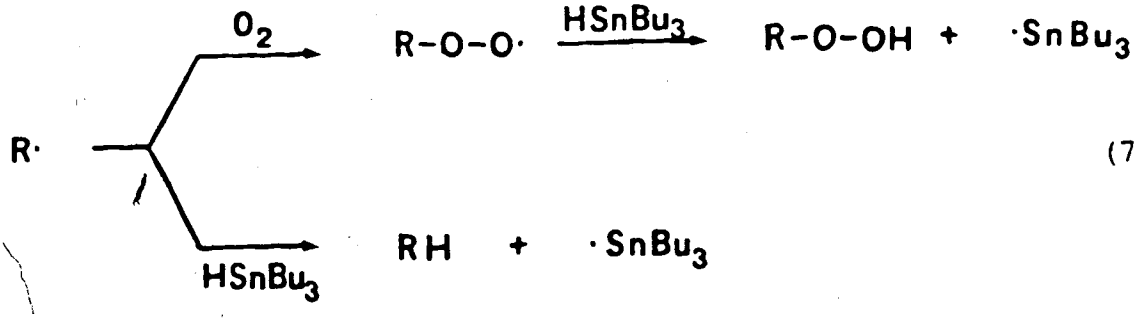


(71)

present in the mixture.[144] Radical chains can also be intercepted by molecular oxygen. The ability of oxygen to prevent substitution of the tertiary carbon in substrates where the potential leaving group is nitro or chloro has been well documented by Kornblum.[52] Oxygen scavenges the radical formed from the transient radical anion and the resulting peroxy radicals presumably are converted into hydroperoxides.

$$R\cdot + O_2 \longrightarrow R\text{-}O\text{-}O\cdot \longrightarrow R\text{-}O\text{-}OH \qquad (72)$$

However, the reduction of tertiary nitro compound I with tri-n-butyltin hydride was not noticeably affected by the oxygen when reactions were carried out in undegassed ampules. Although no evidence is at hand, a possible explanation for the lack of interference by molecular oxygen is the ease of hydrogen abstraction from the tin hydride even by the less reactive peroxyradical.[145]



(73)

The results obtained in the dark uninitiated reactions at 38°C and 90°C suggest a key question about the nature of the initiation step in these processes. At least four initiation mechanisms can be considered to account for these observations:

The first is homolysis of hexa-n-butyldistannane, which appears always to be present in the tri-n-butyltin hydride. The low values for the bond dissociation energy of the Sn-Sn bond[146] suggest that tin radicals can be easily generated by homolytic cleavage, when the energy requirements are satisfactorily met.

$$Bu_3Sn-SnBu_3 \xrightarrow{\Delta} 2\ Bu_3Sn\cdot \qquad (74)$$

The extent to which the distannane compounds undergo dissociation has been the subject of several conflicting reports. Some reports indicate that in dilute solutions the compounds are dissociated, while in more concentrated solutions they exist in the completely associated form. Other reports indicate no evidence for dissociation. For example, Krauss and Sessions[147] state that cryoscopic measurements indicate that hexamethyldistannane is almost completely dissociated into trimethylstannyl radicals in dilute solutions. As supporting evidence for dissocia-

tion Bullard[148] prepared 1,1,1-triethyl-2,2,2-trimethyldistannane by heating to reflux a mixture of hexamethyldistannane and hexaethyldistannane in benzene.

A second mechanism which deserves consideration involves electron transfer from hexa-n-butyldistannane to the tert-nitro compound.

$$R\text{-}NO_2 + Bu_3Sn\text{-}SnBu_3 \longrightarrow R\text{-}NO_2^{\cdot-} + Bu_3Sn\text{-}\overset{+\cdot}{S}nBu_3 \quad (75)$$

$$Bu_3Sn\text{-}\overset{+\cdot}{S}nBu_3 \longrightarrow Bu_3Sn^{+} + \cdot SnBu_3 \quad (76)$$

Organometals of the type R_4Sn and R_6Sn_2 can potentially be good electron donors by virtue of the powerful inductive effect exerted by the alkyl groups. The occurrence of this initiation step has been suggested for the radical reactions of hexaalkyldistannanes[149] and tetraalkylstannanes.[150-152] The tin-tin bond of the distannane radical cation generated in equation 75 is expected to be more labile than the diamagnetic precursor.

Electron transfer from tri-n-butyltin hydride to the tertiary nitroparaffin is the third mechanistic possibility:

$$R\text{-}NO_2 + HSnBu_3 \longrightarrow R\text{-}NO_2^{\cdot-} + H\overset{+\cdot}{S}nBu_3 \quad (77)$$

$$H\overset{+\cdot}{S}nBu_3 \longrightarrow H^{+} + \cdot SnBu_3 \quad (78)$$

The occurrence of the initiation step at low temperature and its inhibition by m-dinitrobenzene suggests the possibility that tin hydride itself can act as the electron transfer reagent in the same manner as proposed for tetraalkylstannanes and hexaalkyldistannanes. Similarly to these substrates, it can be proposed that the reactants are in equilibrium with their charge transfer complexes, and that the charge transfer complex dissociates to $R\text{-}NO_2^{-\cdot}$ and $H\overset{+\cdot}{S}nBu_3$ either thermally or photochemically promoted. The latter process could also account for the photochemical initiation. The suggestion of electron transfer from the tin hydride is consistent with the spontaneous initiation observed in a number of reactions involving metal hydrides. Tanner[135] reported that in the reduction of benzyl halides with tri-n-butyltin hydride, the induced homolysis reaction appears to take place only with the more reactive substrates. Kochi[156] also suggests that an inner sphere electron transfer was involved in the spontaneously initiated addition of triethyltin hydride to tetracyanoethylene in solvents toluene and cyclohexane.

A fourth possibility, the thermolysis of the tri-n-butyltin hydride can be considered:

$$HSnBu_3 \xrightarrow{\Delta} H\cdot + \cdot SnBu_3 \qquad (79)$$

The relatively weak H-Sn bond[154] suggests that small amounts of tin radicals could also be generated by homolysis of the tin hydride.

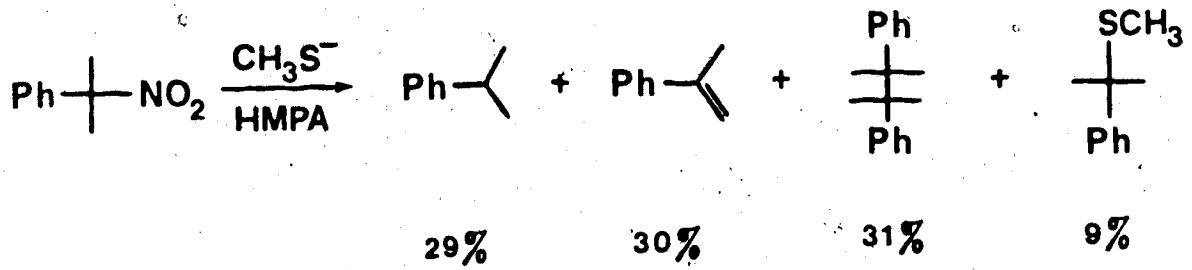
Some insight into the initiation step in the uninitiated reactions was obtained by examining the reduction of nitro compound I in the dark at 38°C and 90°C with equimolar amounts of tin hydride and distannane. Electron transfer from hexabutyldistannane or thermolysis of Sn-Sn bond could be discarded as the initiating act on the basis of the observation that the yields of product Ia were comparable to those obtained under identical conditions in the absence of added distannane. A similar conclusion could be obtained from the fact that this substrate was not affected by hexabutyldistannane in the absence of tin hydride.

If tin radicals cannot be generated from hexabutyldistannane under the experimental conditions used in this work, thermolysis of H-Sn bond is even less likely to occur since the bond dissociation energies for Sn-Sn are lower (46.7±4 kcal/mole)[146] than the bond dissociation energies for H-Sn (65.0 kcal/mole).[154] The small amount of reaction which occurs at 38°C in the uninitiated reactions of compounds I, II, and IV is probably not the result of thermolysis, since the change in the extent of reaction, for a change in temperature of 52°C, does not appear to be of sufficient

magnitude (compare the following reactions: Table I, reaction 5 and 9; Table II, reaction 4 and 3; Table III, reaction 5 and 3). The observation that the tin hydride reduction of benzyl halides[135] at 90°C in solvent benzene occurs spontaneously only with the more reactive substrates supports this point of view. From the foregoing facts we propose that the initial step in the uninitiated reactions involves an electron transfer from the tin hydride to the nitro compound as shown in equation 77.

From the point of view of synthetic utility, the reduction of tertiary nitro compounds with tin hydride compares favorably with Kornblum's method. Aside from the high yields the tin hydride reduction method has the added advantage that side reactions are less likely to occur. For example, the reduction of α-nitrocumene with sodium thiomethoxide in HMPA, which is the least successful example in this series, affords a mixture of four products where only 29% corresponds to cumene.[140]

(80)



The almost identical yields of cumene and α-methylstyrene suggest that these products derive from disproportionation of the cumyl radical. On the other hand, the substantial amount of bicumyl, which arises from radical-radical combination, also testifies to the reluctance of the cumyl radical to enter into reaction with the mercaptide ion. The reduction of this substrate with tri-n-butyltin hydride in benzene affords cumene as major product (79% yield) and only trace amounts of α-methylstyrene and bicumyl are detected. The difference in the reactions is undoubtedly due to the ease of hydrogen transfer with the tin hydride compared to the less facile transfer reaction with thiomethoxide. In the latter case, the relatively stable cumyl radical undergoes dimerization and disproportionation in preference to hydrogen abstraction.

EXPERIMENTAL

A. Materials.

n-Undecane (99% pure) and octadecane (97% pure) were purchased from Aldrich Chemical Co. and used without further purifications.

Cumene (Eastman Kodak Co.) was distilled at 84-85°C/100 mm prior to use.

α-Methylstyrene (Aldrich Chemical Co.) was purified by two consecutive distillations and the fraction b.p. 162-163°C/700 mm was collected.

Tri-n-butyltin hydride and hexabutyldistannane (Alfa Research Chemicals and Materials) were used as purchased.

m-Dinitrobenzene (Fisher Scientific Co.) was purified by recrystallization from ethanol: m.p. 88-90°C (lit[155] 90°C).

Durene (Aldrich Chemical Co.) was recrystallized from aqueous ethanol: m.p. 79-81°C (lit[155] 79°C).

Benzoyl peroxide (Fisher Scientific Co.) was purified by recrystallization from dichloromethane-methanol: m.p. 102-105°C (lit[155] 106-108°C).

Hexamethylphosphoramide (Aldrich Chemical Co.) was distilled from calcium oxide at 127°C/20 mm and stored over molecular sieves 4A.

Dimethylformamide (Fisher Scientific Co.) was dried over calcium sulphate for one day, distilled at 72-73°C/

40 mm, and stored over molecular sieves 4A.

Dimethylsulphoxide was dried over powdered barium oxide, distilled (74-75°C/12 mm) and stored over molecular sieves 4A.

Commercial benzene (Caledon Laboratories Ltd.) was shaken with concentrated sulphuric acid (10% v/v) 7 times, washed with water (3 times), 10% sodium carbonate solution, water, and then dried over anhydrous calcium chloride. The benzene was fractionally distilled from sodium wire, the middle fraction, b.p. 77-78°C/705 mm, collected and subjected to fractional recrystallization at low temperature (sodium chloride - ice bath).

Nitrocyclohexane. This compound was prepared according to the method outlined by Nametkin,[156] using cyclohexane (40 mL, 0.36 mol) and nitric acid (60 mL, d 1.2 g/mL). The crude product was distilled at 110°C/40 mm: n_D^{22} 1.4604 (lit[156] n_D^{19} 1.4612); IR (neat) 6.45, 7.24 (NO_2) μm.

The lithium salt of nitrocyclohexane. Using the literature procedure,[157] nitrocyclohexane (18.8 g, 0.146 mol) was converted to its lithium salt by reaction with a methanolic solution of lithium methoxide. The product was collected in quantitative yield as an off white powder.

2-Bromo-2-cyanopropane. This material was prepared

from isobutyronitrile (25 g, 0.36 mol) and bromine (58 g, 0.36 mol) in the presence of phosphorus tribromide (98 g, 0.36 mol) by the procedure reported by Stevens.[158] The crude reaction product was distilled at 138-140°C/699 mm.

2-Cyano-2-nitropropane. This compound was synthesized by the method reported by Kornblum.[140] A DMF solution (400 mL) of urea (38 g, 0.63 mol), sodium nitrite (28.4 g, 0.41 mol) and 2-bromo-2-cyanopropane (40.8 g, 0.275 mol) yielded a crude product, which after distillation (70-75°C/10 mm) gave 7.6 g (24.4%) of 2-cyano-2-nitropropane: m.p. 34-36°C (lit[140] 35.5-36°C).

2-(Nitrocyclohexyl)isobutyronitrile (I). This tert-nitro compound was prepared by the reaction of 2-cyano-2-nitropropane (8.8 g, 0.08 mol) with the lithium salt of nitrocyclohexane (16.2 g, 0.12 mol) in DMSO (330 cc), according to the procedure reported by Kornblum.[140] Recrystallization of the impure material from hexane gave a white solid (8.7 g, 55.7%): m.p. 108.5-110°C (lit[140] 108-109°C); NMR ($CDCl_3$) δ 1.45 (s, 6 H), 1.2-2.0 (m, 8 H), 2.5-2.9 (m, 2 H); IR ($CHCl_3$) 4.46 (CN), 6.47, 7.24 (NO_2) μm; MS m/e 150, 81, 69.

Anal. Calcd for $C_{10}H_{16}N_2O_2$: C, 61.19; H, 8.21; N, 14.28. Found: C, 61.28; H, 8.31; N, 14.33.

Sodium thiomethoxide. This material was obtained by passing methyl mercaptan (5 g, 0.1 mol), through a solu-

tion of the sodium salt of 2-propanol,[140] (1.8 g, 0.08 mol of sodium in freshly distilled 2-propanol). The final product, obtained in quantitative yield was a white powder.

2-Cyano-2-cyclohexylpropane (Ia). This compound was obtained from the reaction of 2-(nitrocyclohexyl)isobutyronitrile (0.4 g, 2 mmol) and sodium thiomethoxide (0.42 g, 6 mmol) in DMSO using the method outlined by Kornblum.[140] The crude product, a yellow oil, was purified by column chromatography (silica gel and hexane-ether) and then by distillation (87-88°C/3 mm, lit[140] 70°C/1 mm) to yield a colorless liquid: NMR ($CDCl_3$) δ 1.34 (s, 6 H), 1.07-2.1 (m, 11 H); IR (neat) 4.46 (CN) μm.

N-α-Cumylformamide. This compound was prepared from α-Methylstyrene (118 g, 1 mol) by treatment with sodium cyanide (55 g, 1.1 mol) and concentrated sulphuric acid (250 g) in glacial acetic acid, using the procedure reported by Ritter and Kalish.[169] Two consecutive Kugelrohr distillations of the crude product, a yellow oil, at 124-128°C/1 mm (lit[53] 93°C/0.1 mm) yielded 41 g (25%) of N-α-cumylformamide, a colorless oil.

α-Aminocumene. This tert-amino compound was obtained by the alkaline hydrolysis of N-α-cumylformamide (40 g, 0.245 [redacted][159] Distillation of the crude product (83-

86°C/10 mm. Lit[53] 94°C/26 mm) gave 17.6 g (53%) of a colorless liquid, n_D^{22} 1.5190 (lit[160] n_D^{25} 1.5175-1.5185), having a NMR (CCl_4) spectrum δ 1.26 (s, 2 H), 1.37 (s, 6 H) 7.1-7.6 (m, 5 H) which was consistent with α-aminocumene.

α-Nitrocumene (IV). The general procedure for the transformation of tert-amino into tert-nitro compounds described by Kornblum[161] was followed. Permanganate oxidation of α-aminocumene (15 g, 0.11 mol) gave the product (5.8 g, 32%), whose physical properties were consistent with those given in the literature[53]: n_D^{22} 1.5191 (lit[162] n_D^{20} 1.5204); NMR ($CDCl_3$) δ 1.97 (s, 6 H), 7.43 (s, 5 H); IR (neat) 6.51, 7.40 (NO_2) μm; MS m/e 119.

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.54; H, 6.81; N, 8.38.

Lithium salt of 2-nitropropane. This lithium salt was prepared in quantitative yield by the reaction of 2-nitropropane (17.8 g, 0.2 mol) with a methanolic solution of lithium methoxide.[157]

p-Cyano-α-nitrocumene (II). Using the literature procedure,[163] p-nitrobenzonitrile (14.8 g, 0.1 mol) was subjected to reaction with the lithium salt of 2-nitropropane (19.0 g, 0.2 mol) in HMPA. The crude product, a yellowish solid, was purified by column chromatography on neutral alumina using benzene as eluent, and then re-

crystallized twice from pentane to give a white solid whose physical properties were identical to those reported for p-cyano-α-nitrocumene: mp 62-63°C (lit[163] 59.5-60.5°C); NMR ($CDCl_3$) δ 1.96 (s, 6 H); 7.6 (m, 4 H); IR ($CHCl_3$) 4.47 (CN), 6.46 (NO_2) μm; MS m/e 144, 116, 89.

Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.73. Found: C, 62.84; H, 5.30; N, 14.76.

p-Cyanocumene (IIa). Treatment of p-cyano-α-nitrocumene (3.8 g, 20 mmol) with sodium thiomethoxide (4.2 g, 60 mmol) in HMPA[140] gave a yellow oil which was subjected to column chromatography on silica gel (benzene-ether, 49:1). After removing the solvent, the material was purified by gas chromatography using a 10% OV 101, Chromosorb WAW DMCS, 10' x 1/4" stainless steel column. The collected colorless oil was p-cyanocumene: NMR ($CDCl_3$) δ 1.27 (d, 6 H), 2.97 (h, 1 H), 7.25-7.75 (m, 4 H); IR (neat) 4.46 (CN) μm; MS m/e 145, 130.

4-Nitrophenyl phenyl sulfone. The synthesis of this compound was carried out by treating p-dinitrobenzene (21.0 g, 0.125 mol) with sodium benzene sulfinate (23.0 g, 0.140 mol) in DMSO.[163] The resulting brown solid was recrystallized three times from absolute ethanol to afford an off white solid: mp 141.5-143°C (lit[164] 140-142°C).

4-Phenylsulfonyl-α-nitrocumene. 4-Nitrophenyl,

phenylsulfone (13.5 g, 50 mmol) was converted to 4-phenylsulfonyl-α-nitrocumene from its reaction with the lithium salt of 2-nitropropane (9.3 g, 98 mmol) in HMPA.[163] Two recrystallizations of the impure material from absolute ethanol afforded a white solid: mp 118-120°C (lit[163] 117-117.5°C); NMR ($CDCl_3$ δ 1.97 (s, 6 H), 7.46-7.70 (m, 5 H), 7.88-8.17 (m, 4 H).

2,3-Dimethyl-2-(p-benzenesulfonylphenyl)-3-nitrobutane (III). Using the literature procedure,[53] 4-phenylsulfonyl-α-nitrocumene (3.05 g, 10 mmol) was subjected to reaction with the lithium salt of 2-nitropropane (10.6 g, 110 mmol) in HMPA (100 ml). The crude product obtained from this reaction was recrystallized twice from methanol to give a white solid: mp 141.5-143.5°C (lit[53] 143-143.5°C); NMR ($CDCl_3$) δ 1.48 (s, 12 H), 7.40-7.65 (m, 5 H), 7.80-8.05 (m, 4 H).

Anal. Calcd for $C_{18}H_{21}NO_4S$: C, 62.25; H, 6.05; N, 4.03; S, 9.22. found: C, 61.90; H, 6.16; N, 3.98; S, 9.21.

2,3-Dimethyl-2-(p-benzenesulfonylphenyl)butane (IIIa). This compound was obtained by reduction of 2,3-dimethyl-2-(p-benzenesulfonylphenyl)-3-nitrobutane (0.44 g, 1 mmol) with sodium thiomethoxide (0.26 g, 3.7 mmol) in DMF using the method described by Kornblum.[140] The crude product was recrystallized twice from hexane to

give a white solid: mp 76-77°C (lit[140] 79.5-80.5°C). NMR ($CDCl_3$) δ 0.72 (d, 6 H), 1.21 (s, 6 H), 1.90 (h, 1 H), 7.40-7.63 (m, 5 H), 7.80-8.02 (m, 4 H).

B. Methods and Procedures.

1. Physical Constants.

All melting point values are uncorrected and were obtained with a Reichert melting point apparatus.

Refractive indexes were measured on a Bausch & Lomb refractometer.

2. Microanalyses.

Microanalyses were performed in the Microanalytical Laboratory, Chemistry Department, University of Alberta, Edmonton.

3. Spectral Measurements.

Infrared spectra (IR) were recorded on a Perkin Elmer 457 spectrophotometer. Nuclear Magnetic Resonance (NMR) spectra are proton spectra and were obtained on either a Varian Associates A-56/60 A, a Perkin Elmer R-32 90 MHz, or a Varian HA-100/Digilab - 12 inch Magnet spectrometer. Chemical shifts are expressed in δ units. The following symbols are used to denote multiplicity: singlet, s; doublet, d; heptet, h; multiplet, m. Mass Spectra (MS) were obtained using a A.E.I. MS-50 high

resolution Mass Spectrometer coupled to a Data General Nova 2 DS-50, with an ionizing voltage of 70 eV. Gas chromatography - mass spectra (Glpc-ms) data were obtained using a Varian Aerograph 1400 gas chromatograph coupled to a A.E.I. MS-12 medium resolution mass spectrometer with a Data General Nova 3 DS-55. Columns are specified in the individual experiments.

4. Gas Liquid Partition Chromatography (glpc) Analyses.

Glpc analyses were carried out using a Hewlett Packard 5840 A gas chromatograph provided with either a normal injector system for packed columns or a H.P. 18835-B capillary inlet system for capillary columns. A thermal conductivity detector was utilized for analysis with packed columns, while a flame ionization detector was used in case of capillary chromatography. Both detectors were coupled to a Hewlett Packard 5840 A terminal integrator.

In order to quantify the products in reaction mixtures, calibration data were obtained by analyzing mixtures of known composition of standard (s) and authentic material (x). Glpc response calibration factors, f s/x, of the standard relative to the product were obtained from the equation:

$$f_{s/x} = \left(A_s/A_x\right)\cdot\left(M_x/M_s\right)$$

where A's represent peak areas, and M's number of moles.

Under the same glpc conditions as those used to analyze the mixtures of known compositions, these factors can be used to calculate the number of moles of products formed and the number of moles of unreacted material in the reaction mixtures:

$$M_x = f_{s/x} \cdot \left(A_x / A_s \right) \cdot \left(M_s \right)$$

The specifications of the columns used throught the course of this work are given in the individual experiments.

5. High Pressure Liquid Chromatograph (hplc) Analyses.

Hplc analyses were performed with a Perkin Elmer, Series 2 liquid chromatograph, supplied with a Perkin Elmer LC-55B Spectrophotometric UV detector and a Differential Refractometer R.I. detector, and coupled to a Varian CDS 401 Data System.

Two types of columns were used: (1) Stainless Steel columns (3.9 mm x 30 cm μ Porasil, 3000 plates per column) and (2) Radial PAK-A reverse phase permanently bonded octadecylsilane, compressed by a RCM-100 module. The particular type of column, as well as, the standard and solvent system used, are specified in the individual experiments. As in glpc analysis, quantifications of

products were carried out using f s/x values obtained from mixtures of known composition of standard and authentic material.

6. General Procedure for Reactions.

Reaction ampules were Pyrex tubes joined to 10/30 joints. The ampules were cleaned with chromic acid solution, water, concentrated ammonium hydroxide, and distilled water, then oven dried at 120°C. The reactants were placed in the ampules, degassed by three freeze-thaw cycles at 2-3 μm (-198°C), and sealed under vacuum. The degassed mixtures were subsequently allowed to react under the desired conditions.

C. A General Procedure for the Reaction of Nitroalkanes with Tri-n-butyltin Hydride in Solvent Benzene. Reduction of 2-(Nitrocyclohexyl)isobutyronitrile (I).

An aliquot sample (0.5 ml) of a stock solution which was 0.08 molar in the compound I and 0.024 molar in n-undecane (internal standard) was placed in an ampule wrapped with aluminum foil. Another 0.5 ml of benzene solution of tri-n-butyltin hydride (0.24 molar) was added and the ampule was degassed and then sealed. The mixture was subjected to reaction in an oil bath at 90°C, in the dark,

dark for a standard time (18 h). The ampule was opened and analyzed by glpc using a 10% UCON Polar 50 H 2000, Chromosorb W. AW 60-80 mesh, 13' x 1/8" stainless steel column. The chromatogram showed 6 major peaks. The structures of the compounds related to these glpc peaks were established by a comparison of their retention times and glpc-mass spectra with those of authentic samples. Three of the peaks correspond to tri-n-butyltin hydride, tetrabutylstannane, and hexabutyldistannane. Two peaks correspond to the starting material and the reduction product Ia. Quantification of these peaks against n-undecane afforded 46% of I and 36% of Ia. The sixth peak corresponds to the internal standard.

One or more experiments were carried out to test the effect of each of the following: concentration of tri-n-butyltin hydride, temperature, initiation by light, benzoyl peroxide, and hexabutyldistannane, inhibition by m-di-nitrobenzene and O_2. The results and specific conditions for these experiments are listed in Table I.

The Reduction of α-Nitrocumene(IV) with Tri-n-butyltin Hydride in Solvent Benzene.

The reactions of α-nitrocumene with tri-n-butyltin hydride in benzene were performed under analogous conditions to those outlined in the general procedure (degassed mixtures thermostated at a given temperature

for 18 h in the dark or light). The experiments were those designed to test the effect of concentration of tri-n-butyltin hydride, temperature, initiation by benzoyl peroxide or light and inhibition by m-dinitrobenzene. Analyses were carried out by either glpc using a 10% UCON Polar, Chromosorb W AW, 60-80 mesh, 13' x 1/8" stainless steel column or by hplc using a 10 cm Radial PAK-A cartridge (reverse phase permanently bonded octadecylsilane) and a 1:1 water-acetonitrile solvent system. The structure of the compounds related to the peaks observed in the chromatograms were determined as indicated in the general procedure. Determination of moles of products was done against n-undecane (internal standard in glpc) or durene (external standard in hplc). The results and specific conditions of these experiments are listed in Table III.

The Reduction of p-Cyano-α-nitrocumene (II) with Tri-n-butyltin Hydride in Solvent Benzene.

The reactions of nitrocompound II with tri-n-butyltin hydride in benzene were carried out in an identical manner to that described in the general procedure (degassed mixtures thermostated at 90°C or 38°C for 18 h in the dark). These reactions involved test for initiation with benzoyl peroxide and temperature effect. The reaction mixtures were analyzed by glpc

using a 3% OV-101, Chromosorb W AW DMCS, 60-80 mesh, 10' x 1/8" stainless steel column. Besides the peaks assigned to tin compounds (tri-n-butyltin hydride, tetrabutylstannane, and hexabutyldistannane) and internal standard (octadecane), two major peaks are observed. They correspond to p-cyanocumene (IIa) and p-cyano-α-nitrocumene (II). The yield of these products was determined as described in the general procedure. Results and specific conditions of these reactions are listed in Table II.

Reduction of p-Cyano-α-nitrocumene with Tri-n-butyltin Hydride in Benzene. A Synthetic Method.

A mixture of p-cyano-α-nitrocumene (327 mg, 1.719 mmol), tri-n-butyltin hydride (1.517 mg, 5.204 mmol), and benzoyl peroxide (33.5 mg, 0.138 mmol) in benzene (18 mL) was heated to reflux for 18 h under a nitrogen atmosphere. The solvent benzene was removed by distillation. A dilute solution of iodine in diethylether was added to destroy the excess of tin hydride. The tin salts present in the mixture were precipitated as the fluoride salts by addition of an aqueous solution of potassium fluoride.[165] The fluoride salt was removed by filtration and the organic layer washed with an aqueous solution of sodium thiosulphate, water, and dried over anhydrous magnesium sulphate. The

ether was removed by distillation and the residue, after column chromatography (silica gel, pentane), and distillation, yielded 187.2 mg (75%) of p-cyanocumene, n_D^{20} = 1.5190 (lit 1.5194[166] and 1.5196[140]). NMR ($CDCl_3$) δ 1.27 (d, 6 H), 2.97 (h, 1 H), 7.25-7.75 (m, 4 H).

The Reduction of 2,3-Dimethyl-2-(p-benzenesulfonyl-phenyl)-3-nitrobutane (III) with Tri-n-butyltin Hydride in Solvent Benzene.

The reactions of nitro compound III were performed as indicated in the general procedure, except that no internal standard was used. These reaction involved test for initiation with benzoyl peroxide. The reaction mixtures were analyzed by hplc using a 3.9 mm x 30 cm μ-Porasil stainless steel column (3000 plates) and a 4:1 n-hexane-chloroform solvent system. m-Dinitrobenzene was used as external standard. The results of these experiments are listed in Table II.

PART II

INTRODUCTION

Organotin monohydrides have been found to reduce aldehydes and ketones to their corresponding alcohols under a variety of reaction conditions. These reactions were initially reported as occurring according to the following general equation:

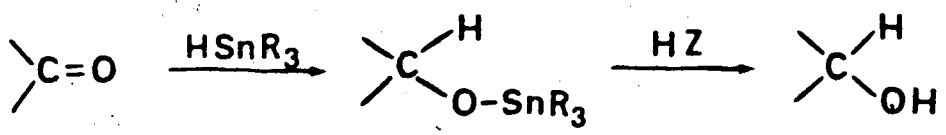
$$\rangle C{=}O + 2\,R_3SnH \longrightarrow \rangle C\langle^{H}_{OH} + (R_3Sn)_2 \qquad (81)$$

The reduction of these carbonyl compounds was first reported by Van der Kerk and Noltes.[167] They found that triphenyltin hydride could reduce methyl vinyl ketone and phenyl vinyl ketone, the products being the alcohol and hexaphenyldistannane. Later, in 1961 Kuivila[168] investigated the reaction of benzaldehyde with triphenyl- and tri-n-butyltin hydride. The aldehyde was reduced in the absence of solvent by both tin hydrides to yield 86% of benzyl alcohol. Under comparable conditions, 4-methylcyclohexanone and 4-tert-butylcyclohexanone could also be reduced by triphenyltin hydride to produce the alcohols in high yields. In both cases the major product was the trans-isomer. The reduction mechanism was reported to proceed by transfer of hydrogen to the sub-

strate.

Since then a large number of aldehydes and ketones have been converted into alcohols by using different trialkyltin hydrides. These include chloral and pentafluorobenzaldehyde,[169-170] aliphatic[171] and aromatic aldehydes.[171-173] The ketones that have been studied include aliphatic,[171-172,174] carbocyclic[171,175-176] and aromatic ketones.[169-171] The yields, obtained from the reductions carried out in either neat solutions or in solvents, methanol, cyclohexane, isobutyronitrile, toluene, etc., are generally high. Studies on the reactivity of the tin hydrides indicated that $HSnPh_3$ is more reactive than $HSnBu_3$[132,168] while in another study of the reduction of electrophilic ketones[170] the order of reactivity was reported to be $HSnEt_3 > HSnMe_3 > HSnBu_3 >> HSnPh_3$.

Today it is generally accepted that the reduction of ketones may occur under ionic or under free-radical generating conditions. In both cases the process involves a net initial addition of $HSnR_3$ to the carbonyl group to generate an alkoxystannane which upon hydroly-

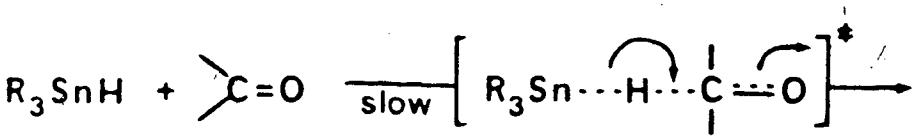


(82)

Z = OH , OR , SnR_3 .

sis, solvolysis or hydrostannolysis gives the corresponding alcohol.

Two different mechanistic pathways have been proposed to account for the formation of the alkoxystannane, a heterolytic and a homolytic pathway. The heterolytic mechanism, which involves a hydride transfer, was initially suggested by Newmann and Heymann[171] and subsequently confirmed by other works.[170]



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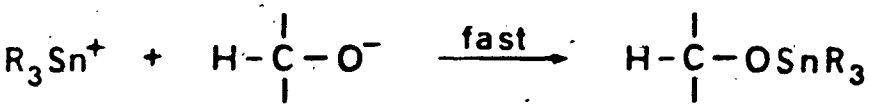
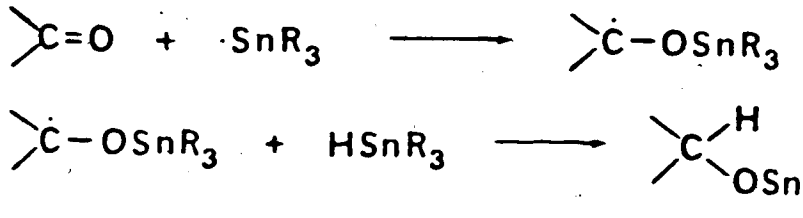


(84)

The heterolytic pathway was proposed to explain the observation that the rate of reduction increased with the increasing polarity of the solvent and that electron releasing substituents at tin and electron withdrawing substituents α to the carbonyl likewise increased the rate of reduction. Reactions conducted in solvent methanol in the absence of α,α-azobisisobutyronitrile (AIBN) or light were not affected by galvinoxyl. The reductions were also found to be catalyzed by $ZnCl_2$ and by acid. In the case of ionic addition, the attack of the nucleophile determined the stereochemistry of the addition.

The homolytic pathway has been shown to be catalyzed either by light or by AIBN, or inhibited by galvinoxyl,

and is proposed to involve a free-radical chain addition.[171,177]



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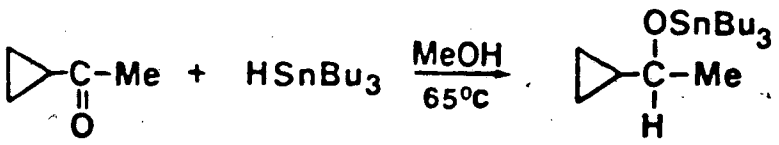
(86)

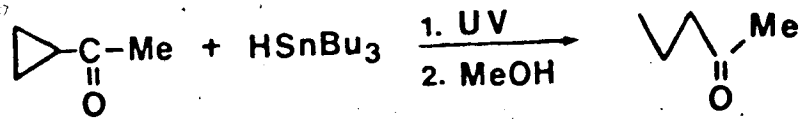
In this mechanism, the stereochemistry of the products is determined during the hydrogen atom transfer.

More information concerning the free-radical chain mechanism has been obtained by analyzing the reactions of α-cyclopropyl and α-cyclobutyl ketones.[178-182] The reduction of α-cyclopropyl ketones with tri-n-butyltin hydride in refluxing methanol leads to the alcohol as only product[178] (eq. 87).



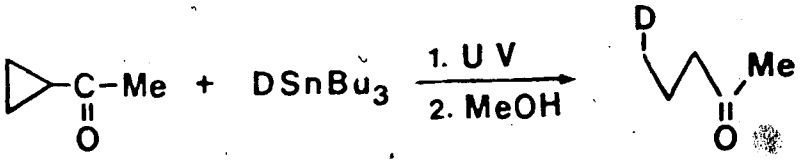
(87)

The initial hydrostannation presumably arose from an ionic mechanism. However, when the reaction was conducted in the presence of AIBN or under U.V. irradiation followed by methanolysis the product was the open chain ketone (eq. 88).



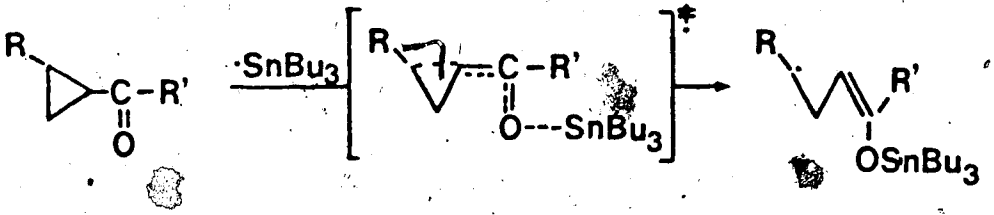
(88)

When cyclopropyl methyl ketone was treated with $DSnBu_3$ under the same conditions (U.V., methanol) the product was the γ-deuterated open chain ketone.[178]



(89)

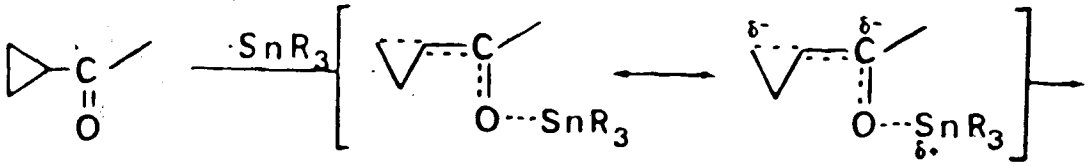
The opening of the cyclopropane ring was inferred to be concomitant with the addition of the stannyl radical to the carbonyl oxygen.



(90)

The rate and direction of ring opening was proposed not to be controlled by the relative stability of the ring

opened radicals formed but by stereoelectronic factors and polar effects[179-180] which governed the relative stability of the proposed transition states. A study of the reactivity with tri-n-butyltin hydride of two series of cyclopropyl ketones (m- and p-substituted by 2-phenylacetylcyclopropanes and m- and p-substituted benzoylcyclopropanes) under radical generating conditions shows positive ρ values using the Hammett correlation. The results were interpreted as consistent with a polar transition state for the radical-promoted ring opening.[180]



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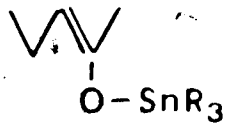
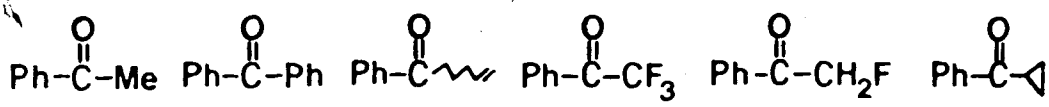


Recently the chemistry of trialkyltin hydrides has been proposed to involve electron transfer with a variety of substrates. Tanner[135] suggested a radical-chain mechanism involving electron transfer for the reduction of benzyl iodides with tri-n-butyltin hydride in solvent benzene. Subsequently, the results of a study of the

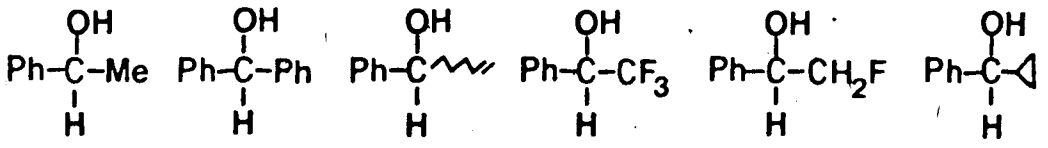
reduction of methyl iodide by trialkyltin hydrides has been likewise interpreted as proceeding by electron transfer.[183] Most recently, Tanner[184] demonstrated that, following the same type of reaction process, the replacement of the nitro group in tertiary nitro compounds could be effected by tri-n-butyltin hydride reduction when carried out under free-radical conditions. Since this alternative pathway, the electron transfer process, appears to be involved in tin hydride reductions, it was of interest in light of the newly proposed reaction scheme, to reexamine in some mechanistic detail the well documented reduction of organic carbonyl compounds by these reagents. For this purpose, the reduction of a series of six different aromatic ketones and cyclohexanone by either triphenyl or tri-n-butyltin hydride was studied in solvents benzene, acetonitrile and methanol. The ketones used in this work were acetophenone (V), benzophenone (VI), 1-phenyl-5-hexen-1-one (VII), α,α,α-trifluoroacetophenone (VIII), ω-fluoroacetophenone (IX), cyclopropyl phenyl ketone (X), and cyclohexanone (XI). The reactions were conducted using a standard set of conditions (degassed samples, 61°C, 16 h), but changing one variable at a time in order to establish the applicability of each mechanistic process.

RESULTS

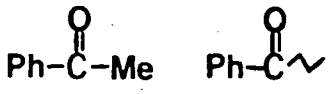
Acetophenone (V), benzophenone (VI), 1-phenyl-5-hexen-1-one (VII) and α,α,α-trifluoroacetophenone (VIII), could be reduced either by triphenyl or tri-n-butyltin hydride, the products being α-methylbenzyl alcohol (Va), benzhydrol (VIa), 1-phenyl-5-hexen-1-ol (VIIa) and α-trifluoromethylbenzyl alcohol (VIIIa). Reduction of ω-fluoroacetophenone (IX) gave two products, acetophenone (V) and α-fluoromethylbenzyl alcohol (IXa). Similarly, cyclopropyl phenyl ketone (X) gave α-cyclopropylbenzyl alcohol (Xa) and butyrophenone (Xb).



V VI VII VIII IX X



Va VIa VIIa VIIIa IXa Xa



V Xb

The reductions were effected in solvents of different polarity: benzene, acetonitrile, and methanol under a set of standard conditions which ensured the decomposition of the initiator, AIBN ($t_{1/2}$ = 18 h) and the ability to differentiate between the reactivity of the two tin hydrides (degassed ampules, 61°C, dark, 16 h). One or more experiments were carried out to test the effect of the initiator (AIBN), the inhibitor (m-DNB), concentration of triphenyltin hydride, polarity of the solvent, and the structure of the tin hydride. Yields of products and unreacted starting materials were determined by glpc. The results are listed in Tables V-X.

Uninitiated Reactions. Mixtures of ketones and triphenyl or tri-n-butyltin hydride in solvent benzene were only sparingly reactive in the absence of additives. The yields of products in the reductions using triphenyltin hydride ranged from traces to less than 6% (Tables V-X, reaction 1 in each table), while the reductions by tri-n-butyltin hydride afforded less than 1% of the reduction products (Tables V-X, reaction 8 in each table). A similar pattern was observed for the reductions of ketones by triphenyltin hydride in solvents acetonitrile (Tables V-VII, IX-X, reaction 10 in each table) and methanol (Tables V-VII, X, reaction 14 in each table). Exceptions to these general observations were

TABLE V

Reduction of Acetophenone (V) with Organotin Hydrides[a]

Reaction[b]	Solvent	Conditions	Product, Yield %[c]	
			CH_3-CH(OH)-Ph	Unreacted Ketone
1	Benzene	-	traces	94.6 ± 1.0
3	Benzene	AIBN (4%)	46.5 ± 0.5	49.7 ± 0.0
4	Benzene	AIBN (8%)	57.0 ± 0.5	37.3 ± 0.8
5	Benzene	AIBN (4%), m-DNB (6%)	0	96.0 ± 1.0
6	Benzene	AIBN (4%)[e]	86.6 ± 3.8	9.9 ± 0.4
8[d]	Benzene	-	traces	95.7 ± 0.3
9[d]	Benzene	AIBN (4%)	5.7 ± 0.3	88.4 ± 0.4
10	Acetonitrile	-	traces	96.0 ± 0.2
12	Acetonitrile	AIBN (4%)	37.5 ± 0.1	57.8 ± 0.1
13	Acetonitrile	AIBN (4%), m-DNB (6%)	traces	97.9 ± 0.4
14	Methanol	-	1.5 ± 0.0	96.4 ± 0.4
15	Methanol	m-DNB (6%)	0.6	93.6
16	Methanol	AIBN (4%)	53.0 ± 1.4	44.5 ± 0.3
17	Methanol	AIBN (4%), m-DNB (6%)	1.0 ± 0.0	97.3 ± 0.0

See Footnotes Page 83.

TABLE VI

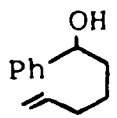
Reduction of Benzophenone (VI) with Organotin Hydrides[a]

Reaction[b]	Solvent	Conditions	Products, Yield %[c]	
			OH PH-CH-Ph	Unreacted Ketone
1	Benzene	-	1.5 ± 0.5	92.7 ± 1.7
2	Benzene	m-DNB (6%)	traces	95.8 ± 0.9
3	Benzene	AIBN (4%)	31.8 ± 4.5	60.6 ± 3.9
4	Benzene	AIBN (8%)	39.3 ± 2.5	56.4 ± 1.8
5	Benzene	AIBN (4%), m-DNB (6%)	0	94.4 ± 2.4
6	Benzene	AIBN (4%)[e]	72.7 ± 2.7	24.1 ± 3.8
8[d]	Benzene	-	traces	97.0 ± 2.0
9[d]	Benzene	AIBN (4%)	1.9 ± 0.3	92.8 ± 1.0
10	Acetonitrile	-	traces	101.7 ± 1.0
12	Acetonitrile	AIBN (4%)	23.3 ± 0.3	74.0 ± 0.0
13	Acetonitrile	AIBN (4%), m-DNB (6%)	0	104.2 ± 0.6
14	Methanol	-	<1.0	99.4 ± 0.4
16	Methanol	AIBN (4%)	25.5 ± 0.9	73.1 ± 1.5

See Footnotes Page 83.

TABLE VII

Reduction of 1-Phenyl-5-hexen-1-one (VII) with Organotin Hydrides[a]

Reaction[b]	Solvent	Conditions	Products, Yield %[c]	
				Unreacted Ketone
1	Benzene	-	traces	95.0 ± 0.8
3	Benzene	AIBN (4%)	38.7 ± 0.3	56.2 ± 0.9
5	Benzene	AIBN (4%), m-DNB (6%)	0	96.7 ± 1.4
6	Benzene	AIBN (4%)[e]	61.0 ± 0.2	34.9 ± 0.6
8[d]	Benzene	-	0	97.0 ± 1.2
9[d]	Benzene	AIBN (4%)	7.4 ± 0.2	90.5 ± 0.4
10	Acetonitrile	-	traces	100.4 ± 0.5
12	Acetonitrile	AIBN (4%)	38.1 ± 1.4	58.4 ± 0.6
14	Methanol	-	<1.0	98.5 ± 0.5
16	Methanol	AIBN (4%)	50.7 ± 0.3	47.0 ± 0.6

See Footnotes Page 83.

TABLE VIII

Reduction of α,α,α-Trifluoroacetophenone (VIII) with Organotin Hydrides[a]

Reaction[b]	Solvent	Conditions	Products, Yield %[c]	
			CF_3-CH(OH)-Ph	Unreacted Ketone
1	Benzene	-	4.4 ± 0.7	91.0 ± 0.5
2	Benzene	m-DNB (6%)	traces	95.1 ± 1.4
3	Benzene	AIBN (4%)	90.6 ± 0.2	8.4 ± 0.4
5	Benzene	AIBN (4%), m-DNB (6%)	traces	91.6 ± 0.6
8[d]	Benzene	-	<1.0	97.2 ± 0.5
9[d]	Benzene	AIBN (4%)	47.5 ± 0.4	48.9 ± 0.0
10	Acetonitrile	-	31.6 ± 3.4	62.6 ± 1.6
11	Acetonitrile	m-DNB (6%)	10.0	72.5
12	Acetonitrile	AIBN (4%)	61.5 ± 1.2	34.3 ± 1.8
14	Methanol	-	66.3 ± 6.8	32.6 ± 5.4
15	Methanol	m-DNB (6%)	38.7 ± 1.8	57.5 ± 1.2
16	Methanol	AIBN (4%)	68.4 ± 3.8	28.8 ± 1.7

See Footnotes Page 83.

TABLE IX

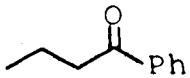
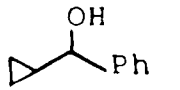
Reduction of ω-Fluoroacetophenone (IX) with Organotin Hydrides[a]

Reaction[b]	Solvent	Conditions	Products, Yield %[c]		
			CH_3-CO-Ph	CH_2F-CH(OH)-Ph	Unreacted Ketone
1	Benzene	-	4.9 ± 0.0	1.2 ± 0.1	91.0 ± 0.6
2	Benzene	m-DNB (6%)	traces	traces	99.0 ± 0.6
3	Benzene	AIBN (4%)	87.0 ± 0.3	<1.0	6.8 ± 0.0
5	Benzene	AIBN (4%), m-DNB (6%)	0	<1.0	96.3 ± 0.1
8[d]	Benzene	-	<1.0	traces	97.0 ± 0.5
9[d]	Benzene	AIBN (4%)	55.2 ± 0.2	traces	32.1 ± 0.7
10	Acetonitrile	-	1.7 ± 0.0	0	97.3 ± 0.5
11	Acetonitrile	m-DNB (6%)	0.3 ± 0.0	0.5 ± 0.0	100.6
12	Acetonitrile	AIBN (4%)	77.2 ± 1.8	0	15.8 ± 1.2
14	Methanol	-	5.3 ± 0.0	41.4 ± 0.6	51.8 ± 0.4
15	Methanol	m-DNB (6%)	0.6 ± 0.1	39.4 ± 0.3	59.9 ± 0.3
16	Methanol	AIBN (4%)	65.8 ± 0.5	1.8 ± 0.0	28.8 ± 0.1

See Footnote Page 83.

TABLE X

Reduction of Cyclopropylphenyl Ketone (X) with Organotin Hydrides[a]

Reaction[b]	Solvent	Conditions	Products, Yield %[c]		
					Unreacted Ketone
1	Benzene	-	1.0	1.5 ± 0.0	95.7 ± 1.7
3	Benzene	AIBN (4%)	27.7 ± 0.7	5.0 ± 0.0	63.0 ± 2.7
4	Benzene	AIBN (8%)	32.8 ± 0.5	6.8 ± 0.0	54.2 ± 1.0
5	Benzene	AIBN (4%), m-DNB (6%)	0	traces	97.5 ± 0.5
6	Benzene	AIBN (4%)[e]	37.7 ± 1.2	9.8 ± 0.2	47.4 ± 0.9
7	Benzene	AIBN (4%)[f]	42.2 ± 1.1	15.6 ± 0.2	36.4 ± 0.8
8[d]	Benzene	-	0	traces	96.9 ± 1.2
9[d]	Benzene	AIBN (4%)	18.1 ± 0.5	traces	73.1 ± 0.4
10	Acetonitrile	-	traces	traces	100.3 ± 0.0
12	Acetonitrile	AIBN (4%)	26.3 ± 0.0	4.3 ± 0.0	69.0 ± 0.3
13	Acetonitrile	AIBN (4%), m-DNB (6%)	0	traces	102.0 ± 0.2
14	Methanol	-	traces	traces	100.0 ± 0.7
16	Methanol	AIBN (4%)	27.2 ± 0.0	3.7 ± 0.2	66.7 ± 0.3
17	Methanol	AIBN (4%), m-DNB (6%)	0	0	101.3 ± 0.3

See Footnotes Page 83.

Footnotes

a. A mole ratio 1:1 of ketone and triphenyltin hydride was used in all of the reactions, except when indicated.

b. Two individual runs were carried out for each reaction. The error values are standard deviations from the mean.

c. In solvent benzene n-tridecane was used as internal standard for ketones V and VI and n-heptadecane for ketones VII, VII, IX, and X. For all of the ketones p-di-tert-butylbenzene was the internal standard in solvents acetonitrile and methanol.

d. A mole ratio 1:1 of ketone and tri-n-butyltin hydride was used in these reactions.

e. The mole ratio ketone: triphenyltin hydride was 1:2.

f. The mole ratio ketone:triphenyltin hydride was 1:4.

α,α,α-trifluoroacetophenone (VIII) and ω-fluoroacetophenone (IX). Ketone VIII gave alcohol VIIIa in 31.6% yield in acetonitrile (Table VIII, reaction 10) and 66.3% in methanol (Table VIII, reaction 14). Ketone IX in methanol yielded 41.4% of α-fluoromethylbenzyl alcohol (VIa) and 5.3% of acetophenone (V) (Table IX, reaction 14).

Initiation by AIBN. The reactions of ketones with triphenyltin hydride in solvents benzene, acetonitrile and methanol were unambiguously initiated by the addition of small amounts of AIBN (4%) to give a reasonable yield of reduction products (Tables V-X, compare reactions 1 and 3, 10 and 12, 14 and 16 in each table). The change in the extent of the reaction of α,α,α-trifluoroacetophenone (VIII) and ω-fluoroacetophenone (IX) in benzene was more dramatic since the corresponding reduction products were obtained in almost quantitative yields (Table VIII-IX, compare reactions 1 and 3 in each table). The reduction product VIIIa, obtained from the reaction of ketone VIII with triphenyltin hydride in methanol, in the presence of AIBN (4%), was not formed in a substantially different yield than that obtained from the uninitiated reaction (Table VIII, reaction 14 and 16). On the other hand, the uninitiated reaction of ketone IX in methanol afforded α-fluoromethylbenzyl

alcohol (IXa) and acetophenone (V) in 41.4% and 5.3% yield, respectively. When this reaction was carried out under similar conditions, but in the presence of AIBN (4%), the comparative yields of products were reversed. Products IXa and V were formed in 1.8% and 65.8% yield, respectively (Table IX, reactions 14 and 16). The initiation by AIBN of the reactions with tri-n-butyltin hydride in benzene is less effective. Most of the ketones gave low yields of products, (Tables V-VII,X, reaction 9 in each table), with the exception of α,α,α-trifluoroacetophenone (VIII) which afforded 47.5% of alcohol VIIIa (Table VIII, reaction 9) and ω-fluoroacetophenone (IX) which gave 55.2% of acetophenone (V) (Table IX, reaction 9). It is obvious that under the experimental conditions used in this work triphenyltin hydride is more reactive than tri-n-butyltin hydride. When the reduction of cyclohexanone (XI) with triphenyltin hydride was attempted in solvents benzene, acetonitrile and methanol, using AIBN (4%), cyclohexanol was obtained in low yield (<4%). Because of the low yield of reduction product, this ketone was not further investigated.

The Effect of m-Dinitrobenzene. The uninitiated reductions of α,α,α-trifluoroacetophenone (VIII) and ω-fluoroacetophenone (IX) by triphenyltin hydride in

solvents benzene and methanol could be totally or partially inhibited by the addition of small amounts (6%) of m-dinitrobenzene (Tables VIII and IX, compare reactions 1 and 2, 10 and 11, 14 and 15 in each table). Ketone IX, for example, in solvent methanol in the presence of m-dinitrobenzene afforded 39.4% of α-fluoromethyl benzyl alcohol (IXa) and only 0.6% of acetophenone. The yields of these products in the uninitiated reaction, respectively, were 41.4% and 5.3%. In the same solvent, methanol, ketone VIII yielded 38.7% and 66.3% of alcohol VIIIa, in the presence and absence of m-dinitrobenzene. The AIBN induced reductions of all of the ketones were also inhibited by m-dinitrobenzene (6%), and regardless of the solvent and the structure of the ketone no reduction products were observed under these conditions (Tables V-X, reactions 3 and 5; Tables V-VI, X, reactions 12 and 13; Tables V, X, reactions 16 and 17).

Competitive Reactions of α,α,α-Trifluoroacetophenone (VIII) and ω-Fluoroacetophenone (IX) with Triphenyltin Hydride. The relative rates of the initiated reaction of ketones VIII and IX with triphenyltin hydride were obtained from competitive reductions, by determining the relative initial and final amounts of each ketone. The estimated k_{VIII}/k_{IX} values were 2.30 ± 0.01 and 9.86 ± 0.33 in benzene and acetonitrile respectively.

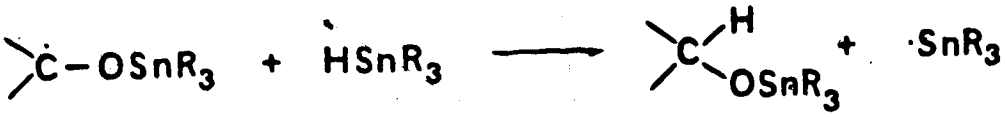
Polarographic Measurements. The half-wave potentials obtained from the polarographic current-voltage curves for the reduction of triphenyl- and tri-n-butylstannyl cations to the corresponding stannyl radicals, in dimethoxymethane were -1.43 and -1.35 v vs Ag^+/Ag respectively. For α,α,α-trifluoroacetophenone (VIII), ω-fluoroacetophenone (IX) and acetophenone (V), the half-wave potentials were -2.0, -2.05, and -2.51 v vs Ag^+/Ag.

DISCUSSION

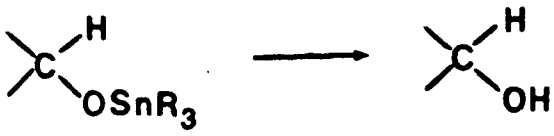
The reductions of acetophenone (V), benzophenone (VI) and 1-phenyl-5-hexen-1-one (VII) are seen to occur by a free-radical chain mechanism (Scheme 17):

Scheme 17

(92)



(93)



(94)

In solvent benzene, the ketones V and VI were not reduced significantly by either triphenyltin hydride or tri-n-butyltin hydride in the absence of an initiator (Tables V, VII, reaction 1 in each table). Benzophenone (VI), however, was reduced to a small extent (1.5%) by triphenyltin hydride in the absence of AIBN (Table VI, reaction 1). The small amount of uninitiated reaction was shown to occur by a homolytic process since the formation of the product was inhibited by m-dinitrobenzene (Table VI, reaction 2). The uninitiated reactions are seen to take place not only with benzophenone but with the fluorinated ketones VIII and IX (Tables

VIII-IX, reaction 1 in each table). Both of these ketones showed inhibition by m-dinitrobenzene when the reactions were carried out in solvent benzene (Tables VIII-IX, reaction 2 in each table). However, when VIII and IX were reduced in the more polar solvent methanol, reduction of VIII was only partially inhibited while only one of the two products, acetophenone, formed from the reduction of IX was inhibited (Tables VIII-IX, reactions 14 and 15 in each table). The partial inhibition observed during the reaction of the fluorinated ketones in the more polar solvent methanol, suggested the possibility that two reduction pathways (radical and heterolytic) were involved (see discussion pages 98-99). The inhibition of the uninitiated reductions is inconsistent with a hydride transfer process (see page 45, Part I of this thesis). The thermal homolysis of the tin-hydride bond ($D(R_3Sn-H)$ = 65.0 kcal/mol)[154] is not significant under the reaction conditions (61°C) (see page 50, Part I of this thesis). By analogy with the proposed initiation step in the reduction of benzyl iodides[135] and tertiary nitro compounds,[185] the initiation step for the tin hydride reductions of the ketones which proceeds in the absence of initiator presumably occurs by an electron transfer process (eq. 95).

(95)

The homolytic process initiated by electron transfer appears to be more favorable for the more electronegatively substituted ketones. This observation coupled with the fact that tri-n-butyltin hydride was less reactive than triphenyltin hydride, suggested that the ease of initiation and possibly the propagation reaction were moderated by the electron donor and acceptor properties of the reactants. Although the differences are not dramatic, the above observations are in accord with the order obtained for the estimated half-wave potentials of the ketones and the trialkylstannyl cations. Table XI shows that benzophenone (VI) and the fluorinated ketones VIII and IX are better electron acceptors than acetophenone (V). Also consistent with the donor-acceptor suggestion was the observation that tri-n-butylstannyl radical was shown to be slightly harder to oxidize than the triphenylstannyl radical (from the measurement of the reduction of the cations, $\Delta E_{1/2} = 0.08$ v). It is recognized, of course, that the order observed for the ease of reduction of the ketones would also be the same

Table XI

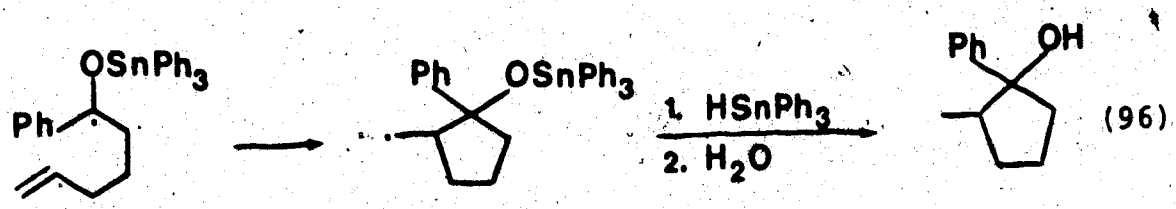
Ketone	$E_{1/2}$	$E_{1/2}$[185]	Uninitiated Reactions Yield of product (%)
Ph-CO-CH_3 (V)	-2.61v	-2.4	0
Ph-CO-Ph (VI)	-	-2.04	1.5
Ph-CO-CH_3 (VIII)	-2.00v		4.4
Ph-CO-CH_2F (IX)	-2.05v		6.1

as that predicted for any of the other proposed mechanisms of reduction, although it is not clear that the reactivity of the tin hydrides would be in the order found. In fact, for the heterolytic reductions, the order of reactivity of the tin hydrides is reported to be reversed.[170]

The reduction of ketones V-VII with triphenyltin hydride in solvent benzene was initiated by the addition of catalytic amounts of AIBN (Tables V-VII, reactions 3 and 4 in each table). The length of the chain could be estimated as being 16-24 units long (assuming an efficiency of 0.5 for AIBN)[186] since the addition of 4% of initiator led to the formation of the reduction products in 32-47% yield.

It was expected that the triphenyltin hydride

reduction of 1-phenyl-5-hexen-1-one (VII) under free-radical generating conditions could afford 2-methyl-1-phenylcyclopentanol from an internal attack of the transient radical on the double bond as shown in equation 96.



(96)

These cyclization processes have been observed in radical reactions of substrates of the type 5-hexen-1-X.[187] However, the anticipated cyclic material was not formed even in the reactions where the yields of reduction product were relative high (Table VII, reactions 3 and 6). This suggests that the cyclization of the alkoxystannyl radical has to compete with a much faster process, the hydrogen abstraction from the tin hydride. Apparently the transient radical is totally trapped by the tin hydride before any cyclization takes place. An estimate of the rate of cyclization to the five membered ring of the stannylketyl can be obtained from the known rate of cyclization (0.9×10^5 sec^{-1}) of the radical generated from 6-bromo-6-methyl-1-heptene with tri-n-butyltin hydride.

Since the cyclization of the 1-phenyl-5-hexenyl radical should occur at a rate < 10^5 sec^{-1} at 61°C[188] in competition with the transfer of hydrogen from tri-n-butyltin hydride (5×10^7 $mole^{-1}$ sec^{-1} at 100°C)[133] and since no cyclized material is obtained from the ketone reduction carried out under similar concentration conditions[187] the rate of cyclization must be $<10^2$-10^3 sec^{-1}.

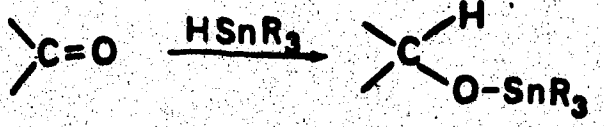
The addition of m-dinitrobenzene inhibited totally the formation of the products in the AIBN initiated reductions (Tables V-VII, reaction 5 in each table).

Van der Kerk and Noltes reported that the reduction of ketones may take place by a two-step process which leads to the alcohol and the distannane.[167]

(97)

However, no compelling experimental data were reported for these reductions.

On the other hand, it is generally accepted that the reduction may also occur by a one-step process, the product being the alkoxystannane.



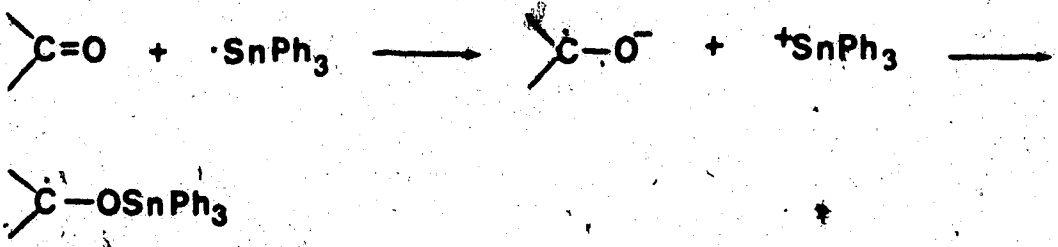
(98)

In the one-step mechanism the final product, the alkoxystannane, can be further solvolyzed to give the alcohol. In the two-step mechanism the alcohol is formed by hydrostannolysis of the alkoxystannane intermediate. The stoichiometry for the reductions of ketones V-VII could not be unequivocally deduced from the observed yields of products, since under the condition that the reactions were studied these substrates afforded less than 50% of reduction products. However, the intermediacy of the alkoxystannane was confirmed by a comparison of the ^1H NMR spectrum of the reaction mixture resulting from the reaction of acetophenone (V) and triphenyltin hydride in benzene-d_6 with that of an authentic sample of α-methylbenzyl alcohol in the same solvent. The spectrum of the reaction mixture showed a multiplet at 5.14 ppm while the authentic material showed a multiplet at 4.63 ppm ($\Delta\delta$ = 0.51 ppm). A comparison of the chemical shift of α-hydrogens of tri-n-butyltin methoxide and tri-n-butyltin ethoxide with the chemical shift of α-hydrogens of the parent alcohols showed chemical shift differences of $\Delta\delta$ 0.38 and $\Delta\delta$ 0.37 ppm. On this basis the absorption at 5.14 ppm in the spectrum of the reaction mixture was assigned to the α-hydrogen of the alkoxystannane.

The reductions of ketones V-VII with tri-n-butyltin hydride with added initiator (AIBN 4%) was shown to

proceed by a very short or probably non-chain radical process (Tables V-VII, reaction 9 in each table).

In the free radical chain mechanism (equations 92-94) the nature of the reaction between the carbonyl substrate and the stannyl radical to form the alkoxy-stannyl radical (eq. 92) has not been unequivocally established. A free radical addition has been suggested, but in light of the mechanistic pathways involving stannyl radicals recently proposed by Tanner[135,184] and Kochi[183] an electron transfer process as represented in equation 99 can not be ruled out.



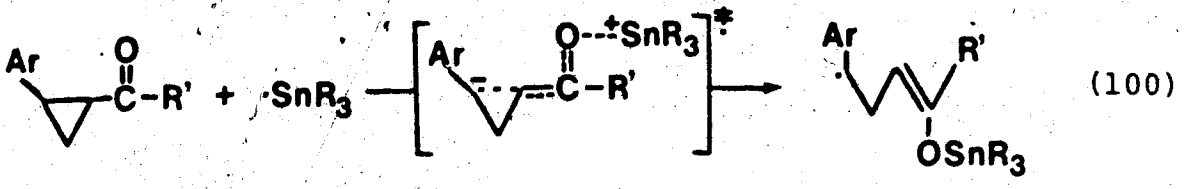
(99)

The ketyl radical anion stannyl cation pair thus formed could collapse to form the incipient alkoxy radical and would be indistinguishable from the intermediate formed from radical addition. A reduction process occurring by such a mechanism should be dramatically affected by the polarity of the solvent because of the charge separation in the transition state of the rate controlling step. However, reductions of ketones V-VII under uninitiated or initiated conditions in the more polar solvents acetonitrile and methanol did not show substantial differences

in the yields of products from those observed in the less polar solvent benzene (Table V-VII, reactions 3, 12, and 16 in each table). The foregoing facts apparently militate against the occurrence of an electron transfer process in the propagation sequence of the reduction of ketones V-VII. An analysis of the results of the reduction of cyclopropyl phenyl ketone (X) with both tin hydrides led to similar conclusions as those arrived at from the other ketones V-VII. The AIBN initiated reactions gave both the ring opened product, butyrophenone (Xb) and the ring closed material, α-cyclopropylbenzyl alcohol (Xa). The products were consistent with either an electron transfer-hydrogen abstraction sequence or a radical addition process. The overall yield of products as well as the ratio Xb/Xa did not change dramatically regardless of the polarity of the solvent (Table X, reactions 3, 12, and 16). This suggested that the reaction proceeded by a short chain radical mechanism which probably involves addition of the stannyl radical to the carbonyl oxygen.

Substituted cyclopropyl ketones have been previously reduced with tin hydride reagents. These reductions have been carried out in methanol on cyclopropyl methyl ketone under heterolytic conditions and yielded cyclopropylcarbinol.[178] When the reductions were performed

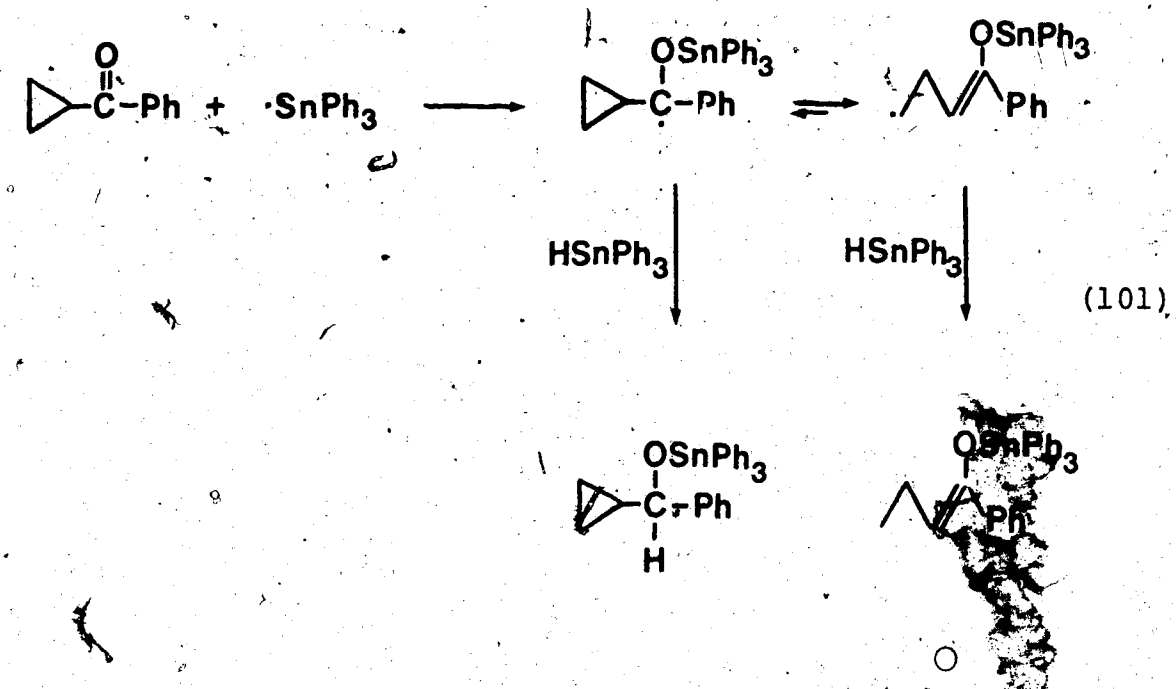
under homolytic conditions (AIBN initiation) in toluene, only open chain ketones were obtained. From the studies on the mechanism of the free radical reduction the authors suggested that the ring opened product was formed by a concerted homolytic process.[180]



(100)

In accord with these observations the major product for reduction of ketone X was ring opened material, however, minor amounts of alcohol, Xa, were also found. When the reduction of ketone X with triphenyltin hydride in benzene was carried out with increasing amounts of tin hydride relative to ketone, the overall yields of the products were increased and the ratio Xb/Xa changed from 5.5 to 2.7 (Table X, reactions 3, , and 7). Contrary to the previous reports[180] it appears that at higher concentration of tin hydride the radical formed by the addition of the stannyl radical to the substrate can be trapped to give cyclopropylcarbinol at a rate competitive with ring opening. The concentration

dependence of the product ratio demands that at least two intermediates are involved (eq. 101).



(101)

The fluorinated ketone VIII showed uninitiated reduction in the three solvents used. In the less polar solvent benzene the reduction product was totally inhibited by m-dinitrobenzene (Table VIII, reactions 1 and 2) while in the more polar solvents acetonitrile and methanol only partial inhibition occurred (Table VIII, reactions 10 and 11, 14 and 15). The partial inhibition suggested the possibility that with the increasing polarity of the solvent the reduction proceeded by both homolytic and heterolytic pathways. Previous reports for reductions of ketones conducted in methanol concluded that the reduction products were formed from a hydride

transfer process.[171,175] The AIBN induced reductions of α,α,α-trifluoroacetophenone (VIII) carried out in benzene by triphenyl- and tri-n-butyltin hydride were shown to proceed by longer chains than those observed for the other ketones previously investigated. The length of the chains in benzene were estimated as being 45-46 and 24 units long, respectively, since the addition of 4% of initiator led to the formation of the reduction product in 91% and 48% yield (Table VIII, reactions 3 and 9). A comparison of the ^1H NMR spectrum for an initiated reaction of VIII carried out in benzene-d_6 with triphenyltin hydride with that of authentic α-trifluromethylbenzyl alcohol showed that the final product in the reaction mixture was the alkoxystannane. A multiplet for the α-hydrogen is observed at 5.17 ppm which can be assigned to H-C(CF_3)($OSnPh_3$)(Ph) since the α-hydrogen in the alcohol VIIIa shows a multiplet at 4.35 ppm ($\Delta\delta$ = 0.72 ppm). As argued previously the formation of the alkoxystannane could be the result of either radical addition or electron transfer-hydrogen abstraction.

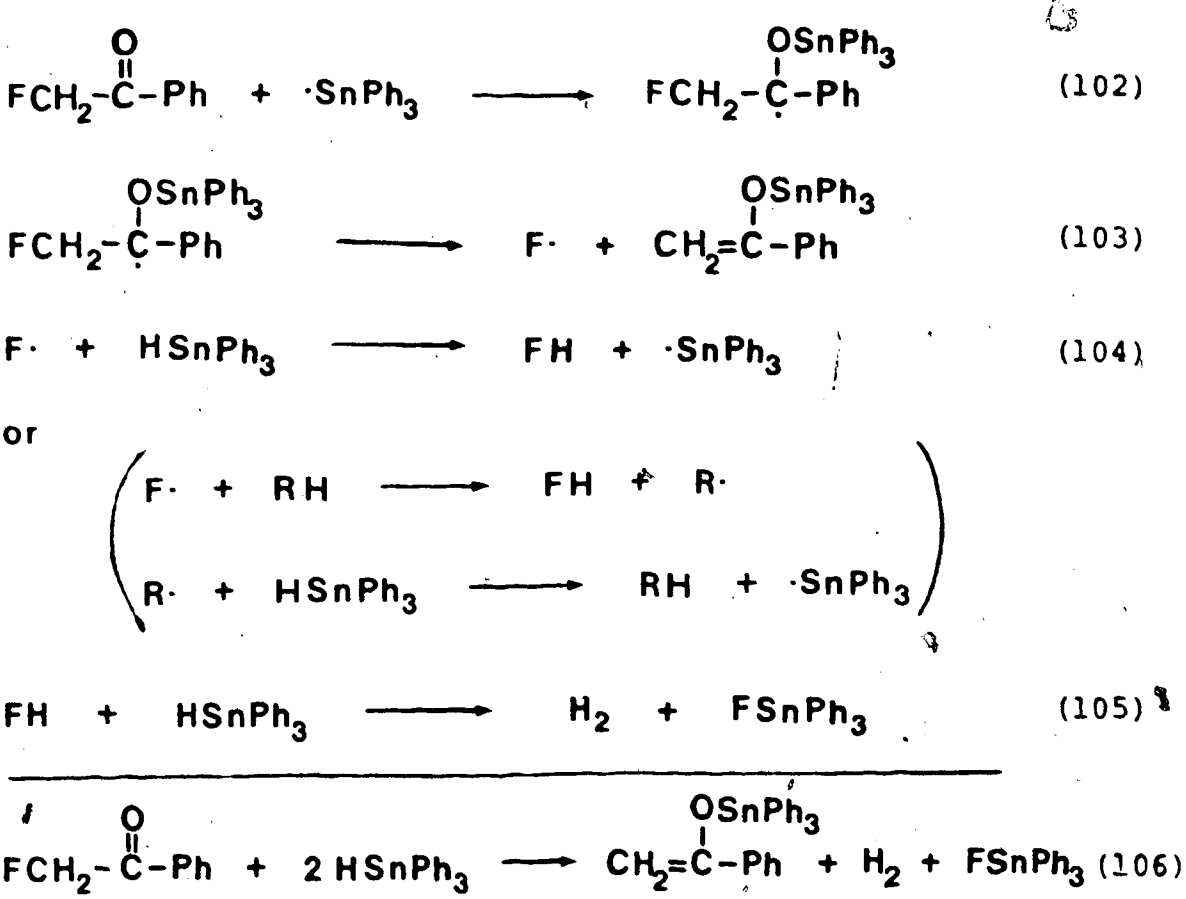
The reduction of ketone VIII in acetonitrile did show some difference between the uninitiated and the initiated reactions (Table VIII, reactions 10 and 12). This difference was even less dramatic in solvent methanol (Table VIII, reactions 14 and 16). Although no

clear cut evidence is at hand, it appears that under free radical generating conditions the duality of mechanisms observed in the uninitiated reactions disappears and the formation of the reduction product occurs only by the faster homolytic process. This suggestion is supported by the analysis of the results of the reduction of ketone IX in solvent methanol. The formation of product IXa in the uninitiated reaction was shown by the inhibition studies to be the result of a heterolytic process, while acetophenone whose formation was inhibited by m-dinitrobenzene arose from a homolytic pathway (Table IX, reactions 14 and 15). However, when the reduction was carried out in the presence of AIBN (4%), the reaction took an entirely different course and the formation of acetophenone was dramatically increased while the heterolytic product IXa was only formed in small amounts (1.8%). The above results argued that the defluorinated product came from the radical process.

Two radical chain mechanisms can be envisioned to account for the formation of acetophenone. The mechanism represented in Scheme 18 involves a radical addition of the stannyl radical to the carbonyl oxygen.

The stannylketyl radical formed by addition of the stannyl radical to the substrate may undergo Lewis acid assisted β-scission,[189] the radical fragment being a

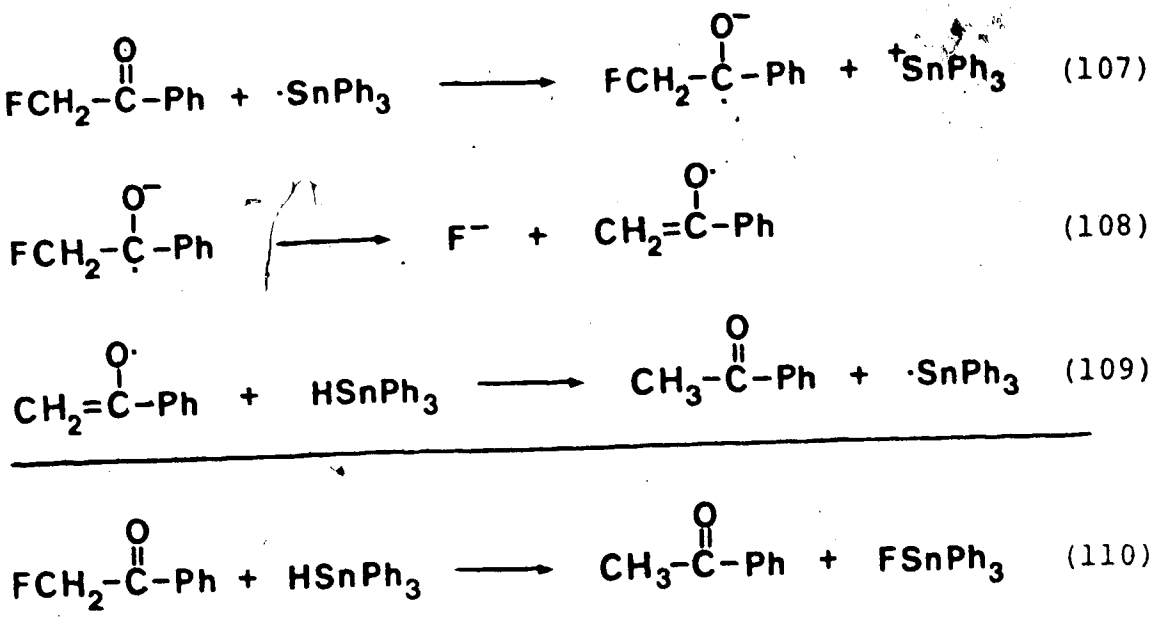
Scheme 18



fluorine atom. The high reactivity of F· and the ease of hydrogen abstraction from tin hydride necessarily should lead to the formation of HF which subsequently reacts with another molecule of triphenyltin hydride to produce H_2 and triphenyltin fluoride.[190] In this mechanistic sequence the formation of the alkoxystannane requires at least 2 moles of triphenyltin hydride for each mole of starting material.

The second mechanistic pathway involves an electron transfer from the stannyl radical to the ketone as shown in Scheme 19.

Scheme 19



In this mechanism acetophenone can be formed in yield higher than 50% from a 1:1 stoichiometric relationship.

A ^1H NMR examinaton of a reaction mixture (1:1 mole ratio) of ω-fluoroacetophenone and triphenyltin hydride in the presence of AIBN (4%) in solvent benzene-d_6 showed that the final product was acetophenone (s, 2.13 ppm) since no indication of vinyl protons was observed. Glpc analysis of this mixture revealed that acetophenone was formed in 80% yield. On the other hand, when the initiated reaction of IX in solvent benzene was subjected to analysis for the formation molecular hydrogen, non-condensable gases were found to correspond to only 4-7%, the amount of nitrogen produced from the decomposition of the initiator.

The observations that the reduction of ketone IX gave acetophenone and not alkoxystannane in high yield (>50% at a 1:1 stoichiometric ratio of IX and tin hydride) that no hydrogen was produced during the reaction, and that the production of acetophenone was the result of a radical chain process, argued that the mechanism was indeed the electron transfer process depicted in Scheme 19. Although no clear evidence is at hand, it seems likely that the reduction of the even more electronegatively substituted ketone VIII proceeds by the same mechanistic pathway. This conclusion was further substantiated by carrying out competitive reactions of ketones VIII and IX with triphenyltin hydride under initiating conditions in solvents benzene and acetonitrile. The competitive reactions showed a substantial solvent effect and the values of the relative rates k_{VIII}/k_{IX} in benzene and acetonitrile were, respectively 2.30 and 9.86. This observed solvent effect is consistent with an electron transfer process which should depend heavily on the polarity of the solvent.

EXPERIMENTAL

A. Materials

n-Tridecane (99% pure) and n-heptadecane (99% pure) (Aldrich Chemical Co.) were used as purchased.

p-Di-tert-butylbenzene (Aldrich Chemical Co.) was recrystallized from ethanol-hexane: m.p. 77-78°C (lit[155] 80°C). The material was shown by glpc (FFAP 10%, Chromosorb W AW DMCS, 5' x 1/8" column) to be >99% pure.

Tri-n-butyltin hydride (Alfa Research Chemicals and Materials) was distilled and the fraction 68-74°C/0.3 mm was collected.

Triphenyltin hydride, tetrabutylstannane, and hexabutyldistannane (Alfa Research Chemicals and Materials) were used as purchased.

Benzoyl peroxide (Fisher Scientific Co.) was purified by recrystallization from dichloromethane-methanol: m.p. 102-105°C (lit[155] 106°C).

α,α'-Azobisisobutyronitrile (Aldrich Chemical Co.) was recrystallized from ethanol-water: m.p. 101-102°C (lit[191] 103°C).

Cyclohexanone (British Drug Houses), cyclopropyl-phenyl ketone (Aldrich Chemical Co.) and butyrophenone (Matheson Coleman & Bell) were used without further purifications. Benzophenone (Fisher Scientific Co.) was recrystallized from ethanol: m.p. 47-48°C (lit[155]

48.1°C). Acetophenone (Fisher Scientific Co.) was distilled at 93-95°C/10 mm (lit[155] 202.6°C/760 mm).

Benzhydrol (Koch-Light Laboratories Ltd.) and α-methylbenzyl alcohol (Aldrich Chemical Co.) were used as purchased. Cyclohexanol (Mallinckrodt Chemical Works) was heated to reflux over freshly ignited calcium oxide, distilled at 153°C/700 mm, and stored over molecular sieves 4 A.

Benzene (Caledon Laboratories Ltd.) was purified as indicated in part one of this thesis and stored over molecular sieves 3 A.

Acetonitrile (Caledon Laboratories Ltd., HPLC grade) was stored over molecular sieves 3 A and used without further purification.

Absolute methanol (Terochem Laboratories Ltd.) was dried by treatment with magnesium activated by iodine and stored over molecular sieves 3 A.

Tri-n-butyltin methoxide. This compound was prepared from the reaction of tri-n-butyltin chloride (10 g, 30 mmol) with a methanolic solution of sodium methoxide (0.8 g of sodium wire in 20 mL of absolute methanol).[192] Distillation of the crude product at 75-78°C/0.25 mm (lit[192] 101°C/2 mm) gave a colorless liquid: NMR ($CDCl_3$) δ 0.65-1.8 (m, 27 H), 3.65 (s, 3 H).

Anal. Calcd for $C_{13}H_{30}OSn$: C, 48.63; H, 9.41. Found: C, 48.94; H, 9.54.

Tri-n-butyltin ethoxide. This compound was made as described for tri-n-butyltin methoxide, except that the solvent used was absolute ethanol. The crude product was distilled at 97°C/1 mm to give a colorless oil: NMR ($CDCl_3$) δ 0.65-1.8 (m, 27 H), 1.18 (t, 3 H), 3.78 (q, 2 H).

Anal. Calcd for $C_{14}H_{32}OSn$: C, 50.18; H, 9.62. Found: C, 50.21; H, 9.69.

Hexaphenyldistannane. Using the literature procedure,[193] anhydrous stannous chloride (3.8 g, 0.02 mol) was subjected to reaction with phenyllithium (0.06 mol). An ether solution of triphenyltin chloride (7.7 g, 0.02 mol) was added and the reaction mixture heated to reflux for 3 h. Two recrystallizations of the crude product from benzene-ether gave a white solid: m.p. 233-234°C (lit[193] 229-231°C).

α,α,α-Trifluoroacetophenone (VIII). This ketone was obtained by treating trifluoroacetic acid (34.2 g, 0.3 mol) with an ether solution of phenylmagnesium bromide (0.9 mol in 600 ml solution).[194] The crude product, a yellowish oil, was distilled twice, and the fraction 69-70°C/30 mm collected (lit[195] 75°C/37 mm): IR (neat) 5.78 (CO) μm; MS m/e 174, 105.

α-Trifluoromethylbenzyl alcohol (VIIIa). This material was prepared by the reduction of α,α,α-trifluoroacetophenone with lithium aluminum hydride in

ether. Distillation of the crude product at 58°C/2.3 mm gave a colorless oil, which was further purified by gas chromatography using a 10% FFAP, Chromosorb W AW DMCS, 3' x 1/4" stainless steel column: NMR ($CDCl_3$) δ 2.95 (d, 1 H), 4.95 (m, 1 H), 7.30-7.56 (m, 5 H); MS m/e 176, 107.

1-Phenyl-5-hexen-1-ol (VIIa). The synthesis of this alcohol was carried out by adding benzaldehyde (9.0 g, 0.085 mol) to an ether solution of 4-pentenyl magnesium bromide (from 12.5 g (0.085 mol) of 1-bromo-4-pentene and 2.1 g (0.086 mol) of magnesium in 250 ml of ether).[196] The impure material obtained from this reaction, a colorless oil, was distilled twice and the fraction 76-92°C/1 mm collected: NMR ($CDCl_3$) δ 1.20-2.12 (m, 6 H), 2.44 (s, 1 H), 4.55 (t, 1 H), 4.85-5.86 (m, 3 H), 7.12-7.40 (m, 5 H); MS m/e 176, 158, 107.

1-Phenyl-5-hexen-1-one (VII). This ketone was prepared by oxidation of the preceeding alcohol (3.0 g, 0.017 mol) with manganese dioxide (15 g, 0.17 mol) in pentane.[196] After the inorganic material was removed and the solvent evaporated, the residue was purified by vacuum distillation and the fraction 75-77°C/3 mm (lit[196] 77-78°C/3 mm) was collected: NMR ($CDCl_3$) δ 1.60-2.22 (m, 4 H), 2.95 (t, 2 H), 4.94-5.92 (m, 3 H), 7.38-7.60 (m, 3 H), 7.90-8.00 (m, 2 H); IR (neat) 5.93 (CO) μm; MS m/e 174, 120, 105.

2-Methyl-1-phenylcyclopentanol. This tert-alcohol

was prepared by the Grignard reaction of 2-methylcyclopentanone (2 g, 0.02 mol).[197] The purification of the crude product was carried out by vacuum distillation (115-118°C/10 mm, lit[197] 124-127°C/14 mm) and then by gas chromatography using a 10% FFAP, Chromosorb W AW DMCS, 5' x 1/4" stainless steel column: NMR ($CDCl_3$ δ 0.84 (d, 3 H), 1.52-2.35 (m, 8 H), 7.21-7.68 (m, 5 H); MS m/e 176, 158, 133, 120, 105.

Fluoroacetic acid. Fluoroacetamide (50 g, 0.65 mol) was converted to fluoroacetic acid using the method reported by Buckle,[198] but a mixture of nitric oxide and nitrogen dioxide was used rather than nitric acid and arsenous oxide. After the excess nitrous fumes were removed, distillation at ordinary pressure (160-162°C) gave 42 g (83%) of the product: NMR ($CDCl_3$) δ 5.04 (d, 2 H, J 47.7 cps), 11.53 (s, 1 H).

Fluoroacetyl chloride. This material was prepared from fluoroacetic acid (39 g, 0.5 mol) and α,α,α-trichlorotoluene (108 g, 0.55 mol) in the presence of a catalytic amount of zinc chloride.[199] The crude product of the reaction was distilled at ambient pressure and the fraction 69-73°C collected. A second distillation at 70-71°C (lit[199] 71.5-72.0°C) gave 40.5 g (84%) of fluoroacetyl chloride, a colorless oil: NMR ($CDCl_3$) δ 5.20 (d, J 48.0 cps); IR (neat) 5.51 (CO), 13.07 (C-Cl) μm.

ω-Fluoroacetophenone (IX). Using the literature

procedure,[200] this ketone was prepared from fluoroacetyl chloride (38.6 g, 0.40 mol) and benzene (39 ml) in the presence of aluminum trichloride (120 g). The reaction crude was distilled at 70-72°C/1.5 mm (lit[200] 65-70/1 mm) to give a colorless liquid whose physical properties were consistent with ω-fluoroacetophenone: mp 26-27°C (lit[200] 27-28°C); NMR ($CDCl_3$) δ 5.57 (d, 2 H, J 47.5 cps), 7.36-8.10 (m, 5 H); IR (neat) 5.86 (CO) μm; MS m/e 138, 105.

α-Fluoromethylbenzyl alcohol(IXa). This compound was prepared by reduction of the preceeding ketone with lithium aluminum hydride in ether. In the distillation of the crude product, the material boiling at 95-99°C/8 mm was collected (lit[201] 97-102°C/8 mm): NMR ($CDCl_3$) δ 3.15 (s, 1 H), 4.48 (m, 3 H), 7.40 (s, 5 H); MS m/e 140, 120, 107.

α-Cyclopropylbenzyl alcohol (Xa). This alcohol was obtained by reduction of cyclopropyl phenyl ketone with lithium aluminum hydride in ether. The crude product was distilled, and the fraction 129-132°C/18 mm collected: NMR ($CDCl_3$) δ 0.2-1.6 (m, 5 H), 2.20 (s, 1 H), 4.10 (d, 1 H), 7.35 (m, 5 H).

B. Methods and Procedures

Physical constant measurements, microanalyses, spectral measurements, and gas liquid partition chromatograph analyses were carried out using the same

instruments described in Part I of this thesis.

In addition to those, ^{1}H-NMR high resolution spectra were obtained using a Bruker WH 400 high field cryo-spectrometer. Gas chromatography-infrared spectra (Glpc-IR) data were obtained using a Nicolet 7199 FT-IR interfaced to a Varian series 3700 gas chromatograph. Polarographic measurements were carried out using a EG & G Princeton Applied Research Model 174-A polarographic analyzer coupled to a X-Y recorder model RE 0074 and to a EG & G model 303 static mercury drop electrode.

C. A General Procedure for the Reaction of Ketones with Organotin Hydrides. The Reduction of Acetophenone (V) with Triphenyltin Hydride in Solvent Benzene.

An aliquot sample (0.2 ml) of a stock solution which was 0.1 molar in ketone V and 0.042 molar in n-tridecane (internal standard) was placed in an ampule wrapped with aluminum foil. Another aliquot (0.2 ml) of a benzene solution of triphenyltin hydride (0.1 molar) and AIBN (0.004 molar) was added. The ampule was degassed by three freeze-thaw cycles and then sealed under vacuum. The mixture was thermostated in an oil bath at 61°C for a standard time (16 h) in the dark. The ampule was opened and the reaction mixture analyzed by glpc using a 10% FFAP, Chromosorb W AW DMCS 60-80 mesh 5' x 1/8" stainless

steel column. The chromatogram showed three major peaks. The structure of the compounds related to these peaks was established by a comparison of their retention times, glpc-mass spectra, and glpc-IR with those of authentic samples. The first peak corresponds to the internal standard. The other two peaks correspond to acetophenone (V) and α-methylbenzyl alcohol (Va). Quantification of these peaks against n-tridecane afforded 49.7% of V and 46.5% of Va.

Duplicate experiments using ketone V, were carried out to test the effect of each of the following: concentration of triphenyltin hydride, initiation by different concentrations of AIBN, inhibition by m-dinitrobenzene, structure of the hydride, and polarity of the solvent. The results and specific conditions of these experiments are listed in Table V.

D. Reduction of Other Ketones by Organotin Hydrides

Experiments at the standard conditions specified in the general procedure (61°C, 16 h, dark, degassed ampules) were also carried out to test the effect of the concentration of the hydride, initiation by AIBN, inhibition by m-dinitrobenzene, structure of the hydride, and polarity of the solvent in the reduction of each of the following ketones: benzophenone (VI), 1-phenyl-5-

hexen-1-one (VII), α,α,α-trifluoroacetophenone (VIII), ω-fluoroacetophenone (IX), and cyclopropyl phenyl ketone (X). In all cases the initial concentration of ketone was c.a. 0.1 molar. All glpc analyses were performed using 10% FFAP, Chromosorb W AW DMCS, 60-80 mesh, 5' x 1/8" stainless steel columns. The structure of the compounds related to the peaks observed in the chromatograms was established as indicated in the general procedure. Determination of moles of products was done against an internal standard. The results and specific conditions are listed in Tables VI to X.

E. Competitive Reaction of α,α,α-Trifluoroacetophenone and ω-Fluoroacetophenone with Triphenyltin Hydride.

α,α,α-Trifluoroacetophenone (1.0 mmol), ω-fluoroacetophenone (1.0 mmol) and p-di-tert-butylbenzene (0.3 mmol) were accurately weighed into a volumetric flask and diluted to 10 mL with benzene. Triphenyltin hydride (1.0 mmol) and AIBN (4×10^{-2} mmol) were weighed into another volumetric flask and the mixture diluted to 10 mL with benzene. An aliquot (0.3 mL) of each solution was pipetted into a reaction tube. The reaction vessel was degassed, and sealed and the mixture allowed to react at 61°C for 3.5 h. The product analysis was effected by glpc using a FFAP 10%, Chromosorb W AW DMCS, 68-80 mesh,

5' x 1/8" stainless steel column. A competitive reaction of these two ketones was also carried out in identical manner in solvent acetonitrile. The relative rates k_{VIII}/k_{IX} in each solvent were estimated from the equation:

$$\frac{k_{VIII}}{k_{IX}} = \left[\frac{\log\left(\frac{\text{area}^{o}\ CF_3COPh}{\text{area}^{o}\ \text{standard}} \Big/ \frac{\text{area}^{f}\ CF_3COPh}{\text{area}^{f}\ \text{standard}}\right)}{\log\left(\frac{\text{area}^{o}\ CH_2FCOPh}{\text{area}^{o}\ \text{standard}} \Big/ \frac{\text{area}^{f}\ CH_2FOOPh}{\text{area}^{f}\ \text{standard}}\right)}\right]$$

where the superscripts o and f refer to the areas in the initial mixture and the final reaction mixture.

F. Polarographic Measurements. The Reduction of Triphenyl and Tri-n-butystannyl Cations in Dimethoxyethane.

Polarographic measurements were carried out in a one compartment glass cell provided with dropping mercury electrode (DME), a reference electrode [0.01 M $AgClO_4$ in dimethoxyethane (0.1 M Bu_4NClO_4)/Ag wire] and a mercury pool counter electrode. The reference electrode made electrical contact with the cathode environment via a glass frit. The solution containing $Ph_3Sn^+ClO_4^-$ was prepared by reaction of triphenyltin chloride or hexaphenyldistannane with silver perchlorate.[202] Hexaphenyldistannane (70 mg, 0.1 mmol) was dissolved in 10 mL of

electrolyte solution (0.1 M tetrabutylammonium perchlorate in dimethoxyethane). Silver perchlorate (8.3 mg, 0.04 mmol) was dissolved in 10 mL of electrolyte solution. The two solutions were mixed and then filtered under a blanket of N_2. An aliquot of the filtrate (10 mL) was placed in the polarographic cell and Triton X-100 added. The mixture was purged with dry nitrogen (8 min). The dc polarographic current-voltage curve was recorded at a rate of 5 mv per s from an initial potential of -0.7 volts. $Bu_3Sn^+ ClO_4^-$ was generated by mixing electrolyte solutions (0.1 M tetrabutylammonium perchlorate in dimethoxyethane) of hexa-n-butyldistannane (1.5×10^{-2} M) and silver perchlorate (6×10^{-3} M). No suppressor (Triton X-100) was used to record the dc polarographic current-voltage curve.

G. Polarographic Reduction of Ketones.

The current-voltage curves for the polarographic reductions of acetophenone (V), α,α,α-trifluoroacetophenone (VIII) and ω-fluoroacetophenone (IX) were obtained from electrolyte solutions (0.1 M tetrabutylammonium perchlorate in dimethoxyethane) of each ketone (10^{-3} M) by using the cell previously described. The half-wave potentials estimated from the current-voltage curves were -2.51 v, -2.0 v and -2.05 v

vs Ag^+/Ag for the ketones V, VIII and IX respectively.

H. Analysis of Non-condensable Gases in the Reduction of ω-Fluoroacetophenone (IX).

An aliquot sample (1 mL) of a stock solution of ketone IX in benzene (0.1 M) was placed in a break seal tube. Another aliquot (1 mL) of a benzene solution of triphenyltin hydride (0.1 M) and AIBN (0.004 M) was added. The tube was degassed, sealed and the mixture allowed to react at 61°C for 16 h. The reaction mixture was frozen and the dead volume evacuated in a ultra high vacuum line. The seal was then broken and the non-condensable gases transferred using a Toppler pump to a bulb of known volume. The temperature and the pressure of the gases were measured and the number of moles estimated from the ideal gas law equation.

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