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TITLE OF THESIS.....STUDIES ON THE MODE OF DECOMPOSITION OF SOME ALKYL CHLOROSULFITES AND TERT-BUTYL PERESTERS.................

UNIVERSITY...UNIVERSITY OF ALBERTA...............

DEGREE FOR WHICH THESIS WAS PRESENTED...Ph.D...............

YEAR THIS DEGREE GRANTED...SPRING 1974...............

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THE UNIVERSITY OF ALBERTA

STUDIES ON THE MODE OF DECOMPOSITION OF SOME ALKYL CHLOROSULFITES AND *tert*-BUTYL PERESTERS

BY

Ⓒ HARRY LUTZER

A THESIS

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

DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA
SPRING, 1974

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled

"STUDIES ON THE MODE OF DECOMPOSITION OF SOME ALKYL CHLOROSULFITES AND *tert*-BUTYL PERESTERS"

submitted by HARRY LUTZER in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Dennis D. Tanner
Supervisor

Karl R. Kopecky

....

....

....

Stephen F. Nelsen
External Examiner

Date..........................

TO MY PARENTS

ABSTRACT

PART I

In order to assess the influence of a β-substituent on the rate of decomposition of a series of dialkyl peresters, a number of *tert*-butyl 3-substituted, 2,2-dimethylperpropionates were decomposed thermally. The rates were measured by monitoring the disappearance, in the infrared, of the carbonyl stretching bands of the peresters.

On the basis of the small variation in the magnitudes of the rate constants and activation parameters observed, it was concluded that anchimerically assisted acceleration of the rate of decomposition by a β-chloro, bromo, iodo or phenylthio substituent does not occur. The rate constants, activation parameters, and the near quantitative amounts of carbon dioxide observed, have established that all the peresters decompose by a one-step, concerted loss of carbon dioxide. The small variations in the rate constants are rationalized on the basis of inductive and steric effects. The products observed from the decomposition of *tert*-butyl-2,2-dimethyl-3-phenylthioperpropionate are rationalized on the basis of the concerted two-bond scission mechanism.

PART II

The reaction of thionyl chloride with various dibenzobicyclo[2.2.2] and [3.2.1] octadienyl alcohols, in several solvents was studied to shed some light upon the mechanism and stereochemical course of the reaction of

alcohols with thionyl chloride.

An intermediate dialkyl sulfite was isolated from the reaction of dibenzobicyclo[2.2.2]octadien-2-ol. No intermediate alkyl chlorosulfite or dialkyl sulfite could be isolated from the [3.2.1] alcohols.

Near quantitative yields of chloride product were observed. Three chlorides were formed in the reaction: 7-chlorodibenzobicyclo[2.2.2]octadiene, exo-4-chlorodibenzobicyclo[3.2.1]octadiene and endo-4-chlorodibenzobicyclo[3.2.1]octadiene. The products obtained are consistent with an ionic mechanism in which an initially formed benzylic [3.2.1] cation produced from both systems, [2.2.2] and [3.2.1], leads to a mixture of exo- and endo-[3.2.1] chlorides. These are the major products observed under all reaction conditions except when the reaction was carried out in toluene. It has been proposed that under these reaction conditions an hydrogen chloride catalyzed rearrangement of the [3.2.1] chlorides to the [2.2.2] chloride can occur.

The results of the reaction of cis-3-deuteriodibenzobicyclo[2.2.2]octadien-2-ol with thionyl chloride demonstrated the stereospecificity of the [3.2.1] to [2.2.2] rearrangement.

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. Dennis D. Tanner, for his guidance and direction of this research.

Special thanks are given to Dr. Naoto Wada and Mr. Alan G. Ryan for their invaluable comments and many suggestions during the preparation of this manuscript.

I wish to thank Mrs. Mary Waters for her patience and efficiency in typing this thesis.

The competent assistance of the technical staff in the Spectroscopy and Microanalytical Laboratories is gratefully acknowledged.

To the Chemistry Department and the National Research Council of Canada I am indebted for financial support during the course of this work.

To my wife, Annabel - many, many thanks.

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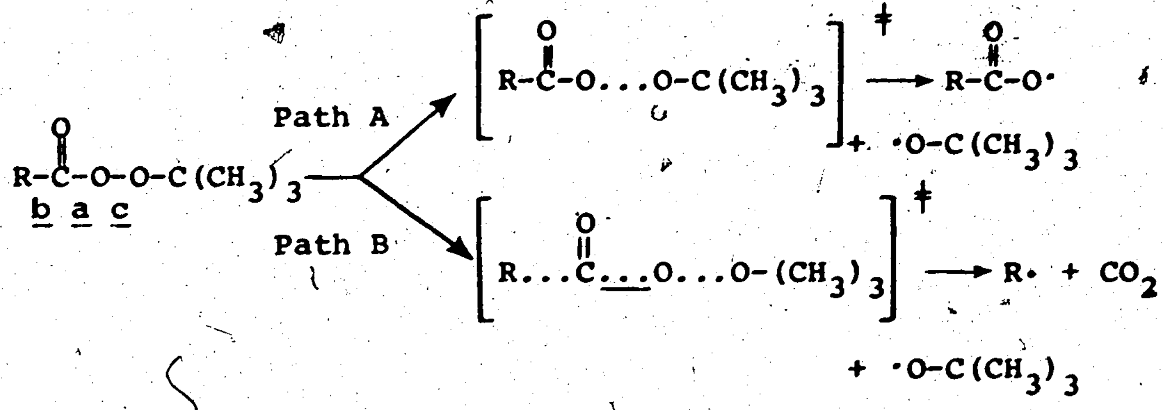
PART I

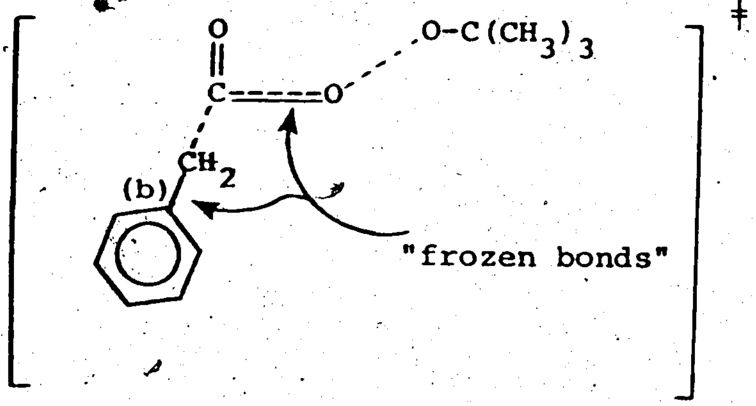
INTRODUCTION

A large number of investigations dealing with the mechanism of the decomposition of tert-butyl peresters have been concerned with the relationship between the structure of the peroxide and its mode of decomposition (1-27). Bartlett and Hiatt (5) postulated that the thermal decomposition of a simple perester can occur by at least two distinct pathways, one-bond scission (path A), and a concerted two-bond scission (path B), as illustrated in Scheme 1.



SCHEME 1

On the basis of their results Bartlett and coworkers (5), have proposed a criterion to allow a distinction to be made between the modes of decomposition of a perester: the decomposition of a perester in a stepwise fashion (path A), or a concerted fashion (path B). They suggested that when the alkyl radical, R, is of equal or greater stability than is tert-butyl, there is a simultaneous cleavage of the alkyl to carbonyl carbon bond (b) and peroxide oxygen-oxygen bond (c), producing carbon dioxide and the alkyl radical in the rate determining step. However, when R· is not as stable as the tert-butyl radical (eg. methyl or phenyl) only bond c cleaves in the rate determining step to give alkyl carbonyl-oxy and tert-butoxy radicals. Bartlett and Hiatt (5) developed a relationship between the mode of decomposition and the enthalpy and entropy of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, obtained from the decomposition of the peresters stated. As the concerted nature of the decomposition increases, (an increase in the stability of the radical R·), $\Delta H^{\ddagger}$ decreases due to a lowering of the energy barrier to reaction. This decrease in energy is, however, achieved only at the expense of $\Delta S^{\ddagger}$, which becomes more negative. These enthalpy changes reflect certain rotational restrictions in the transition states of peresters leading to stable radicals by concerted loss of carbon dioxide. For example, in the decomposition of tert-butyl phenylperacetate, which is proposed to decompose by a concerted two-bond scission, neither bond b nor the bond between the carbonyl carbon and peroxide oxygen is free to rotate in the transition state. Bond b must be "frozen" to allow the resonance delocalization of the unpaired electron developed in the incipient benzyl radical (I), and the bond between the carbonyl carbon and peroxy oxygen must be "frozen" to eliminate the benzyl radical and the tert-butoxy radical from the carbon dioxide in a trans manner.



(I)

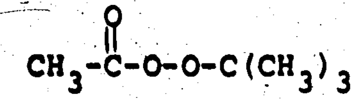
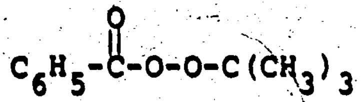
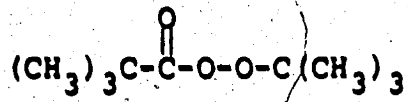
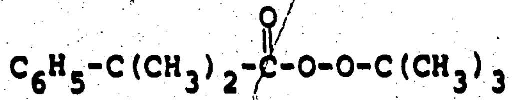
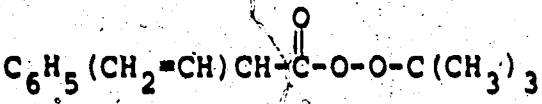
On the other hand, no bonds are "frozen" in the transition state for the non-concerted decomposition of tert-butyl peracetate and thus it was anticipated that this perester would give a higher enthalpy and entropy of activation. The activation parameters, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for tert-butyl phenylperacetate are 29 kcal/mole and 4 e.u. respectively; for tert-butyl peracetate $\Delta H^{\ddagger} = 38$ kcal/mole and $\Delta S^{\ddagger} = 17$ e.u. For the entire series of peresters studied here, Bartlett and Hiatt were able to demonstrate the correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, which suggests that the favorable $\Delta H^{\ddagger}$ for the decomposition of the more unstable peresters was obtained at the expense of restrictions of rotational degrees of freedom, which were reflected in a small $\Delta S^{\ddagger}$. It was possible to discern from their data, ranges of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ characteristic of decompositions involving transition states having restriction of rotation about 0, 1, 2, or 3 bonds. The rates and activation parameters for a number of illustrative substrates are listed in Table 1.

It is important to emphasize that the principles put forth by Bartlett and Hiatt should be used as qualitative tools only. Clearly, Bartlett and Hiatt were only postulating a limited correlation between activation parameters and the number of bonds with restricted rotation in the transition state. Some workers have employed the postulates of Bartlett and Hiatt rigorously and have set limits on the magnitude of the activation parameters for the purpose of distinguishing between concerted or non-concerted decomposition. For example, Martin (14) stated that peresters which decompose by a step-wise mechanism (path A) are associated with values of $\Delta H^{\ddagger} > 35$ kcal/mole and $\Delta S^{\ddagger} > 13$ e.u. Similarly, Lorand (20) put forth a correlation between concerted decomposition and activation parameters where it was suggested that concerted two-bond scission can occur only when $\Delta H^{\ddagger} \leq 32$ kcal/mole and $\Delta S^{\ddagger} \leq 12$ e.u.

Pryor (28) criticizes such rigorous applications of the Bartlett-Hiatt criteria. He cites examples to illustrate that solvent effects can have a very marked influence on activation parameters. Bloomquist and Ferris (2), for

TABLE 1

Decomposition Rates and Activation Parameters of a Number of *tert*-Butyl Peresters $RCOOOC(CH_3)_3$, Studied in Chlorobenzene at 60°

Perester	Half-life at 60°, (min)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)	Restricted rotations
 $CH_3-\overset{O}{\overset{\|}{C}}-O-O-C(CH_3)_3$	5×10^5	38.0	17	0
 $C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-C(CH_3)_3$	3×10^4	33.5	7.8	0
 $(CH_3)_3C-\overset{O}{\overset{\|}{C}}-O-O-C(CH_3)_3$	3×10^2	30.6	12	1
 $C_6H_5-C(CH_3)_2-\overset{O}{\overset{\|}{C}}-O-O-C(CH_3)_3$	12	26.1	5.8	2
 $C_6H_5(CH_2=CH)CH-\overset{O}{\overset{\|}{C}}-O-O-C(CH_3)_3$	4	23.0	-1.1	3

example, found that the decomposition of tert-butyl perbenzoate in phenyl ether led to quite different activation parameters than when the decomposition was carried out in para-chlorotoluene (Table 2). This result would lead one to conclude that tert-butyl perbenzoate decomposes by a non-concerted mechanism in phenyl ether, and by a concerted mechanism in para-chlorotoluene. Albeit that this is an extreme case it does, however, underline one of the serious limitations of the Bartlett-Hiatt criteria. Perhaps, even subtle solvent changes could blur the differences between the activation parameters of some peresters. Therefore, it is important to restrict the Bartlett-Hiatt test to data from a single solvent.

Pryor (28) pointed out another limitation of the usefulness of the activation parameter test, and that is the imprecision involved in determining $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. For the decomposition of tert-butyl 2,2-dimethylperpropionate in cumene Lorand and coworkers (20) report activation parameters of $\Delta H^{\ddagger} = 27.6$ kcal/mole and $\Delta S^{\ddagger} = 3.6$ e.u. Fort and Franklin (21) also studied the decomposition of this perester in cumene and found $\Delta H^{\ddagger} = 25.5$ kcal/mole and $\Delta S^{\ddagger} = -2.9$ e.u. It is difficult, therefore, to use the activation parameters to compartmentalize precisely peresters either as regards the number of bonds that are rotationally restricted, or that are undergoing scission at the transition state. Pryor suggests that the most

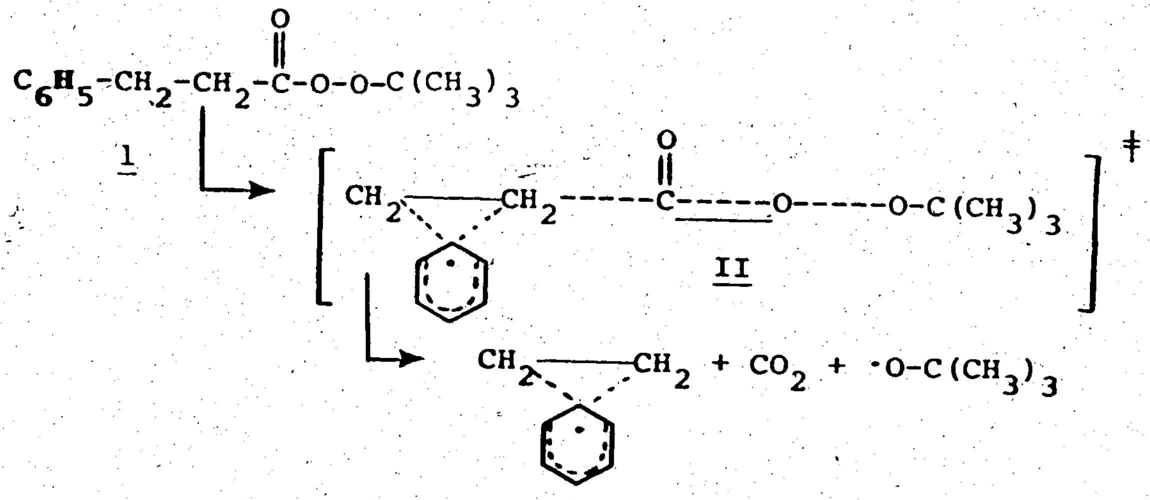
TABLE 2

Activation Parameters of the Decomposition of *tert*-Butyl Perbenzoate

Solvent	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)
Phenyl ether	37.5	15.8
p-Chlorotoluene	33.5	7.8

restrictive classification that can be made is that peresters with $\Delta H^{\ddagger} > 33$ kcal/mole probably decompose by simple one-bond homolysis with no restricted rotations in the transition state, and those with $\Delta H^{\ddagger} < 27$ kcal/mole probably decompose by a concerted mechanism with one or more bonds restricted in the transition state.

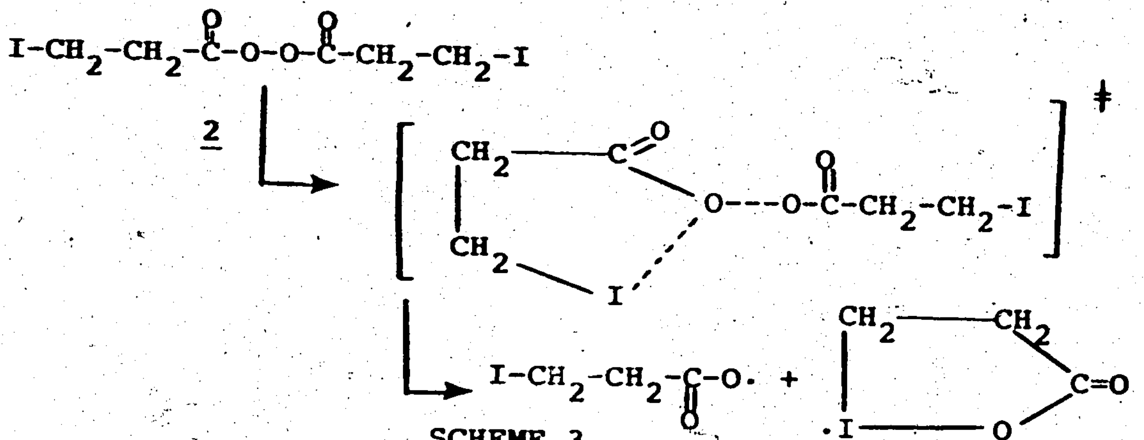
Another facet of the structure-reactivity relationship in perester decomposition has been the effect of neighbouring groups on both the mechanism of the decomposition and its absolute rate relative to the unsubstituted perester (12-14, 29). To examine the possibility of neighbouring group participation by a β-phenyl substituent, Martin (13) studied the kinetics and mechanism of the decomposition of *tert*-butyl 3-phenylperpropionate (1). An acceleration of the rate of decomposition could in theory occur *via* a transition state similar to II (Scheme 2).



SCHEME 2

The activation parameters for the decomposition of this perester fell in the same region as those for the decomposition of tert-butylperacetate (tert-butyl 3-phenylperpropionate, $\Delta H^{\ddagger}$ = 35 kcal/mole, $\Delta S^{\ddagger}$ = 13 e.u., tert-butyl peracetate, $\Delta H^{\ddagger}$ = 38 kcal/mole, $\Delta S^{\ddagger}$ = 17 e.u.). On the basis of the Bart -Hiatt criteria, Martin concluded that the decomposition of this perester occurred *via* a non-concerted one-bond scission (path A). Therefore, he proposed that the phenyl group was not effective in the acceleration of the decomposition of this perester by stabilization of the incipient 2-phenylethyl free radical.

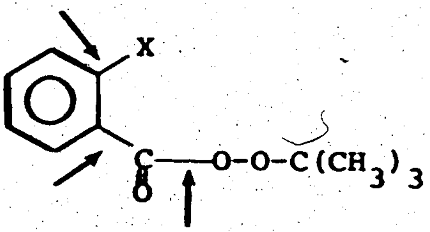
An example of neighbouring group participation by β-substituted heteroatoms in the thermal decomposition of diacyl peroxides was demonstrated by Leffler and coworkers (29c). The rate of decomposition of bis(β-iodopropionyl) peroxide 2 was accelerated by a factor of 17 over that of the parent peroxide, and the magnitudes of the activation parameters were compatible with a cyclic five-membered transition state, as illustrated in Scheme 3.



SCHEME 3

Martin and coworkers (12) found that bond homolysis was accelerated by neighbouring iodide and sulfide groups in the decomposition of some tert-butyl peresters. Very large acceleration of the first-order thermal decompositions of tert-butyl ortho-substituted perbenzoates, 3, was provided by sulfide and to a lesser extent by iodide, relative to tert-butyl perbenzoate. The relative rates of decomposition of these peresters at 40° in chlorobenzene, and their activation parameters, are listed in Table 3.

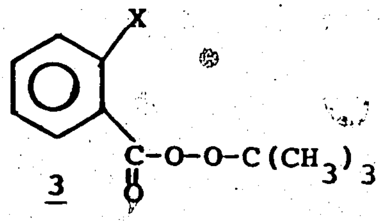
The rate enhancement by both sulfide and iodide substituents was ascribed to neighbouring-group participation in a homolytic bond cleavage, the O-O bond cleavage being accompanied by simultaneous O-S or O-I bond formation. The lowering of the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ upon comparison with those of the unsubstituted perester, X = H, with the ortho-substituted peresters, X = I and X = $S-C_6H_5$, is consistent with a transition state in which there is restricted rotation about three bonds, as indicated by the arrows in the structure below.



Fisher and Martin (12d) speculated that the decomposition

TABLE 3

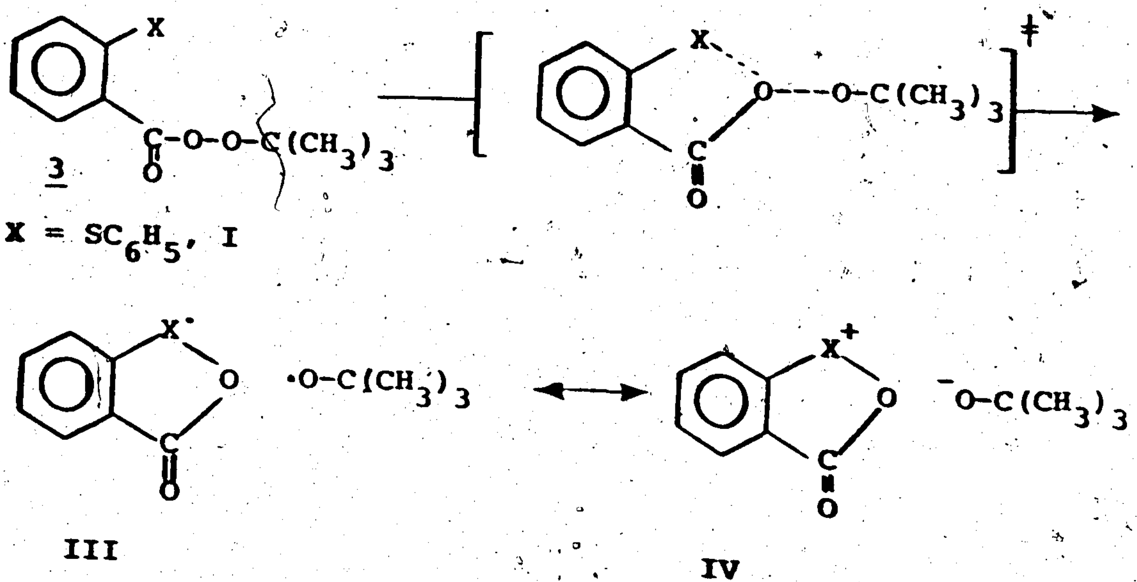
Decomposition of tert-Butyl ortho-Substituted Perbenzoates at 40° in Chlorobenzene [a]

 3	Relative rate	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
$X = SC_6H_5$	6.53×10^4	23.0	-3.4
X = I	80.5	28.0	-0.8
X = H	1	34.1	10.0

---

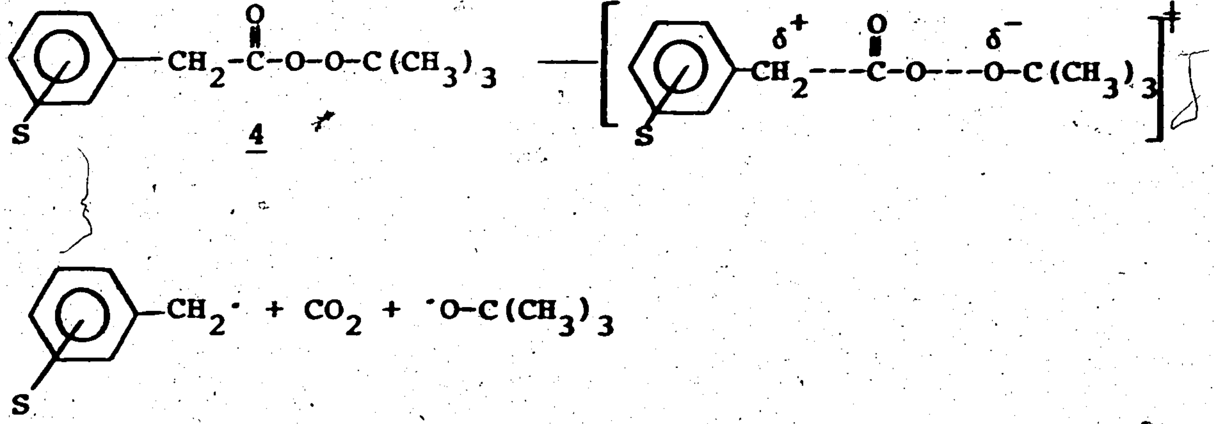
[a] The kinetic data was reported by Martin and coworkers (12).

of *tert*-butyl *ortho*-iodo and *ortho*-phenylthioperbenzoate proceeded *via* a cyclic five-membered transition state, in which stabilization is gained at the expense of rotational freedom as depicted by structures III and IV in Scheme 4.



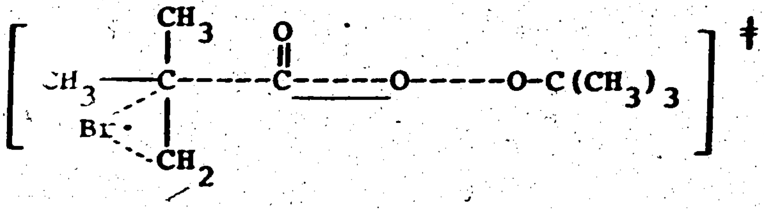
SCHEME 4

Decomposition rates obtained for substituted peresters have been shown to be subject to polar effects as well as effects attributed to anchimeric assistance. Polar effects have a strong influence on the rate of fragmentation of peroxy esters. It was demonstrated by Bartlett and Ruechardt (10) that the rates of decomposition of substituted *tert*-butyl peroxyphenylacetates (4), follow a Hammett relation ($\rho\sigma^+$), with a ρ = -1.09, for the thermal decomposition of these peresters in chlorobenzene at 90.66°. The correlation of the rate constants with the Hammett equation with the use of σ^+ has been interpreted as arising from a direct resonance interaction between the substituent group and the reaction center (Scheme 5).



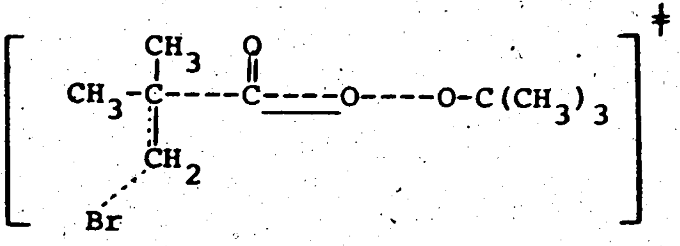
SCHEME 5

There exists the possibility that anchimeric acceleration of the rate of decomposition of tert-butyl-3-bromo-2,2-dimethylperpropionate could occur via a cyclic transition state similar to V.



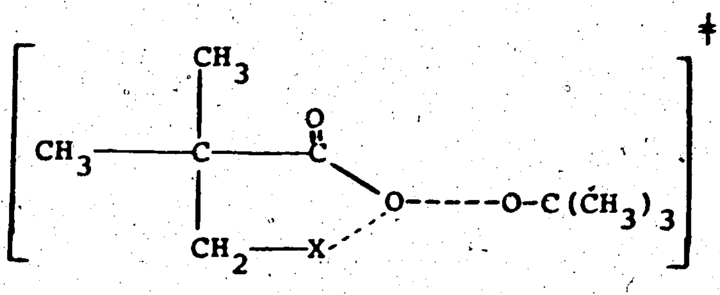
V

Neighbouring group participation by the bromine substituent could also proceed <u>via</u> a concerted, multi-bond cleavage leading to the transition state depicted by structure VI.



VI

Similarly, anchimeric assistance by the β-chloro, β-iodo and β-phenylthio substituents could occur <u>via</u> the types of transition states depicted for the β-bromo perester. In addition, there exists the possibility of anchimeric assistance by β-iodo and β-phenylthio substituents <u>via</u> a cyclic five-membered transition state such as VII.

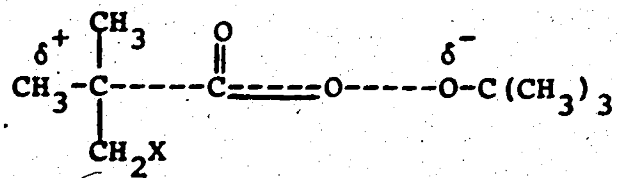


VII

This transition state is analogous to the one postulated by Fisher and Martin (12d) for the decomposition of <u>tert</u>-butyl <u>ortho</u>-substituted perbenzoates, or the one postulated by Leffler (29c), for the decomposition of bis(β-iodopropionyl) peroxide.

It would be expected that neighbouring group participation via any one of the transition states illustrated above should lead to substantial acceleration of the rate of decomposition of the perester, compared to the unsubstituted case. The examination of the activation parameters for their decomposition might shed some light upon the nature of the transition state in this decomposition.

Polar effects caused by the various β-substituents must also be considered (VIII).



$$\overset{\delta^{+}}{CH_3}-\overset{CH_3}{\underset{CH_2X}{C}}\text{-----}\overset{O}{\overset{\|}{C}}\text{=====}O\text{-----}\overset{\delta^{-}}{O}-C(CH_3)_3$$

VIII

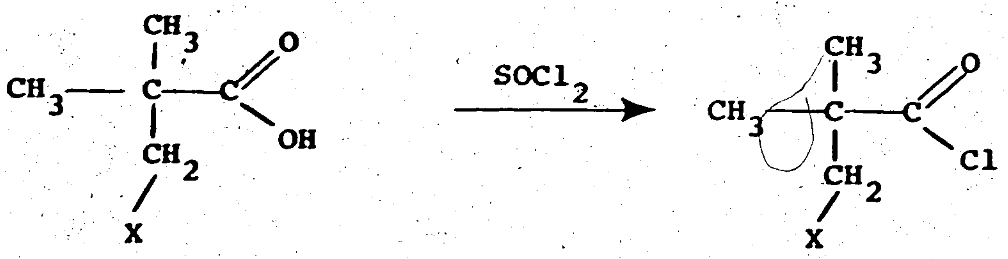
If X is a strongly electron-donating group, it would be predicted that the rate of decomposition would be increased by stabilization of the cationic center on the tertiary carbon. And the opposite effect would prevail for an electron-withdrawing group.

In view of the above considerations it was decided to study the thermal decomposition of the various tert-butyl β-substituted perpropionates.

RESULTS

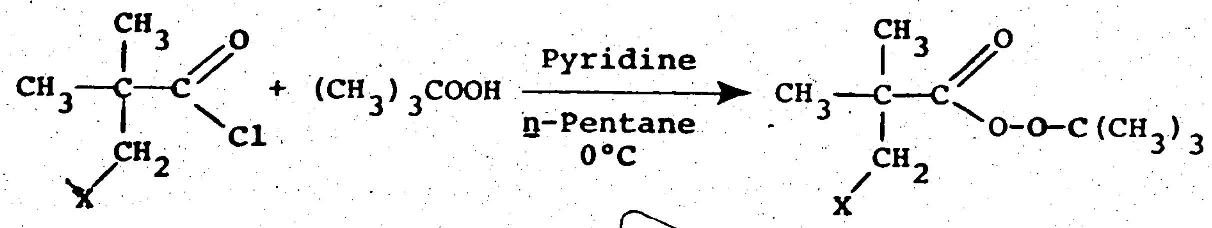
Preparation of the Starting Peresters

The tert-butyl 3-substituted 2,2-dimethylperpropionates ($X-CH_2C(CH_3)_2-CO_3-C(CH_3)_3$, 17-22, were synthesized by converting the corresponding 3-substituted 2,2-dimethylpropionic acids 5-10, into their 3-substituted 2,2-dimethylpropanoyl chlorides 11-16, and treating the acid chlorides with tert-butyl hydroperoxide in the presence of pyridine.



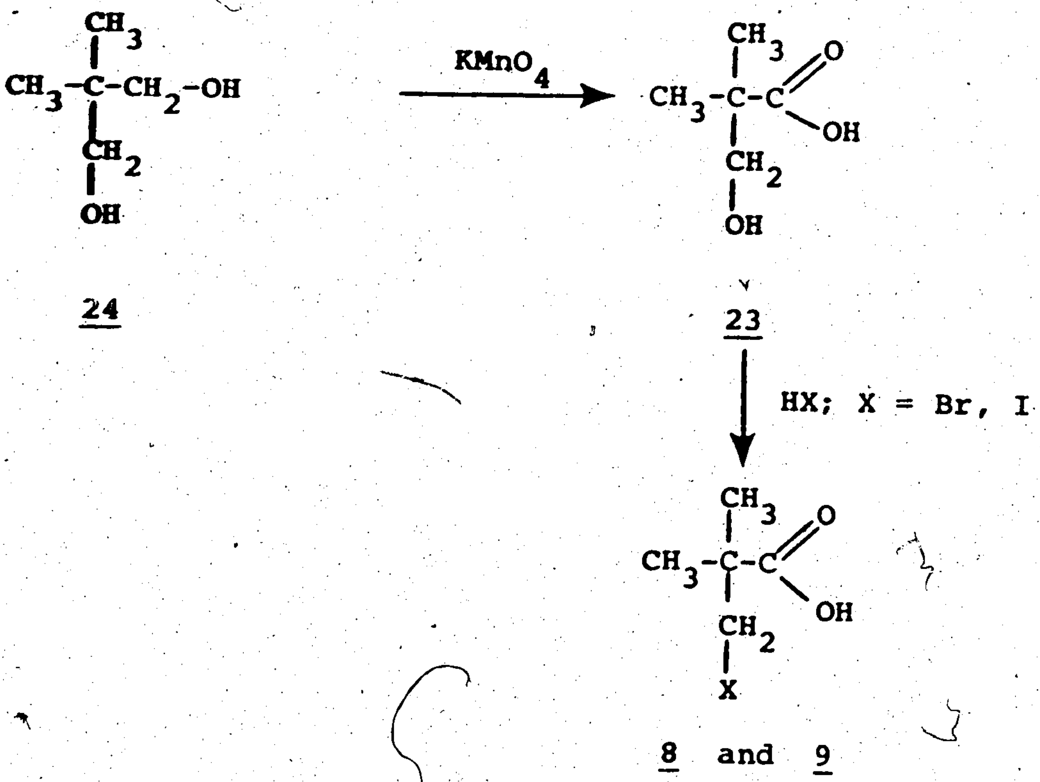
5 $X = H$
6 $X = C_2H_5$
7 $X = Cl$
8 $X = Br$
9 $X = I$
10 $X = C_6H_5S$

11 $X = H$
12 $X = C_2H_5$
13 $X = Cl$
14 $X = Br$
15 $X = I$
16 $X = C_6H_5S$



17 $X = H$
18 $X = C_2H_5$
19 $X = Cl$
20 $X = Br$
21 $X = I$
22 $X = C_6H_5S$

The acids 5-7 were commercially available. Acids 8 (X = Br) and 9 (X = I), were synthesized by the reaction of 3-hydroxy-2,2-dimethylpropionic acid (23) with the appropriate hydrogen halide. Acid 23 was synthesized by potassium permanganate oxidation of 2,2-dimethyl-1,3-propane diol (24).

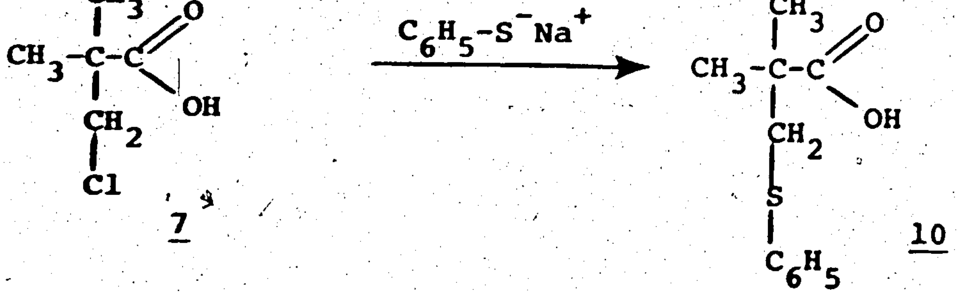


24

23

8 and 9

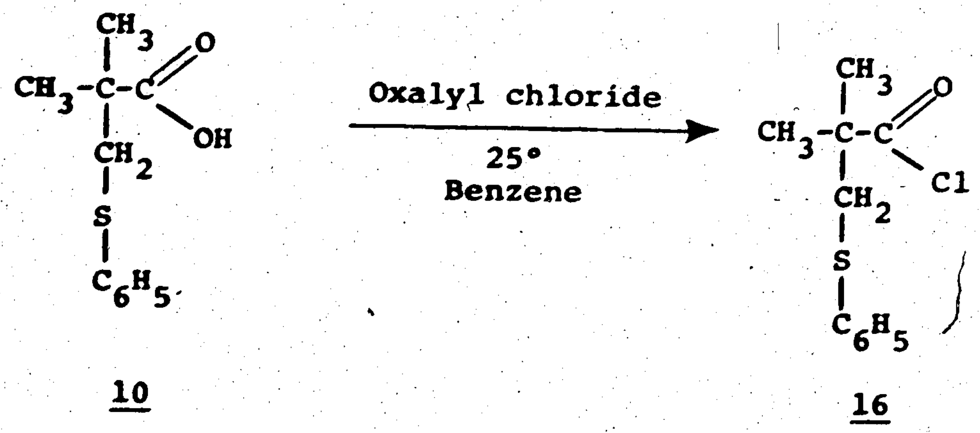
The acid 10 was synthesized by the reaction of 3-chloro-2,2-dimethylpropionic acid (7) with sodium phenylthioxide:



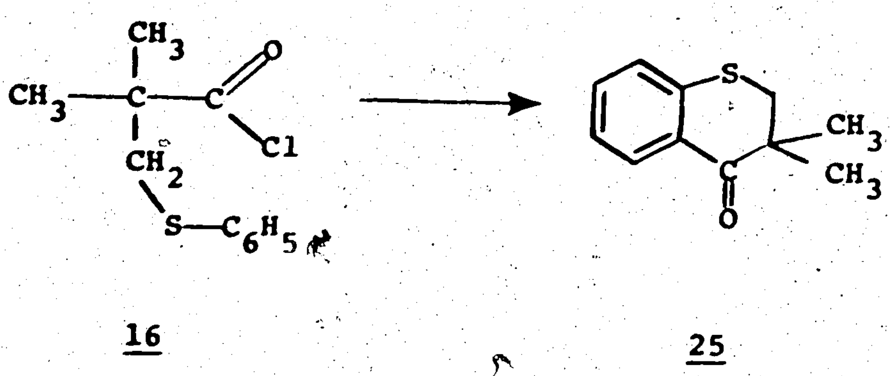
7

10

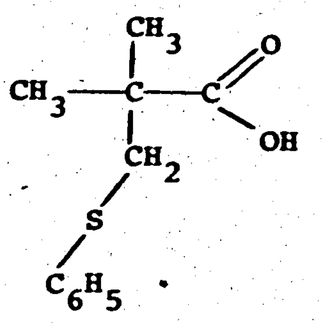
2,2-dimethyl-3-phenylthiopropionic acid (10) was converted into 2,2-dimethyl-3-phenylthiopropionyl chloride (16) by means of reaction with oxalyl chloride in benzene.



The more vigorous conditions for converting the acid into the acid chloride with thionyl chloride at 80°, could not be used for the preparation of this particular acid chloride, since under these reaction conditions the acid chloride underwent an intramolecular cyclization to yield thiocromanon (25).



2,2-Dimethyl-3-phenylthiopropionyl chloride (16) could not be converted into tert-butyl-2,2-dimethyl-3-phenylthioperpropionate (22) by the usual procedure described for all the other peresters. Under these reaction conditions no perester formed, but instead two acids were realized as major products, 10 and 26.



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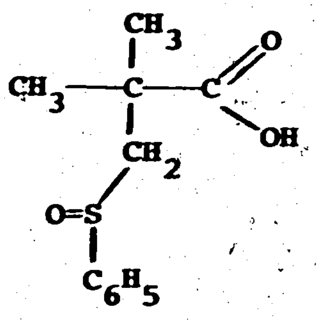


26

A different procedure for the conversion of the acid chloride, 16, to the corresponding tert-butyl perester, 22, was employed. The modified procedure involved the simultaneous addition of pyridine and the acid chloride to a pentane solution of tert-butyl hydroperoxide (see experimental page 64). The perester 22, thus synthesized, was free of all extraneous bands in the hydroxyl and carbonyl regions of the infrared spectrum.

The peresters 17-22 were purified by repeated recrystallizations at -78° from n-pentane, or by column chromatography at 0°. The purity of the various peresters was determined by their nmr and infrared spectra, elementary analysis, and the reproducibility of their unimolecular rates of decomposition.

Kinetics

The tert-butyl 3-substituted 2,2-dimethylperpropionates (17-22) were thermally decomposed in cyclohexane at the appropriate temperatures. The rates were determined by measuring the decrease in intensities of the infrared carbonyl absorptions of the peresters at 1760-1775 cm^{-1}. The kinetic data for the decomposition of these peresters are summarized in Table 4. From the rate constants shown in Table 4 it was possible to calculate the activation parameters. The magnitudes of the activation parameters are also illustrated in Table 4.

The thermolysis of cyclohexane solutions of peresters 17 and 18 gave 98 and 99% yields of the theoretically calculated amount of carbon dioxide and followed steady first-order kinetics to greater than 80% reaction (30). The insensitivity of the rate constant to a change in percent decomposition suggests that induced decomposition was not a complication here. The rate constants for the thermal decomposition of peresters 17 and 18 in cyclohexane at 55°, 65° and 75°, and their activation parameters are listed in Table 4.

The rates of decomposition of peresters 19 (X = Cl) and 20 (X = Br), in various solvents did not show simple first-order kinetics; a plot of log P_o/P vs time did not give a straight line (30). It was found that at high percent decomposition, some acceleration of the rate of

TABLE 4

Rate Constants and Activation Parameters for the Thermal Decomposition of the tert-Butyl 3-Substituted 2,2-Dimethylperpropionates ($X-CH_2-C(CH_3)_2-CO_3-C(CH_3)_3$) at Several Temperatures, in Cyclohexane

Substrate X	Temp °C	Rate constant $k \times 10^5, sec^{-1}$	Relative rates	Activation parameters $\Delta H^‡$ (kcal/mole)	$\Delta S^‡$ (e.u.)
Cl^a	55	0.355 ± 0.014	0.345 ± 0.007	30.7 ± 1.4	10.0 ± 4.3
	65	1.48 ± 0.04	0.368 ± 0.005		
	75	5.65 ± 0.10	0.390 ± 0.010		
Br^a	55	0.950 ± 0.028	0.922 ± 0.010	28.2 ± 1.4	4.0 ± 3.3
	65	3.58 ± 0.19	0.890 ± 0.016		
	75	12.3 ± 0.6	0.841 ± 0.007		
H	55	1.03 ± 0.02	1	29.3 ± 1.4	7.8 ± 4.1
	65	4.02 ± 0.16			
	75	14.5 ± 0.6			
$C_6H_5S^a$	55	1.63 ± 0.04	1.58 ± 0.01	27.[illegible] ± 0.7	3.8 ± 0.7
C_6H_5S	55	1.61 ± 0.04	1.56 ± 0.01		
$C_6H_5S^a$	75	19.8 ± 0.4	1.37 ± 0.03		
C_2H_5	55	1.66 ± 0.01	1.61 ± 0.02	28.[illegible] ± 0.9	[illegible].0 ± 2.7
	65	6.31 ± 0.25	1.57 ± 0.00		
	75	22.3 ± 0.4	1.54 ± 0.04		
I^a	55	2.91 ± 0.08	2.83 ± 0.03	27.9 ± 0.3	[illegible].7 ± 1.4
	75	37.6 ± 0.70	2.59 ± 0.10		

---

[a] Iodine was added to exclude catalyzed decomposition (0.04 mole/l).

decomposition had taken place when radical scavengers such as DPPH, galvinoxyl or iodine were not present in the solution. For example, the rate constant for the decomposition of the 3-bromo perester, 20, in cumene at 65°, was observed to increase with time. This result is illustrated in Table 5. The amount of carbon dioxide measured under these reaction conditions was less than 50% of the amount expected for the decarboxylation reaction. The decomposition of the perester was accompanied by a steady increase in the formation of 3-bromo-2,2-dimethylpropionic acid. Similarly, the decomposition of β-bromo perester, 20, in cyclohexane without added iodine led to only 11% of the theoretically calculated amount of carbon dioxide, and 87% (mole/mole of perester) of the β-bromo acid, 8, was isolated. It was anticipated that the radicals $(CH_3)_2\text{-}\dot{C}\text{-}CH_2\text{-}X$ (X = Cl, Br), formed in the decomposition of the parent peresters, could liberate a Cl· or Br· atom by β-elimination; subsequent abstraction of hydrogen from the solvent would lead to the formation of the corresponding hydrogen halide. The hydrogen halide formed in the reaction most likely leads to an acid catalyzed decomposition of the peresters. In the presence of iodine neither the acceleration of the rate of decomposition nor acid formation was observed. With added iodine first-order kinetics were observed.

The decomposition of perester 19 (X = Cl) in chloro-

TABLE 5

Decomposition of *tert*-Butyl 3-bromo-2,2-dimethylperpropionate (20)[a,b] in Cumene at 65°

Decomposition time (hours)	$k \times 10^5$, sec^{-1}
0.5	5.81
1.0	6.40
2.0	7.32
4.0	8.67

---

[a] A total of 0.199 mmoles were used in the decomposition study.

[b] The concentration of the perester solution was 0.03986 moles/l.

benzene gave a quantitative amount of carbon dioxide (30). Decomposition of peresters 20 (X = Br) and 21 (X = I), in cyclohexane with added iodine also gave quantitative amounts of carbon dioxide, 99% and 97% respectively. The rate constants and the activation parameters for the thermal decomposition of peresters 19-21 are listed in Table 4.

For the 3-phenylthio perester, 22, catalyzed decomposition was not a complication when the kinetics for its decomposition were studied; the magnitude of the rate constant for the decomposition in cyclohexane at 55° was the same within the limits of experimental error, whether the decomposition was carried out in cyclohexane with or without added iodine (1.63×10^{-5} sec^{-1}). Under either of the decomposition conditions the rate constants obtained for perester 22 were essentially the same as those for the other peresters in the series, as illustrated in Table 4.

Product Studies

The products of decomposition of perester 22 (X = C_6H_5-S) were thoroughly examined. The perester was heated in cyclohexane at 75° for 10 half-lives and the products of the decomposition were analyzed. The data are outlined in Table 6.

TABLE 6

Products of Decomposition of *tert*-Butyl 2,2-dimethyl-3-phenylthioperpropionate in Cyclohexane at 75°

Product	Amount (mg)	Amount (mmole)	Perester moles/mole
Carbon dioxide	30.8	0.673	0.94
tert-Butyl alcohol	46.3	0.625	0.90
Isobutylene	33.8	0.603	0.84
β-Methylallylphenylsulfide	18.0	0.110	0.16
Cyclohexylphenylsulfide	64.1	0.334	0.47
Diphenyldisulfide	21.3	0.098	0.14

DISCUSSION

Bartlett and Hiatt (5), who studied the kinetics of the thermal decomposition of a wide variety of tert-butyl peresters, $R-CO_3-C(CH_3)_3$, have demonstrated that the decomposition of a perester may occur by one-bond or concerted two-bond scission. They postulated that when the stability of the resultant R· radical is so constituted as to have a degree of stabilization considerably exceeding that of the methyl or phenyl radical, the thermal decomposition of a perester can occur with concerted rupture of an O-O bond and a C-C bond to produce carbon dioxide and the free radicals $(CH_3)_3C-O\cdot$ and R·. In an endeavour to establish whether the increased stability of the tert-butyl radical over a methyl or phenyl radical is sufficient to facilitate a decomposition via a concerted two-bond scission mechanism, Bartlett and Simons (9) undertook to study the kinetics of the thermal decomposition of tert-butyl 2,2-dimethylperpropionate (17) in the temperature range 58-88°, and in the solvent chlorobenzene.

Their kinetic studies showed that the rate of decomposition of perester 17 was accelerated by a factor of 10^3 over tert-butyl peracetate, and by a factor of 10^2 over tert-butyl perbenzoate, and the increase in the rate of decomposition was accompanied by a lowering of the activation parameters (tert-butyl peracetate, $\Delta H^{\ddagger}$ =

38 kcal/mole, $\Delta S^{\ddagger}$ = 17 e.u.; tert-butyl 2,2-dimethylperpropionate, $\Delta H^{\ddagger}$ = 30.0 kcal/mole, $\Delta S^{\ddagger}$ = 11.1 e.u.). Bartlett and Hiatt (5) observed large amounts of carbonyl-containing products (acid and ester) from the decomposition of tert-butyl peracetate. However, tert-butyl 2,2-dimethylperpropionate did not give rise to carbonyl-containing products; instead, 90% of the theoretically calculated amount of carbon dioxide was found. Similarly, Koenig (19) found 91% of the theoretically calculated amount of carbon dioxide during the course of the study of the decomposition of perester 17 in chlorobenzene.

Lorand (20) and Fort (21) studied the thermal decomposition of perester 17 at various temperatures in cumene. Lorand reported a near quantitative yield of carbon dioxide under these decomposition conditions. Yabuuchi (30) of this laboratory, studied the kinetics of the thermal decomposition of tert-butyl 2,2-dimethylperpropionate at 55, 65 and 75° in cyclohexane. He also observed a near quantitative yield of carbon dioxide for the thermal decomposition of perester 17. The rate constants, activation parameters, and yields of carbon dioxide reported by the above authors, for the decomposition of perester 17 at 65°, are listed in Table 7.

Bartlett and Simons (9) and Lorand (20) carried out a detailed study of the products from the decomposition of perester 17. The products, and the yields based on

TABLE 7

Thermal Decomposition of tert-Butyl 2,2-dimethylperpropionate at 65°

	Reference	10^5k, sec^{-1}	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)	CO_2 (moles/mole perester)
a	9	7.0	30.0	11.1	0.90
	19	8.17[b]	-	-	0.91
c	20	5.81	27.6	3.6	0.98
	21	4.53	25.5	-2.9	-
d	30	4.02	29.3	7.8	0.98

---

[a] Decomposition in chlorobenzene.

[b] Calculated rate constant using the activation parameters found by Yabuuchi (30).

[c] Decomposition in cumene.

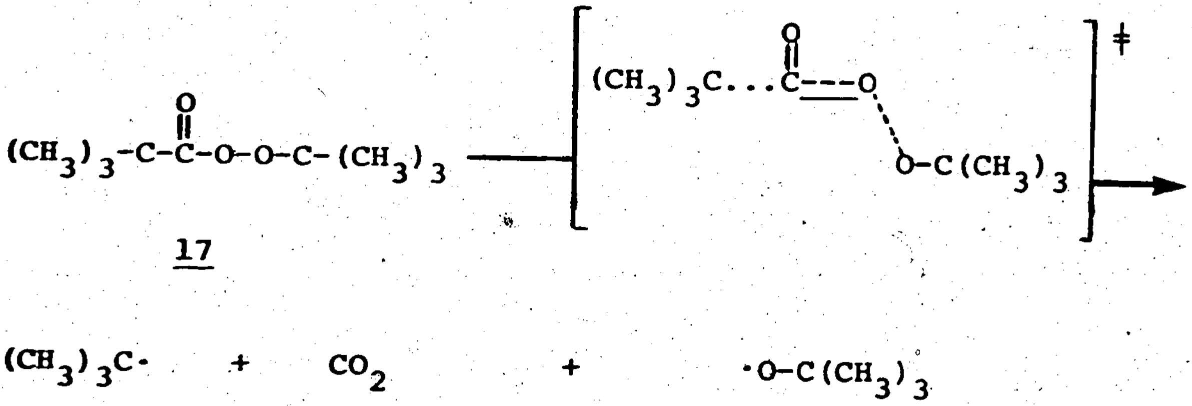
[d] Decomposition in cyclohexane.

moles/mole of perester, found by Bartlett and Simons (9) were: acetone 0.26, tert-butyl alcohol 0.79, isobutylene and isobutane 0.29, and polybutylene 0.46. Lorand found tert-butyl alcohol 0.79, isobutylene 0.40, isobutane 0.30, dicumyl 0.68 and di-tert-butyl ether 0.02. The products can all be rationalized on the basis of the products derived from $(CH_3)_3$-C-O·, R· and carbon dioxide.

The Bartlett-Hiatt criteria predict that peresters which decompose by a mechanism in which the rotation of one bond is restricted in the transition state will show values of $\Delta H^\ddagger$ between 30 and 35 kcal/mole, and $\Delta S^\ddagger$ between 6 and 13 e.u. For those peresters in which there is restricted rotation about two bonds, the values of $\Delta H^\ddagger$ should lie between 26 and 30 kcal/mole and $\Delta S^\ddagger$ between 4 and 6 e.u. If there is a further bond whose rotation is restricted, $\Delta H^\ddagger$ is predicted to lie between 22 to 26 kcal/mole and $\Delta S^\ddagger$ between 4 to -5 e.u.

In the case of perester 17 a concerted decomposition requires that the bond from the carbonyl carbon to peroxy oxygen be restricted because of the trans elimination of the tert-butyl and tert-butoxy radicals. The magnitude of the activation parameters found by Bartlett and Simons (9) and by Yabuuchi (30) for perester 17 (Table 4), are compatible with the Bartlett-Hiatt criteria for restricted rotation about one bond in the transition state. However, the activation parameters reported by Lorand (20) for the decomposition of perester 17 in cumene, would predict restricted rotation about two bonds in the transition state, and the activation parameters reported by Fort (21) for the decomposition of perester 17 in the same solvent, would predict restricted rotation about three bonds in the transition state. This lowering of the activation parameters should be reflected in substantial increases in the rate constant for the decomposition of perester 17. Bartlett and Hiatt (5) observed a 75-fold decrease in the rate of decomposition in going from a perester for which there was a predicted restriction of rotation about three bonds to perester 17, for which there is a predicted restriction of rotation about one bond. It seems reasonable to suggest, then, that Bartlett and Hiatt were postulating a limited correlation between activation parameters and the number of bonds with restricted rotation in the transition state. However, their postulates have been extended, at least as a working hypothesis, by some workers to include a correlation between activation parameters and concerted or non-concerted decomposition. For example, Lorand (20) postulated that peresters may decompose via spontaneous, concerted two-bond scission whenever the stability of R· is equal to or greater than that of tert-butyl; $\Delta H^{\ddagger}$ less than or equal to 32 kcal/mole, and $\Delta S^{\ddagger}$ less than or equal to 12 e.u.

The results from the kinetic study of perester 17 listed in Table 7, and the nature of the products reported by Bartlett and Simons (9), and by Lorand (20) for the decomposition of this perester, can be rationalized by proposing a first-order concerted cleavage to yield carbon dioxide, tert-butyl radical and tert-butoxy radical as illustrated in Scheme 6.



SCHEME 6

It can be seen from the data contained in Table 7 that for the decomposition of perester 17, the enthalpy of activation ($\Delta H^{\ddagger}$) varies from 30.0 kcal/mole to 25.5 kcal/mole, and the entropy of activation ($\Delta S^{\ddagger}$) varies from 11.1 to -2.9 e.u. Some of these discrepancies may arise from a lack of precision in the data or from the use of different solvents. Pryor (28) has cited examples in which solvent effects have led to considerable differences in the activation parameters observed in the decomposition of some peresters. Differences in the activation parameters may also arise from the influence of induced decomposition, although all the data listed in Table 7 were obtained by researchers who endeavored to eliminate this complication. For example, Yabuuchi studied the decomposition of perester 17 in pure cyclohexane, and with 0.04 M iodine added, and found the rate constant and activation parameters to be the same within the limits of experimental error. The differences between the activation parameters found by Bartlett and Simons (9) for the decomposition of perester 17 in chlorobenzene, and those found by Lorand (20) and Fort (21) for the decomposition in cumene, may be attributed to the differences in the solvents used. However, the significantly different activation parameters reported by Lorand (20) and by Fort (21) for the decomposition of perester 17, both in cumene, appears to reveal an imprecision which may be involved in determining $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

Fort studied the kinetics of the thermal decomposition of tert-butyl 2,2-diethylperbutanoate ($((C_2H_5)_3C-CO_3-(CH_3)_3)$, and tert-butyl 2,2-dimethylperpentanoate ($CH_3CH_2CH_2C(CH_3)_2-CO_3-C(CH_3)_3$), and compared the rate constants and activation parameters for the decomposition of these two peresters with those of the less substituted tert-butyl 2,2-dimethylperpropionate (17). The rate constants and activation parameters for the thermal decomposition of these peresters at 65° in cumene are given in Table 8.

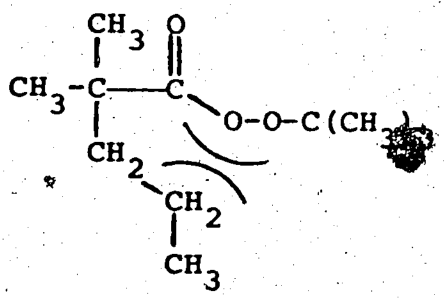
TABLE 8

Thermal Decomposition of Various *tert*-Butyl Peresters

$R-CO_3C(CH_3)_3$ at 65° in Cumene

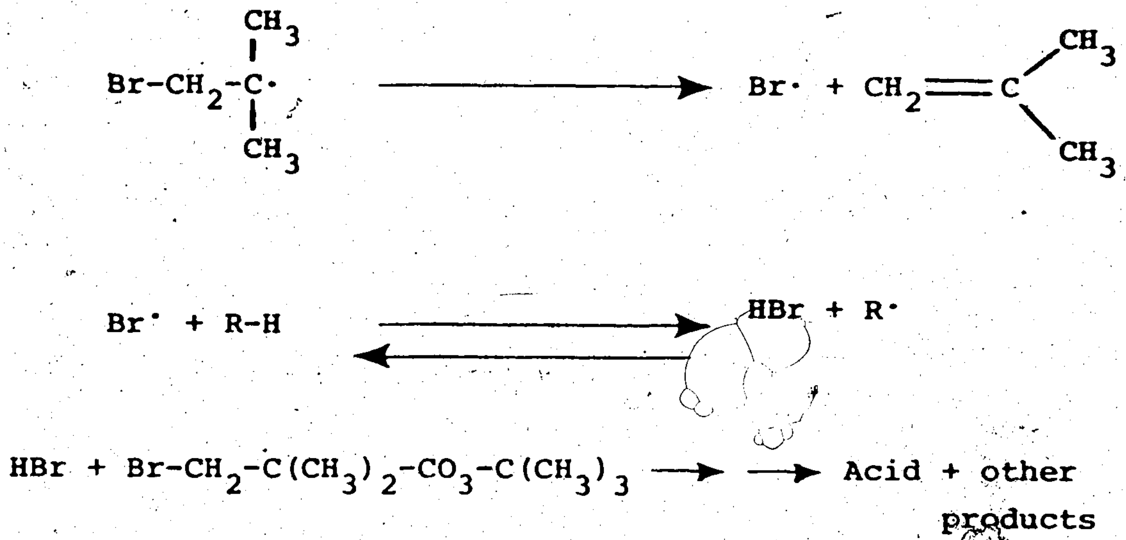
R	k x 10^5, sec^{-1}	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)	Relative rate
$(CH_3)_3C$	4.53	25.5	-2.9	1.0
$CH_3CH_2CH_2C(CH_3)_2$	7.76	25.2	-3.2	1.67
$(CH_3CH_2)_3C$	14.6	24.7	-1.8	3.2

The results in Table 8 show no significant variations in the magnitude of the activation parameters. There is a steady increase in the rate of decomposition as the substitution of the R· radical increases. Fort attributes this increase to the increase in the stability of R· by virtue of the inductive effect of their additional carbons. Yabuuchi (30) studied the kinetics of the decomposition of perester 18 at several temperatures in cyclohexane. The rate constant for the decomposition of this perester at 65° was found to be 6.31×10^{-5} sec^{-1}. The activation parameters observed ($\Delta H^{\ddagger} = 28.8$ kcal/mole, $\Delta S^{\ddagger} = 7.0$ e.u.) were higher than those reported by Fort. An investigation of the products from the thermal decomposition of this perester was not carried out; however, Yabuuchi did observe 99% of the theoretically calculated amount of carbon dioxide. Fort found that the rate of decomposition of perester 18 increased by 42% over perester 17 at 65°; Yabuuchi found this increase to be 36% in cyclohexane. The activation parameters found for perester 18 are well within the limits required for decomposition *via* the concerted two-bond scission mechanism. They do not differ significantly from those reported for perester 17 with the reaction carried out in cumene. It can then be postulated that the mode of decomposition of these two peresters occurs by a similar mechanism, namely concerted two-bond scission. The increase in the rate of decomposition of perester 18 over perester 17 can be rationalized as due to an increase in the stability of R· by virtue of the additional ethyl group. The observed increase in the rate of decomposition as the R group of the perester becomes larger may also be rationalized on the basis of steric grounds. An examination of a space filling model of perester 18 reveals that steric interaction between the β-ethyl substituent with the carbonyl peroxy oxygen of the perester can occur:



The relief of this steric strain could result in an increase in the rate of decomposition of the more substituted peresters over tert-butyl 2,2-dimethylperpropionate (17).

It was observed that both the β-chloro and β-bromo peresters, 19 and 20, did not give first-order kinetics when the decomposition was carried out without an added radical scavenger. The rate of decomposition increased with increasing percent decomposition, and the main products were 3-chloro-2,2-dimethylpropionic acid (7) and 3-bromo-2,2-dimethylpropionic acid (8). This result was attributed to an acid catalyzed decomposition of these peresters as illustrated for the β-bromo perester, <u>20</u>, in Scheme 7 (31).



$$Br{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}\cdot \longrightarrow Br\cdot + CH_2{=}C(CH_3)_2$$

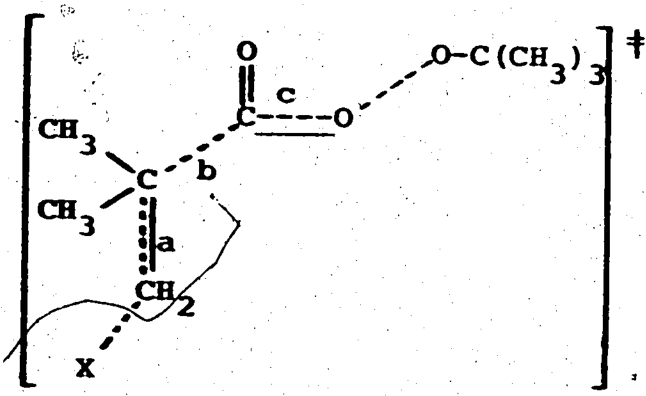
$$Br\cdot + R{-}H \rightleftarrows HBr + R\cdot$$

$$HBr + Br{-}CH_2{-}C(CH_3)_2{-}CO_3{-}C(CH_3)_3 \longrightarrow \longrightarrow \text{Acid + other products}$$

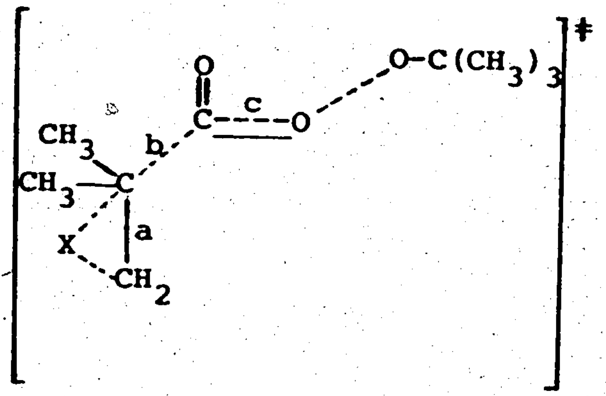
<u>SCHEME 7</u>

The decomposition of the β-halogen peresters, <u>19</u> and <u>20</u>, gave first-order kinetics in cyclohexane solutions with added iodine. It was rationalized that iodine scavenges the radical species quickly and inhibits the formation of HX. Under these conditions catalyzed decomposition was completely eliminated as evidenced by first-order kinetics and absence of carbonyl-containing products; near quantitative amounts of carbon dioxide were found for both of these peresters. The kinetic study of the thermal decomposition of the β-iodo perester, <u>21</u>, was also carried out in a cyclohexane solution with added iodine. The decomposition of the β-phenylthiol perester, 22, gave first-order kinetics under both conditions, neat cyclohexane and cyclohexane with added iodine. The rate constants and activation parameters for the decomposition of peresters 19 and 20, as illustrated in Table 4, do not exhibit any significantly large variation.

Anchimerically assisted acceleration of the rate of decomposition by a neighbouring halogen atom such as chlorine, bromine or iodine could occur via transition states of the type depicted below in which there would be restricted rotation about bonds a and c in IX and a and c in X.



IX

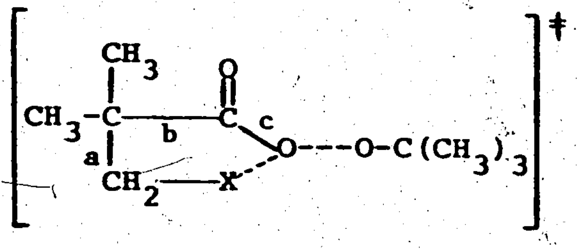


X

This type of stabilization by a neighbouring halogen atom should be reflected by a considerable lowering of the activation parameters when they are compared to those of the unsubstituted perester 17. From the data in Table 1 p. 5 it can be seen that Bartlett and Hiatt observed a lowering of the enthalpy of activation by 7 kcal, and a lowering of the entropy of activation by 13 e.u. when comparing perester 17 with predicted rotation about one bond in the transition state to a perester with predicted restricted rotations about three bonds. Furthermore, this increase in the number of restricted rotations was accompanied by a 75-fold increase in the rate of decomposition. It was anticipated then, if any significant anchimeric acceleration by Cl, Br or I did occur in the decomposition of these *tert*-butyl 3-substituted 2,2-dimethylperpropionates, then the rates of decomposition of these peresters should be substantially higher than those of the unsubstituted analogue, and the increased stabilization of the incipient R· radical *via* transition states IX or X should be reflected by a lowering of the activation parameters.

Examination of the kinetic data of Table 4 shows that only the β-iodo perester, 21, exhibits a small acceleration of the rate of decomposition over the unsubstituted perester, 17. Indeed, the rate constants for both the chlorine and bromine derivatives are lower than those of the unsubstituted perester. Furthermore, the activation parameters for these peresters are the same within the limits of experimental error. In view of these results it must be concluded that anchimeric acceleration of the type as depicted in transition state X, or by concerted elimination as outlined in transition state IX, does not occur to any significant extent. It appears that the relative rates of these peresters are governed by a combination of steric and inductive effects, and these will be discussed subsequently.

As proposed in the introduction, both iodine and sulfur could, by analogy with the tert-butyl ortho-substituted perbenzoates studied by Fisher and Martin (12d), cause anchimerically accelerated bond homolysis in the tert-butyl 3-substituted 2,2-dimethylperpropionates, via a cyclic five-membered transition state VII.

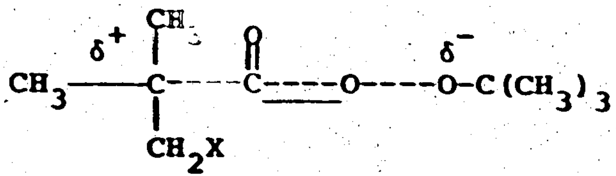


VII

As previously stated a mode of decomposition via such a transition state requires restricted rotation about three bonds (a, b and c), activation parameters consistent with this loss of degree of rotational freedom in the transition state, and a substantial acceleration of the first-order thermal decompositions of the β-substituted peresters, 21 and 22, over the unsubstituted perester, 17. Although both the iodine and sulfur derivatives decomposed at a faster rate than the unsubstituted perester, the increase in the rate of decomposition was not significant enough to allow one to ascribe this to anchimeric assistance. Because the activation parameters of the β-iodo perester, <u>21</u>, and β-phenylthio perester, <u>22</u>, are the same, within the limits of experimental error, the probability of anchimeric assistance by these two substituents *via* the cyclic five-membered transition state VII, is low.

Thus, the kinetic study of the thermal decomposition of the *tert*-butyl 3-substituted 2,2-dimethylperpropionates has not shown any dramatic variations in the rate constants or activation parameters.

Considering the charge-separated structure VIII, it is clear that an increase in the electronegativity of the



$$\mathrm{CH_3}-\overset{\delta^{+}\ \mathrm{CH_3}}{\underset{\mathrm{CH_2X}}{\mathrm{C}}}\cdots\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\cdots\mathrm{O}\cdots\overset{\delta^{-}}{\mathrm{O}}-\mathrm{C(CH_3)_3}$$

VIII

substituent should be less favorable to the partially developed positive charge in the acid portion of the perester. This polar structure will be most destabilized by the electronegative chlorine atom, and this perester actually exhibits the lowest rate of decomposition of the series of peresters studied.

The polar effect of the β-substituent on the ground state energy of the peresters should also be considered. Electron-withdrawing groups like chlorine should reduce repulsive forces between the lone pairs on the two peroxide oxygens and thus increase the stability of the perester. Electron-donating groups should exhibit the opposite effect.

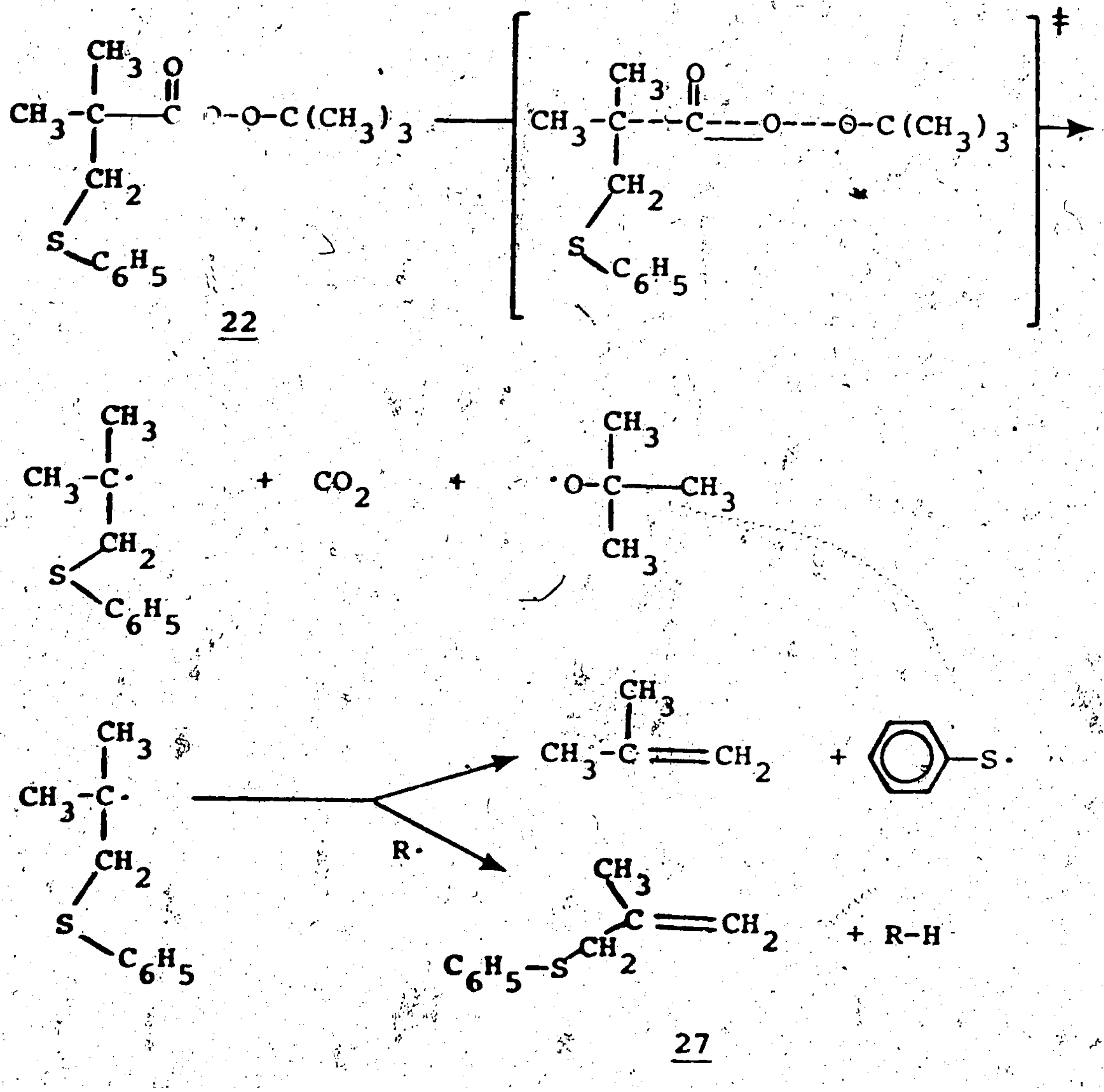
Either argument presented above predicts that the order of the rate of decomposition should be $CH_3CH_2 > H > C_6H_5S > I > Br > Cl$, the inductive order. Experimentally it was found that the order for the rate of thermal decomposition of the peresters studied was $I > CH_3CH_2 > C_6H_5S > H > Br > Cl$, which is not the inductive order. Bartlett and Rueehardt (10) demonstrated the influence of the inductive effect of a chlorine atom upon the rate of thermal decomposition of a _tert_-butyl perester, when they compared the rate constant for the decomposition of _tert_-butyl _meta_-chlorophenylperacetate with that of the unsubstituted perester, _tert_-butyl phenylperacetate, in chlorobenzene at several temperatures. The relative rate of the _meta_-chloro substituted perester to the unsubstituted one was found to be 0.4. A similar retardation of the rate of decomposition due to a chlorine atom was observed for the _tert_-butyl 3-substituted 2,2-dimethylperpropionates ($k_{\underline{19}}/k_{\underline{17}} = 0.4$). It appears that the rate constant for the decomposition of the β-chloro perester, _19_, is governed almost exclusively by the electron-withdrawing inductive effect of the β-chlorine atom.

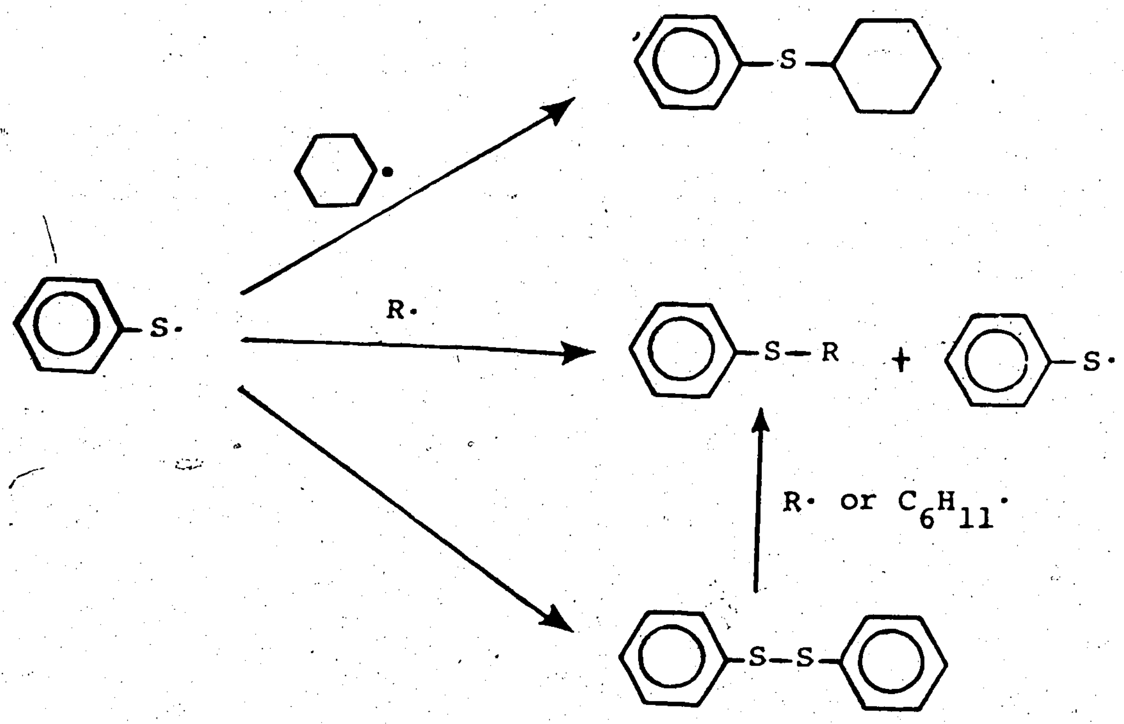
On the basis of the relatively small differences in the electronegativities of the halogen atoms, chlorine, bromine and iodine, one would predict that the rate of decomposition of the β-bromo perester should increase slightly over that of the β-chloro perester, and the β-iodo perester should decompose at a slightly accelerated rate over that of the β-bromo derivative. However, the rate constants of all of the β-halogen peresters would be anticipated to be less than that of the unsubstituted perester. Indeed, if a purely inductive effect prevailed then the rate constants should fit the Hammett-equation with the use of Taft σ^*. Experimentally it was found that the rate constant for the β-bromo perester, 20, was virtually the same as that of the unsubstituted perester, 17, (relative rate of perester 20 to perester 17 was 0.9), and the rate constant for the β-iodo perester, 21, exceeds that of the unsubstituted perester, 17, by a factor of 3. Accordingly a plot of log k vs σ^* was not linear. A purely inductive order also predicts that the β-phenylthio perester, 22, should decompose at a slower rate than the unsubstituted analog. It is difficult to rationalize on the basis of inductive effects why the β-iodo perester, 21, decomposes at a faster rate than both the β-ethyl perester, 18, and perester 17, and why the β-phenylthio perester, 22, decomposes at a faster rate than the unsubstituted perester, 17.

The differences in the rate constants and activation parameters of the various peresters are far too insignificant to permit one to speculate convincingly as to the cause of this observed order in the rates of decomposition. It was speculated earlier that the accelerated rate of decomposition of the β-ethyl perester, <u>18</u>, may be ascribed to steric factors. Similarly, the accelerated rate of decomposition of the β-iodo and β-phenylthio peresters, <u>21</u> and <u>22</u>, over the unsubstituted case, could also be attributed to steric factors. An examination of the structure of the two peresters, <u>21</u> and <u>22</u>, using space filling models reveals an even greater steric interaction between the β-iodo or β-phenylthio substituent and the peroxy oxygen which is bonded to the carbonyl carbon, than for the β-ethyl substituent. This steric interaction appears ~~to be~~ most pronounced for the large iodine atom. The release of this steric strain in the transition state could result in a rate of decomposition greater than that which would be predicted if a purely inductive effect prevailed.

The products of the thermal decomposition of *tert*-butyl 2,2-dimethyl-3-phenylthioperpropionate (<u>22</u>) in cyclohexane, were studied in detail. It was found that the rate constant for the decomposition of this perester was the same whether the decomposition was carried out in cyclohexane with iodine added or in neat cyclohexane.

Similarly, an investigation of the products of decomposition in a cyclohexane solution with iodine added revealed that they were the same as those derived from the decomposition in neat cyclohexane. The decomposition products of perester 22 in pure cyclohexane are summarized in Table 6. The high yield of carbon dioxide (94%) is consistent with the mechanism of concerted decomposition and not with the carbonyl product producing pathway. The products obtained in this study are outlined in Scheme 8.





SCHEME 8

Under the reaction conditions employed for this study the tert-butoxy radical was fixed as tert-butyl alcohol to the extent of 90%. The tert-butoxy radical under these reaction conditions did not undergo a β-scission reaction to yield acetone, a product obtained in other tert-butyl perester decompositions. Bartlett and Ruechardt (10) also found a high yield (90%) of tert-butyl alcohol in their decomposition studies of tert-butyl phenylperacetate in toluene at 95°. In chlorobenzene a considerable amount of acetone was formed. Thus whenever there is a good hydrogen donor the main fate of the tert-butoxy radical is to form tert-butyl alcohol.

In summary, it can be concluded that the tert-butyl 3-substituted 2,2-dimethylperpropionates studied decompose by the concerted two-bond scission pathway, and that anchimeric acceleration of the rate of decomposition by neighbouring group participation of the β-substituent does not occur. The order for the rate of decomposition is not explained by a purely inductive effect. The small differences which do occur, in the order obtained for the decomposition of the tert-butyl 3-substituted 2,2-dimethylperpropionates, may perhaps be attributed to steric factors.

EXPERIMENTAL

GLPC Analysis

An Aerograph 90-P gas chromatograph equipped with a thermoconductivity detector was used throughout. The volatile and low boiling products were analyzed on a 20' x 1/8" FFAP column (4% chromosorb W A/W DMCS 80/100 mesh) at 72°. The high boiling products were analyzed on a 5' x 1/4" SE-30 column (10% chromosorb W A/W 60/80 mesh) at 172°.

Materials

Thionyl chloride was purified according to the procedure described (see experimental p. 172). Oxalyl chloride, from Terochem Laboratories Ltd., was used without further purification. tert-Butyl hydroperoxide was purchased from the Borden Chemical Co. and purified by distillation under reduced pressure (32-35°/15 mm). n-Pentane was washed with concentrated sulfuric acid followed by distillation from phosphorus pentoxide. Cyclohexane, Phillips's Research Grade, was purified by refluxing over sodium metal for several hours followed by distillation. The infrared spectrum of the neat cyclohexane, purified in this manner, showed no extraneous absorption bands in the olefinic region.

Preparation of Peresters and Authentic Samples

Some of the 3-substituted 2,2-dimethylpropionic acids ($X\text{-}CH_2\text{-}C(CH_3)_2\text{-}CO_2H$) were commercially available. 2,2-Dimethylpropionic acid (5), 2,2-dimethylpentanoic acid (6), and 3-chloro-2,2-dimethylpropionic acid (7) were obtained from the Aldrich Chemical Co., and were employed by Mr. Yabuuchi of this laboratory, as starting materials for the preparation of the corresponding peresters. The melting point and/or boiling point, and carbonyl absorption of these acids are listed in Table 9, and their nmr spectra ($CDCl_3$) are listed in Table 10.

Preparation of 3-Bromo-2,2-dimethylpropionic Acid (8)

The β-bromo acid, 8, was prepared by the reaction of fuming hydrobromic acid upon 3-hydroxy-2,2-dimethylpropionic acid (23). The acid, 23, was prepared by potassium permanganate oxidation of 2,2-dimethyl-1,3-propane diol (24), according to the method of Testa (32). The oxidation of 24 by this method netted 37 g (36%) of 3-hydroxy-2,2-dimethylpropionic acid (23). The melting point and carbonyl absorption for this acid is listed in Table 9, and the nmr spectrum ($CDCl_3$), in Table 10.

The carboxylic acid, 23, thus synthesized, was converted to 3-bromo-2,2-dimethylpropionic acid (8) with hydrobromic acid according to a modification of a procedure described by Nerdel (36). Into a 500-ml three-

TABLE 9

Melting Point and/or Boiling Point, and Carbonyl Absorption of Various 3-Substituted 2,2-Dimethylpropionic Acids ($X-CH_2-C(CH_3)_2-CO_2H$)

Substrate X	mp or bp °C	Lit. value	Lit. ref.	$\nu_{C=O}$ cm^{-1}
OH	122-126	123-125	32	1680
H	33-35	34	33	1685
C_2H_5	98-9/9mm	-	34	1695
Cl	126-9/30mm	108-12/10mm	35	1700
Br	51-52	52	36	1705
I	48.5-49.5	54	37	1708
C_6H_5S	115.5-116	115	38	1683
C_6H_5-SO	128.5-130	-	-	1700

TABLE 10

Nmr Spectra of Various 3-Substituted 2,2-Dimethylpropionic Acids ($X-CH_2-C(CH_3)_2CO_2H$)[a]

Substrate	Chemical Shift (τ)			
X	Carbonyl OH	Methylene	Gem-dimethyl	Other
OH	-	6.43 (s)	8.86 (s)	
H	-2.41 (s)			8.78 (s, *tert*-butyl)
C_2H_5	-2.21 (s)	8.54 (m)	8.82 (s)	9.06 (t, methyl)
Cl	-2.45 (s)	6.43 (s)	8.68 (s)	
Br	-1.18 (s)	6.51 (s)	8.63 (s)	
I	-2.31 (s)	6.69 (s)	8.65 (s)	
C_6H_5S	-1.75 (s)	6.82 (s)	8.70 (s)	2.48-2.96 (m, aromatic)
C_6H_5SO	-1.38 (s)	6.86 (s)	8.44 (s), 8.58 (s)	2.08-2.61 (m, aromatic)

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[a] Nmr spectra were taken in $CDCl_3$ with TMS as internal standard.

necked round-bottomed flask fitted with a thermometer, reflux condenser and a fritted glass gas-dispersion tube, were added 38.97 g (0.33 mole) of 3-hydroxy-2,2-dimethylpropionic acid and 218 ml (4.80 mole) of 48% hydrobromic acid. The solution was allowed to stir for 24 hours at 95-100° while a constant flow of hydrogen bromide was bubbled through the solution. The reaction mixture was allowed to cool to 25° and 250 ml of water was added. The entire mixture was extracted several times with ether, and the organic solution was dried over anhydrous magnesium sulfate. After removal of the solvent by rotary vacuum evaporation, 54 g (98%) of a slightly yellow solid remained. After recrystallization from water 3-bromo-2,2-dimethylpropionic acid was obtained as a white crystalline solid. The melting point and carbonyl absorption, and the nmr spectrum (CCl_4) are listed in Tables 9 and 10, respectively.

Preparation of 3-Iodo-2,2-dimethylpropionic Acid (9)

The β-iodo acid, 9, was prepared according to a modification of a method described by Kohn and Schmidt (37). Into a 500 ml three-necked round-bottomed flask, fitted with a reflux condenser, magnetic stirring bar and a thermometer were added 33.6 g (0.29 mmole) of acid 23, 225 ml (2.9 mole) hydriodic acid and 7 g (0.23 mole) of red phosphorus. The solution was allowed to stir under reflux for 12 hours, followed by stirring at 30° for an additional 12 hours. Subsequently, a distillation was carried out at atmospheric pressure and a white crystalline material soon began to solidify on the wall of the reflux condenser. The solid material was periodically flushed out of the condenser with carbon tetrachloride. The distillation was continued until only a viscous residue remained. The residue was extracted several times with carbon tetrachloride and the combined extracts, and the carbon tetrachloride solution of the solid distillate, were dried over anhydrous magnesium sulfate. After evaporation of the solvent 37 g (56%) of a white crystalline material remained. The β-iodo acid, 9, was purified by recrystallization from petroleum ether. The melting point and carbonyl absorption, and nmr spectrum ($CDCl_3$) of this acid are listed in Tables 9 and 10, respectively.

Anal. Calcd for $C_5H_9O_2I$: C, 26.30; H, 3.95. Found: C, 26.49; H, 3.95.

Preparation of 2,2-Dimethyl-3-phenylthiopropionic acid (10)

The acid, 10, was prepared according to a modification of the method used by Truce and Knospe (39) for the preparation of 2,2-dimethyl-3-methylthiopropionic acid. Into a 300 ml round-bottomed flask fitted with a magnetic stirring bar and a reflux condenser were added 130 ml absolute ethyl alcohol and 9.7 g (0.47 mole) sodium metal. The solution was allowed to stir at 30° for 2 hours after which time all of the sodium metal had disappeared. To this mixture was added another solution which had been prepared in the following manner: into a 300 ml round-bottomed flask, fitted with a reflux condenser and a magnetic stirring bar and containing 130 ml of absolute ethanol, were added 25 g (0.52 mole) of freshly distilled phenylthiol and 11.3 g (0.50 mole) of sodium metal. This solution was allowed to stir for 2 hours at 30°.

The combined mixture was subsequently added dropwise into a one liter round-bottomed flask containing a solution of 64 g (0.47 mole) of 3-chloro-2,2-dimethylpropionic acid (7) in 93 ml absolute ethyl alcohol. The resultant mixture was allowed to stir at reflux for 24 hours, after which time the solution was concentrated by means of rotary vacuum evaporation. When the solution was cooled, a white solid residue remained which was subsequently acidified with 10% aqueous hydrochloric acid. The aqueous solution was extracted several times with ether, and the combined ethereal extracts were dried over anhydrous magnesium sulfate. After removal of the solvent by means of rotary vacuum evaporation, 87 g (80%) of a white solid was isolated. The crude product was recrystallized from chloroform/carbon tetrachloride. The melting point and carbonyl absorption, and nmr spectrum ($CDCl_3$) for acid 10 are listed in Tables 9 and 10, respectively.

Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71; S, 15.25. Found: C, 62.50; H, 6.49; S, 15.36.

3-Substituted 2,2-Dimethylpropionyl Chlorides ($X-CH_2-C(CH_3)_2-COCl$)

The procedure for the conversion of the various 3-substituted 2,2-dimethylpropionic acids, to the corresponding 3-substituted 2,2-dimethylpropionyl chlorides, was the same for acids 5 (X = H), 6 ($X = C_2H_5$), 7 (X = Cl), 8 (X = Br) and 9 (X = I). The procedure for the conversion of the acid, 8, to the acid chloride, 14, will be described in detail. Into a 100 ml round-bottomed three-necked flask, fitted with a magnetic stirring bar and a reflux condenser were added 13.6 g (0.075 mole) of 3-bromo-2,2-dimethylpropionic acid (8) and 12.5 g (0.11 mole) of freshly purified thionyl chloride. The mixture was allowed to reflux at 80° for 4 hours. The crude material was distilled under reduced pressure and 8.48 g (59%) of a colorless liquid was collected. Some of the physical constants and carbonyl absorption, and nmr spectra (CCl_4) of the 3-substituted 2,2-dimethylpropionyl chlorides are listed in Tables 11 and 12, respectively.

TABLE 11

Physical Constants and Carbonyl Absorption of Various 3-Substituted 2,2-Dimethylpropionyl Chlorides ($X-CH_2-C(CH_3)_2-COCl$)

Substrate X	Bp °C	Lit. value	Lit. ref.	$n_D^{20°}$	$\nu_{C=O}$ cm^{-1}
H	48/100mm	107	40	1.4126	1795
C_2H_5	59/31mm	45/10mm	34	1.4213	1790
Cl	-	85-6/60mm	41	-	1795
Br	65/10mm	64.5/13mm	36	-	1795
I	90/92/9mm	-	-	1.4808	1795
C_6H_5S	142/5mm	-	-	-	1780

TABLE 12

Nmr Spectra of Various 3-Substituted 2,2-Dimethylpropionyl Chlorides ($X-CH_2-C(CH_3)_2-COCl$)[a]

Substrate	Chemical Shift (τ)		
X	methylene	gem-dimethyl	other
H			[illegible].67 (s, *tert*-butyl)
C_2H_5	8.45 (m)	8.72 (s)	9.06 (t, meth
Cl	6.38 (s)	8.60 (s)	
Br	6.61 (s)	8.52 (s)	
I	6.48 (s)	8.58 (s)	
C_6H_5S	6.79 (s)	8.62 (s)	2.50-2.93 (m, aromatic)

---

[a] The nmr spectra were taken in CCl_4 with TMS as internal standard.

__2,2-Dimethyl-3-phenylthiopropionyl chloride__ (__16__)- A solution of 10.4 g (0.05 mole) of 2,2-dimethyl-3-phenylthiopropionic acid in 100 ml of benzene was prepared in a 500 ml round-bottomed flask fitted with a magnetic stirring bar, a reflux condenser and a dropping funnel. From the dropping funnel was slowly added 112.5 g (0.89 mole) of oxalyl chloride dissolved in 30 ml of benzene. The entire mixture was allowed to stir at 30° for one hour. Subsequently the volatile products and solvent were distilled at reduced pressure at room temperature. A total of 11 g (97%) of a bright yellow liquid was obtained. The physical constants and carbonyl absorption, and nmr spectrum (CCl_4) of this acid chloride are listed in Tables 11 and 12, respectively.

The crude 2,2-dimethyl-3-phenylthiopropionyl chloride was subjected to purification by vacuum distillation. The fraction boiling at 142-143°/5mm was collected as a colorless viscous liquid. An infrared spectrum of the distillate revealed two carbonyl stretching bands at 1672 and 1780 cm^{-1}. The nmr spectrum in carbon tetrachloride showed two methylene absorption bands at τ 6.79 and 7.12, and two different gem-dimethyl-absorption bands at τ 8.62 and 8.78. The integration ratios showed that the ratio of acid chloride, __16__, to the new compound which formed during the distillation was 3:1. A column chromatography purification, employing Woelm neutral alumina and diethyl ether as the eluting solvent, yielded a pure white solid. This compound was characterized as 1-thiocromanon (25); mp 33-35° (lit. 34-35° (38)); ir (CCl_4) $\nu_{C=O}$ 1672 cm^{-1}; nmr (CCl_4) τ 1.93 - 2.13 (multiplet, 1H, aromatic), 2.77 - 3.14 (multiplet, 3H, aromatic), 7.12 (singlet, 2H, methylene) and 8.73 (singlet, 6H, gem-dimethyl).

Anal. Calcd. for $C_{11}H_{12}OS$: C, 68.71; H, 6.29; S, 16.68. Found: C, 68.58; H, 6.31; S, 16.83.

An attempted synthesis of 2,2-dimethyl-3-phenylthiopropionyl chloride by refluxing in neat thionyl chloride, the method employed in the synthesis of the other acid chlorides prepared here, also gave a mixture of acid chloride, 16, and 1-thiocromanon (25). The oxalyl chloride method had the advantage that the reaction could be carried out at room temperature, therefore preventing the formation of 1-thiocromanon.

Peresters

The peresters were prepared from the corresponding acid chlorides. The peresters 17 (X = H), 18 (X = C_2H_5) and 19 (X = Cl) were synthesized by Hiroshi Yabuuchi of this laboratory (30). The method for the conversion of the acid chlorides to the corresponding peresters was the same for the preparation of peresters 17 - 21. 2,2-Dimethyl-3-phenylthiopropionate (22) had to be prepared by a modification of this method.

A mixture of an acid chloride (0.15 mole), freshly purified tert-butyl hydroperoxide (0.255 mole) and 100 ml n-pentane was allowed to stir at 0°. Purified pyridine (0.165 mole) was then added dropwise with stirring over a period of 20 minutes, while the temperature was maintained below 5°. The reaction mixture was then allowed to stand at room temperature for an additional 40 minutes to ensure complete reaction. Subsequently the mixture was poured onto ice. The organic layer was separated and washed successively with cold 10% hydrochloric acid, 10% sodium bicarbonate solution and distilled water, and finally dried over anhydrous sodium sulfate. After removal of the solvent, the remaining crude material (usually 60 - 90% yield) was purified either by recrystallization from n-pentane at -78° or by passing it through a column of Woelm neutral alumina at 0°, using ether as the eluant. The latter method was shown to be particularly effective to remove all traces of impurities. Peroxide contents as determined by iodometric titration developed by Silbert (42), were not very reliable (β-C_2H_5, 86.5%; β-H, 84.7%; β-Cl, 98.3%; β-Br, 98.2%). Bartlett (9) and Koenig (19) also obtained unsatisfactory results by this method for establishing the purity of the peresters synthesized by them. The purity of the peresters was therefore determined by their infrared and nmr spectra, kinetic behaviour and elementary analysis. The refractive indices and carbonyl absorptions, and the nmr spectra (CCl_4) of the peresters are listed in Tables 13 and 14, respectively. The elementary analyses of these peresters are contained in Table 15.

tert-Butyl 2,2-dimethyl-3-phenylthioperpropionate (22) was synthesized in a different manner. An attempt to synthesize this perester from the corresponding acid chloride according to the procedure employed for the other peresters, gave an unsatisfactory result because of the apparent spontaneous decomposition of the perester during the preparation. The major products isolated from this attempted synthesis were two acids. One of these acids was identified as 2,2-dimethyl-3-phenylthiopropionic acid (10) on the basis of its nmr and infrared spectra, and mixed melting point. It was speculated that the other acid formed in the reaction could perhaps be the sulfoxide of 2,2-dimethyl-3-phenylthiopropionic acid. The synthesis of 2,2-dimethyl-3-phenylsulfoxypropionic acid (26) was thus carried out. The procedure employed was similar to the one described in "Organic Synthesis" (43). Into a 100 ml round-bottomed flask fitted with a magnetic stirrer was added 5.0 g (0.024 mole) of 2,2-dimethyl-3-phenylthiopropionic acid in 12 ml of dioxane. The solution was cooled in ice and 5.40 g (0.0252 mole) of meta-sodium periodate

TABLE 13

Refractive Index and Carbonyl Absorption of Various tert-Butyl 3-Substituted 2,2-Dimethylperpropionates ($X-CH_2-C(CH_3)_2-CO_3-C(CH_3)_3$)

Substrate X	$n_D^{25°}$	$\nu_{C=O}$ cm^{-1}	Lit. ref. for synthesis of peresters
H	1.4100	1761	5
C_2H_5	1.4226	1765	21
Cl	1.4390	1765	-
Br	1.4569	1775	-
I	1.5198	1764	-
C_5H_5S	-	1760	-

TABLE 14

Nmr Spectra of Various *tert*-Butyl 3-Substituted 2,2-Dimethylperpropionates ($X-CH_2-C(CH_3)_2-CO_3-C(CH_3)_3$)[a]

Substrate	Chemical Shift (τ)			
X	methylene	gem-dimethyl	*tert*-butyl (peroxy)	other
H			8.76 (s)	8.80 (s, *tert*-butyl)
C_2H_5	8.68 (m)	8.84 (s)	8.74 (s)	(9.08 (t, methyl)
Cl	6.40 (s)	8.68 (s)	8.73 (s)	
Br	6.58 (s)	8.69 (s)	8.74 (s)	
I	6.72 (s)	8.69 (s)	8.73 (s)	
C_6H_5S	6.88 (s)	8.72(s)		2.60-2.97 (m, aromatic)

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[a] The nmr spectra were taken in carbon tetrachloride with TMS as internal standard.

TABLE 15

Elementary Analysis of Various *tert*-Butyl 3-Substituted 2,2-Dimethylperpropionates

$(X-CH_2-C(CH_3)_2-CO_3-C(CH_3)_3)$

X	Carbon, %		Hydrogen, %	
	Calcd	Found	Calcd	Found
C_2H_5	65.31	65.15	10.96	11.14
H	62.04	61.98	10.41	10.30
Br	42.69	42.49	6.77	6.62
Cl	51.80	51.56	8.21	8.40
I	36.02	35.78	5.71	5.72
C_6H_5S	63.79	63.59	7.85	7.97

in 40 ml of water was added. The reaction mixture was allowed to stir for 18 hours. The excess solvent was removed by vacuum distillation; methylene chloride was subsequently added, and the sodium periodate was removed by filtration. The organic solution was washed twice with water. The crude material was freed of iodine by shaking it with sodium thiosulfate in a methylene chloride (20 ml)/water (5 ml) solution. The organic layer was dried over anhydrous sodium sulfate. After removal of the solvent by rotary vacuum evaporation and recrystallization of the crude material from a carbon tetrachloride/chloroform mixture, 5.28 g (97%) of pure 2,2-dimethyl-3-phenylsulfoxypropionic acid (<u>26</u>) remained. The refractive index and carbonyl absorption, and nmr spectrum ($CDCl_3$) of acid <u>26</u> are listed in Tables 9 and 10, respectively.

<u>Anal</u>. Calcd for $C_{11}H_{14}O_3S$: C, 58.38; H, 6.24; S, 14.17. Found: C, 58.11; H, 6.23; S, 14.10. The sulfoxide acid, <u>26</u>, isolated from the attempted perester synthesis was identical with that of independently synthesized acid, <u>26</u>, on the basis of spectral evidence and mixture melting point.

<u>tert</u>-Butyl 2,2-dimethyl 3-phenylthioperpropionate (<u>22</u>) was consequently prepared by a modification of the procedure described for the other peresters. Into a 100 ml three-necked round-bottomed flask submerged in

an ice bath and equipped with a magnetic stirring bar, a reflux condenser and two dropping funnels, was added 1.68 g (0.177 mole) of freshly distilled *tert*-butyl hydroperoxide in 10 ml of purified *n*-pentane. A solution of 2,2-dimethyl-3-phenylthiopropionyl chloride (3.07 g, 0.0135 mole) in 10 ml *n*-pentane, and a solution of pyridine (1.34 g, 0.0170 mole) in 10 ml *n*-pentane, were slowly and simultaneously added to the stirred solution of *tert*-butyl hydroperoxide. After the addition period (20 min), the resultant mixture was poured onto ice. The organic layer was separated, washed successively with cold 10% aqueous hydrochloric acid, cold 10% aqueous sodium carbonate and cold water, and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure while the flask containing the perester was kept at 10°. The oily residue was purified by column chromatography at 0°, as previously described, and 0.530 g (15%) of a colorless oily residue was isolated. 2,2-Dimethyl-3-phenylthioperpropionate (*22*) had an elementary analysis as reported in Table 15, and showed nmr (Table 14) and infrared (Table 13) spectra which were consistent with its assigned structure.

β-Methylallylphenylsulfide (*27*)

The reaction of thiophenol with β-methylallyl chloride to yield β-methylallylphenylsulfide was carried out according to the procedure of Cope, Morrison and Field (44): bp 83 - 84°/2.8 mm (lit. 89°/3.4 mm); the nmr spectrum (neat) was compatible with the one reported for this compound by Kwart and Evans (45).

Anal. Calcd for $C_{10}H_{22}S$: C, 73.11; H, 7.36; S, 19.52.
Found: C, 73.27; H, 7.46; S, 19.64.

Cyclohexylphenylsulfide (28)

The compound, 28, was prepared according to a method similar to that employed by Saville (46). A mixture of 40 ml (0.40 mole) of purified cyclohexane, 54 ml (0.527 mole) of phenylthiol and 1.5 g of AIBN was heated to 75-80° for 40 hours under a constant stream of nitrogen. The resultant reaction mixture was purified by distillation to give a 65% yield of cyclohexylphenylsulfide: bp 126-129°/2.8 mm (lit. 111°/0.1 mm); nmr (neat) τ 2.74 - 3.29 (multiplet, 5H, aromatic), 6.80 - 7.51 (multiplet, 1H, H_1 of cyclohexyl) and 8.00 - 9.65 (multiplet, 10H, cyclohexyl).

Anal. Calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39; S, 16.67.
Found: C, 75.00; H, 8.69; S, 16.70.

Kinetic Studies

The rate of disappearance of the peresters was monitored by following the disappearance of the carbonyl stretching band of the peresters at 1760 - 1775 cm^{-1}.

A Perkin-Elmer infrared spectrophotometer, Model 21 or 421, was employed throughout this study. Products from the decomposition of the peresters did not have any absorptions in this region of the infrared spectrum.

A cyclohexane solution of a perester (0.04 *M*) was initially prepared. In the case of the peresters, **19** (X = Cl), **20** (X = Br), **21** (X = I) and **22** (X = C_6H_5S), iodine (0.04 *M*) was added in order to exclude anticipaed induced decomposition of these peresters. Beer's Law was verified for this system, as evidenced by the straight lines obtained from a plot of log % transmittance *vs* the known concentration of the perester, for a series of standard solutions. Aliquots (1.5 ml) of the solution were degassed by three cycles of the freeze-thaw method and sealed in Pyrex ampoules. The ampoules were then immersed in a bath kept at the appropriate temperature within ± 0.05°. After various reaction periods the tubes were removed from the bath. The first sample was removed after 10 minutes and was regarded as the zero-time sample. Upon removal from the bath, each sample was quenched by immersing the reaction tube in liquid nitrogen. When all of the samples for a particular run had been obtained, they were opened and allowed to warm to room temperature, and the percentage transmittance was measured for each sample at the frequency maximum of the perester carbonyl band in the infrared. The cells used for this purpose were a 0.3 mm AgCl sample cell and a variable NaCl reference cell. For each sample only the region from 1675 to 1975 cm^{-1} was scanned. To obtain an average value for the percentage transmittance T_p, a total of 5 scans over this region was made for each sample. Generally the concentration of the starting perester was so chosen that all samples were in the region of 20 - 80% transmittance; a concentration of 0.04 M generally gave a T_o, (percentage transmittance of the blank), of about 20%. Beer's Law requires that log T_∞ - log T_p should be proportional to the concentration of perester P, where T_∞ is the percentage transmittance of pure solvent, and T_p is the average percentage transmittance of the perester at time t. Experimentally, for predetermined solutions, the plots of perester concentration vs (log T_∞ - log T) were confirmed to be linear for all the peresters studied (T is the percentage transmittance for a known perester concentration). From these calibration curves it was possible to obtain P_o, the initial perester concentration (concentration of the perester in the blank), and P, the perester concentration at time t. The first-order rate constants for perester decomposition at each time t, were obtained by substituting into the rate expression, $k = \frac{2.303}{t} \log P_o/P$. The rate constants obtained for several times t, were the same within the limits of experimental error. For each perester, the rate constants calculated for the various times t, were averaged and reported. The detailed kinetic data for each of the peresters studied are contained in Tables 16 to 22. Duplicate experiments were carried out and the values obtained were the same, within experimental error as those listed in the Tables.

The enthalpy of activation ($\Delta H^{\ddagger}$) could be obtained by calculation from the following equation:

$$\log \frac{k_2}{k_1} = \log \frac{T_2}{T_1} + \Delta H^{\ddagger} \frac{\frac{1}{T_1} - \frac{1}{T_2}}{2.303\ R} \times 10^3$$

The entropy of activation ($\Delta S^{\ddagger}$), was then obtained by substituting this value of $\Delta H^{\ddagger}$ and the values of k and T for any rate constant into the expression

$$k = \frac{k'T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT}$$

where k is the specific first-order rate constant at temperature T, k' is the Boltzmann constant, h is Planck's constant and R is the gas constant. The activation parameters, thus calculated for the various peresters, are summarized in Table 4.

TABLE 16

Decomposition of *tert*-Butyl 2,2-dimethylperpropionate in Cyclohexane

Temp °C	Initial concn, M	Time min.	Decomposition %	Rate constant k x 10^5, sec^{-1}	
55	0.04	0	0	——	1.03 ± 0.02
		210	11.90	1.01	
		330	18.10	1.01	
		480	26.00	1.04	
		840	41.10	1.05	
65	0.04	0	0	——	4.02 ± 0.16
		60	13.00	3.80	
		90	19.40	4.00	
		120	25.10	4.01	
		180	36.30	4.18	
		240	44.00	4.03	
75	0.04	0	0	——	14.5 ± 0.45
		18	14.90	14.9	
		36	28.40	15.1	
		54	37.10	14.3	
		78	46.90	13.9	

TABLE 17

Decomposition of tert-Butyl 2,2-dimethylperpentanoate in Cyclohexane

Temp °C	Initial concn, M	Time min.	Decomposition %	Rate constant $k \times 10^5$, sec^{-1}	
		0	0	—	
		210	18.80	1.66	
		330	27.80	1.65	
55	0.04	492	37.80	1.60	1.66 ± 0.01
		660	48.10	1.66	
		840	56.60	1.66	
		0	0	—	
		60	21.00	6.56	
65	0.04	90	28.50	6.22	6.31 ± 0.25
		120	35.80	6.16	
		180	49.50	6.33	
		240	59.60	6.29	
		0	0	—	
		18	21.40	22.3	
75	0.04	36	37.60	21.8	22.2 ± 0.15
		54	51.30	22.2	
		78	64.70	22.3	

TABLE 18

Decomposition of tert-Butyl 3-chloro-2,2-dimethylperpropionate in Cyclohexane with 0.04 M Iodine

Temp °C	Initial concn, M	Time min.	Decomposition %	Rate constant k x 10^5, sec^{-1}	
		0	0	——	
		780	14.70	0.340	
55	0.04	1680	30.70	0.364	0.355 ± 0.012
		2520	40.80	0.347	
		3800	55.00	0.369	
		0	0	——	
		240	19.60	1.52	
		420	30.70	1.46	
65	0.04	600	40.50	1.44	1.48 ± 0.04
		780	49.20	1.45	
		1020	59.80	1.49	
		1380	71.50	1.52	
		0	0	——	
		60	18.30	5.62	
75	0.04	120	——	——	5.65 ± 0.07
		180	45.20	5.57	
		240	56.30	5.75	

TABLE 19

Decomposition of *tert*-Butyl 3-bromo-2,2-dimethylperpropionate in Cyclohexane with 0.04 M Iodine

Temp °C	Initial concn, M	Time min.	Decomposition %	Rate constant k x 10^5, sec^{-1}	
55	0.04	0	0	——	0.972 ± 0.017
		330	18.30	1.00	
		630	30.40	0.959	
		900	40.20	0.952	
		1260	52.20	0.976	
		1680	61.60	0.950	
65	0.04	0	0	——	3.58 ± 0.19
		120	23.80	3.77	
		180	32.10	3.59	
		270	43.60	3.54	
		360	53.60	4.55	
		480	63.70	3.52	
		840	82.70	3.48	
75	0.04	0	0	——	12.3 ± 0.6
		18	11.90	11.70	
		36	26.80	12.90	
		54	32.80	12.30	

TABLE 20

Decomposition of tert-Butyl 3-iodo-2,2-dimethylperpropionate in Cyclohexane with 0.04 M Iodine

Temp °C	Initial concn, M	Time min.	Decomposition %	Rate constant $k \times 10^5$, sec^{-1}	
55	0.04	0	0	——	2.91 ± 0.07
		138	34.50	2.98	
		202	36.74	2.72	
		270	40.58	2.87	
		341	43.80	2.93	
		438	48.80	2.98	
		516	52.50	2.98	
75	0.04	0	0	——	37.6 ± 0.73
		10	30.50	36.0	
		20	37.70	38.4	
		30	43.30	37.9	
		40	48.90	37.0	
		50	55.00	37.8	
		60	59.60	38.5	

TABLE 21

Decomposition of tert-Butyl 2,2-dimethyl-3-phenylthioperpropionate in Cyclohexane at 55°

Trial	Initial concn, M	Time min.	Decomposition %	Rate constant $k \times 10^5$, sec^{-1}	
1[a]	0.04	0	0	——	1.63 ± 0.04
		93	40.35	1.63	
		225	44.08	1.60	
		348	47.03	1.56	
		483	51.00	1.62	
		602	54.05	1.69	
		739	56.05	1.67	
2	0.04	0	0	——	1.61 ± 0.05
		90	34.03	1.57	
		194	37.24	1.68	
		311	40.25	1.65	
		405	42.70	1.62	
		505	44.30	1.51	
		581	47.13	1.62	

---

[a] Iodine was added (0.04 mol/l).

TABLE 22

Decomposition of tert-Butyl 2,2-dimethyl-3-phenylthioperpropionate in Cyclohexane, at 75° with 0.04 M Iodine

Trial	Initial concn,M	Time min.	Decomposition %	Rate constant k x 10^5,sec^{-1}	
1	0.04	0	0	——	19.43 ± 0.45
		8	28.20	19.64	
		16	30.98	19.61	
		24	33.62	19.30	
		32	35.72	18.19	
		40	39.48	20.04	
		48	41.93	19.78	
2	0.04	0	0	——	19.76 ± 0.04
		8	31.28	20.03	
		16	36.02	19.63	
		24	40.38	19.18	
		32	44.92	19.38	
		49	51.12	20.85	

Product Studies on the Thermal Decomposition of tert-Butyl 2,2-dimethyl-3-phenylthioperpropionate (22)

A total of 0.475 g (0.00169 mole) of the β-phenylthio perester, 22, was accurately weighed into a 50 ml two-necked round-bottomed flask, which was fitted with a break-seal. To the perester was added 40 ml of a cyclohexane with added iodine (0.04 M) solution. The solution was degassed and sealed. The flask was then immersed in a constant temperature oil bath (75°) for 10 hours (10 half-lives). After this reaction period the flask containing the products was attached to a vacuum line, cooled in liquid nitrogen and opened to the line by breaking its break-seal. The volatile gases were then allowed to equilibrate into three traps, the first two cooled to -122° with a pentane/liquid nitrogen slurry, and the third cooled with liquid nitrogen. After 15 minutes, the liquid nitrogen trap containing carbon dioxide was isolated from the other traps. The trap was then warmed to room temperature and the volume of carbon dioxide measured by means of a Toepler pump. The measured carbon dioxide was frozen into a Pyrex tube containing a break-seal. The tube was degassed and sealed and submitted for mass spectral analysis. The cracking pattern, MS-9 spectrometer, confirmed that the gas collected was pure carbon dioxide (0.00160 mole, 95% of the theoretically calculated amount).

The perester, <u>tert</u>-butyl 2,2-dimethyl-3-phenylthioperpropionate, was decomposed in cyclohexane, without iodine to observe the effect of induced decomposition with added iodine. The carbon dioxide isolated was 93% of the theoretically calculated amount.

The gas formed during the decomposition of the peresters was analyzed at 0° by gas chromatography by passing it through a glass column (poly-pack-1, 4' x 1/4") affixed to the vacuum apparatus. Control experiments with authentic gases showed that methane, ethane, carbon dioxide and <u>iso</u>butylene could be separated under these conditions. The gas collected by the method described above, was shown to be pure carbon dioxide.

This method for determining the amount of carbon dioxide given off in the perester decomposition was used for all peresters studied. In each case the amount of carbon dioxide was greater than 93%. The results of these measurements are listed in Table 23.

After the removal of carbon dioxide from the reaction mixture the reaction flask was cooled in liquid nitrogen and was evacuated and sealed. The flask was then cooled in liquid nitrogen, opened, a known amount of benzene was added as internal standard for glpc analysis, and the open neck was immediately covered with a serum stopper. Aliquots of the solution were withdrawn and analyzed by glpc (FFAP, 72°). The pro-

TABLE 23

Measurement of Carbon Dioxide in the Decomposition of *tert*-Butyl 3-Substituted 2,2-Dimethylperpropionates[a, b, c]

Perester Substrate	Mmoles of Perester	Solvent	Mmoles of CO_2	Carbon Dioxide (moles/mole perester)
17 (30)[d]	2.00	cyclohexane	1.95	0.98
18 (30)[d]	2.00	cyclohexane	1.97	0.99
19 (30)	2.00	chlorobenzene	2.06	1.03
20	0.85	cyclohexane	0.85	0.99
21	1.55	cyclohexane	1.50	0.97
22	1.69	cyclohexane	1.61	0.95
22[d]	0.72	cyclohexane	0.71	0.93

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[a] The starting perester concentration was generally 0.04 moles/liter.

[b] The decompositions were carried out with 0.04 molar iodine added except where otherwise indicated.

[c] The peresters were generally decomposed to greater than 10 half-lives.

[d] No iodine was added.

ducts found under these conditions were: isobutylene (84%) and tert-butyl alcohol (90%). Subsequently the solvent and volatile components were evaporated under high vacuum and the solution concentrated to a constant weight. A weighed amount of dibenzyl was added as internal standard, the entire mixture dissolved in a small volume of ether, and the products of the non-volatile residue were analyzed by glpc employing a 5' x 1/4" SE-30 column at 172°. The products found under these conditions were: β-methylallylphenylsulfide (15%), cyclohexylphenylsulfide (47%) and diphenyldisulfide (14%). The volatile products were identified by mass spectroscopy, retention time (compared to authentic samples), and by comparison of their infrared spectra with those of authentic samples. The products from the acid radical of the perester, high boiling liquids or solids, were identified by retention times in glpc, mass spectroscopy, mixture melting point and comparison of their infrared spectra with those of authentic compounds.

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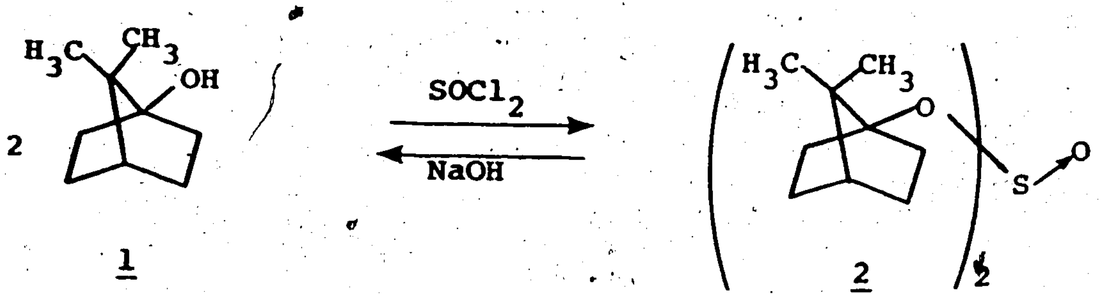
PART II INTRODUCTION

One of the more usual methods of converting alcohols to alkyl chlorides is their treatment with thionyl chloride, $SOCl_2$.

$$ROH + SOCl_2 \longrightarrow RCl + HCl + SO_2$$

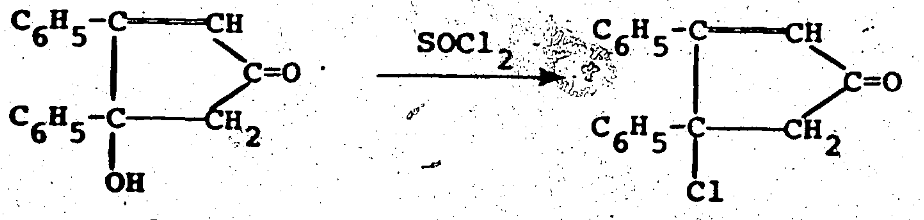
The practical appeal of this reagent is that the two inorganic by-products sulfur dioxide and hydrogen chloride, are gases, and thus can be removed readily from the reaction mixture.

The reaction of thionyl chloride does not proceed readily with some primary or bridgehead alcohols. Whitmore and Rothrock (1) could not obtain a yield greater than 30% of n-butyl chloride from the reaction of n-butanol with neat thionyl chloride. The reaction of neopentyl alcohol with thionyl chloride failed to yield any chloride product. Instead, the starting neopentyl alcohol was reisolated quantitatively. Bartlett and Knox (2) found that the reaction of apocamphanol-1, (1), with thionyl chloride at refluxing temperatures did not lead to chloride product, but instead, 1-apocamphanyl sulfite (2), was isolated in quantitative amount. When the sulfite was warmed with 30% sodium hydroxide solution it gave back the starting alcohol (1).



The reaction of secondary alcohols with thionyl chloride is a very facile one and frequently high yields of alkyl chloride can be obtained. It has been shown that secondary alcohols with thionyl chloride, give the highest yield of chloride in the presence of pyridine or dimethyl- or diethylaniline (3), or when there is a phenyl group attached to the α or β carbon of the carbinol (4). Cram could obtain a 95% yield of 2-chloro-3-phenyl-2-butane from the reaction of 3-phenyl-2-butanol with neat thionyl chloride (5).

Tertiary alcohols also can lead to chlorides in high yield. McKenzie and Clough (6) isolated an 83% yield of tert-amyl chloride from the reaction of tert-amyl alcohol with neat thionyl chloride. In 1932, Allen and Spanagel (7) reported a 66% yield of the chloride, 4, from the reaction of anhydracetone benzil (3) with thionyl chloride.

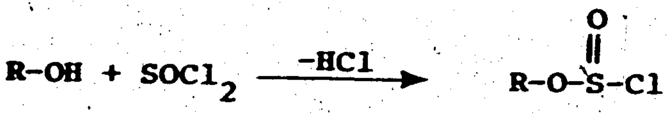


3 4 (66%)

Frequently, however, the reaction of secondary and tertiary alcohols with thionyl chloride is complicated by the formation of a considerable amount of olefin product. Thus, the yield of olefin from the reaction of 2-butanol with thionyl chloride in dioxane is 60%, and cyclohexene can be produced in over 80% yield from the reaction of cyclohexanol with neat thionyl chloride (8c).

The mechanism of the reaction of alcohols with thionyl chloride has been extensively investigated. These mechanistic studies have largely involved the examination of the stereochemistry of the chlorides formed from the reaction of optically active secondary alcohols.

The reaction was postulated by Hughes, Ingold and co-workers (4), to proceed through an intermediate alkyl chlorosulfite (5).

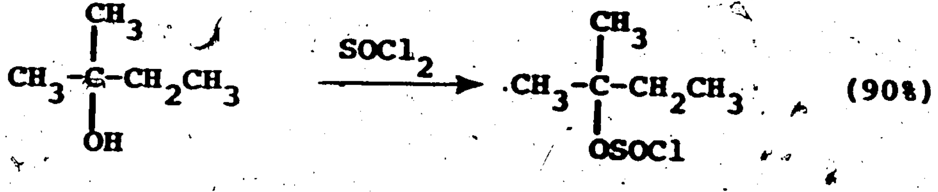


$$\text{R-OH} + \text{SOCl}_2 \xrightarrow{-\text{HCl}} \text{R-O-}\overset{\overset{\displaystyle\text{O}}{\|}}{\text{S}}\text{-Cl}$$

Alkyl chlorosulfite

5

In some cases this ester has been isolated. The first evidence for the formation of chlorosulfite intermediates was cited by McKenzie and Clough (6) in 1913. They successfully isolated the chlorosulfite of tert-amyl alcohol, 6, in excellent yield.



$$CH_3\text{-}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large OH}{|}}{C}}\text{-}CH_2CH_3 \xrightarrow{SOCl_2} CH_3\text{-}\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large OSOCl}{|}}{C}}\text{-}CH_2CH_3 \quad (90\%)$$

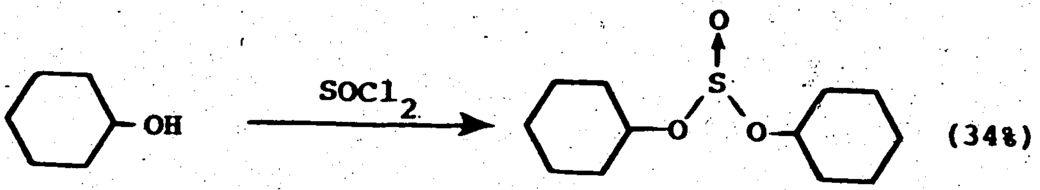
<u>6</u>

tert-amyl alcohol — tert-amyl chlorosulfite

Since then numerous chlorosulfites, which can be liquids or solids, have been isolated (8-11). When these chlorosulfites are heated they decompose to the corresponding alkyl chloride and sulfur dioxide.

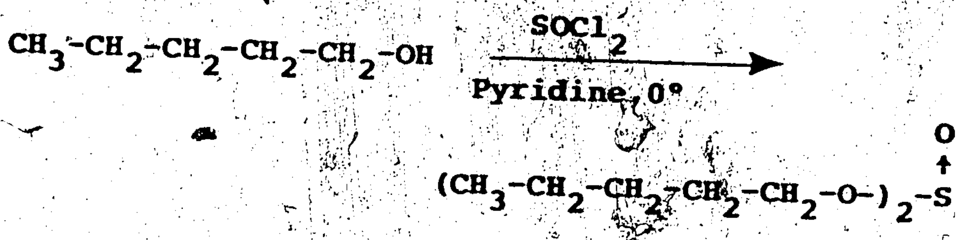
$$ROSOCl \longrightarrow R\text{-}Cl + SO_2$$

A considerable number of cases have been cited in which the reaction of alcohol with thionyl chloride did not yield alkyl chlorosulfite; instead a dialkyl sulfite was formed. Carré and Libermann (12) carried out the reaction of cyclohexanol with neat thionyl chloride at 0° and obtained a mixture of cyclohexene, cyclohexylchlorosulfite and a 34% yield of a liquid boiling at 182°/19 mm which was identified as dicyclohexyl sulfite (7).



7

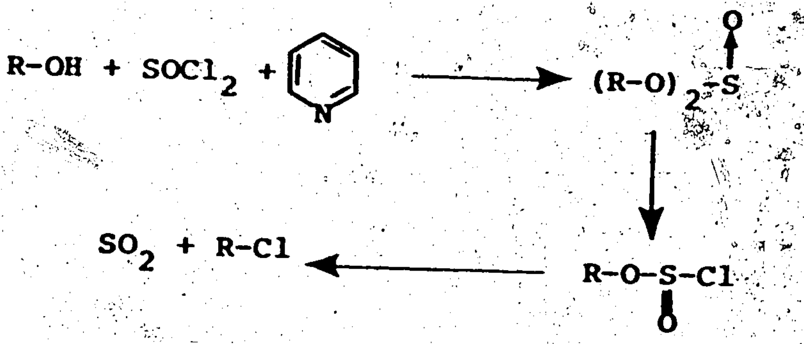
Gerrard (9) found that the slow addition of 1 mole of thionyl chloride to a mixture of 1 mole n-amyl alcohol, and 1 mole pyridine at 0°, gave an excellent yield (83%) of a liquid (bp 173°/20 mm) which was identified as n-amyl sulfite (8).



$$CH_3-CH_2-CH_2-CH_2-CH_2-OH \xrightarrow[\text{Pyridine, }0°]{SOCl_2} (CH_3-CH_2-CH_2-CH_2-CH_2-O-)_2-\overset{O}{\overset{\uparrow}{S}}$$

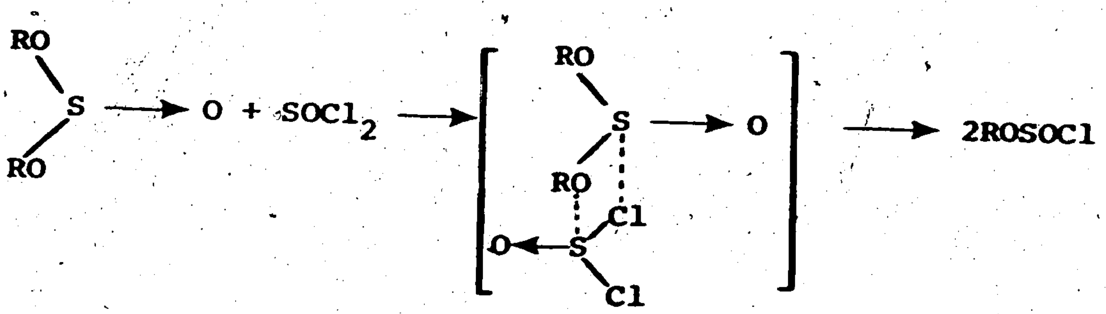
8

By a similar procedure, Gerrard carried out the preparation of di-n-butyl sulfite in 87% yield from n-butyl alcohol. Further, it was found that when the reaction mixture from 1 mole of alcohol, 1 mole of thionyl chloride and 1 mole of pyridine was heated for three hours, the initially formed dialkyl sulfite reacted further with the residual thionyl chloride to form the corresponding chlorosulfite (ROSOCl), which was then catalytically decomposed by the pyridine hydrochloride to alkyl chloride and sulfur dioxide.



This was verified by warming the appropriate chlorosulfite with a small quantity of pyridine hydrochloride and obtaining practically theoretical yields of the chloride, RCl and sulfur dioxide at temperatures far below those required to decompose the chlorosulfites themselves. Thus, the facile decomposition of the alkyl chlorosulfite was attributed to the presence of the chloride anion.

Gerrard (9) formulated the reaction of a dialkyl sulfite with thionyl chloride as being a direct metathetical process occurring between one molecule of dialkyl sulfite and one of thionyl chloride.

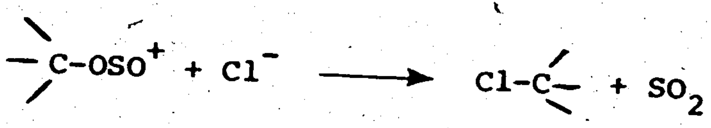


Bartlett (10) undertook to study the kinetics of the reaction between di-n-butyl sulfite and thionyl chloride to yield n-butyl chlorosulfite, in order to determine the validity of the mechanism formulated by Gerrard. It was found that the reaction was not a simple second order metathesis between the two reactants. When the two reactants were present in equal concentrations, the rate was proportional to the concentration of one reactant, and the kinetics were simply first-order. When the reactants were present in inequal concentrations, the reaction was roughly first-order with respect to dibutyl sulfite and not even approximately so with respect to thionyl chloride. The reaction was powerfully catalyzed by chloride ion, but not by hydrogen chloride. The results obtained were consistent with an ionic chain reaction involving steps (1) and (2).

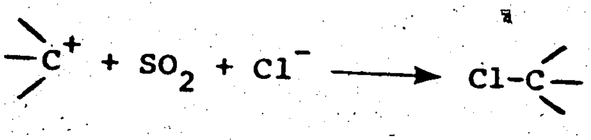
$$Bu_2SO_3 + Cl^- \xrightarrow{k_1} BuOSOCl + BuO^- \qquad (1)$$

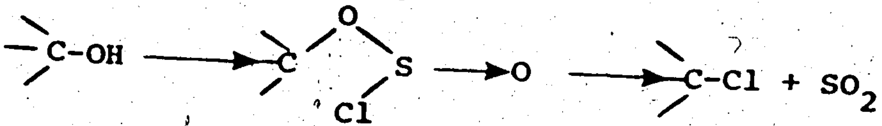
$$SOCl_2 + BuO^- \xrightarrow{k_2} BuOSOCl + Cl^- \qquad (2)$$

When a mechanism involving the formation of a chlorosulfite as an intermediate had been established, it then became necessary to establish the manner in which this intermediate decomposes to give alkyl chlorides. Three possible routes for the thermal decomposition of the chlorosulfite were proposed by Hughes, Ingold and co-workers (4).


(inversion)

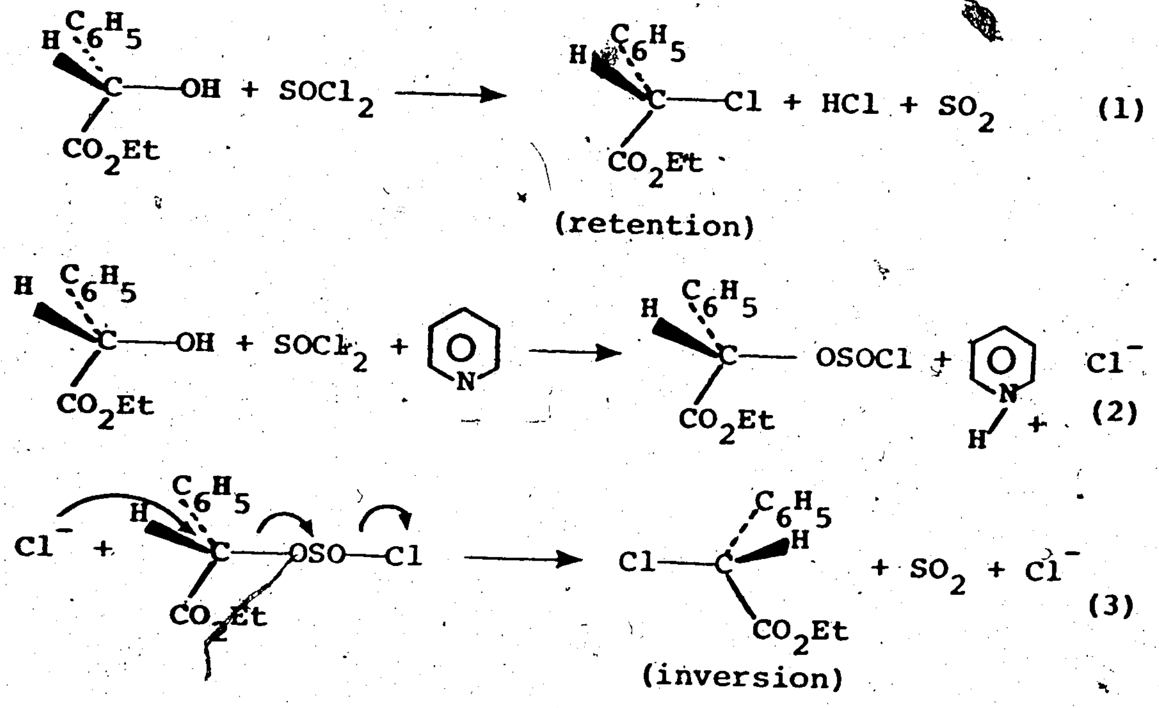
(S_N2)


(S_N1)


(retention)

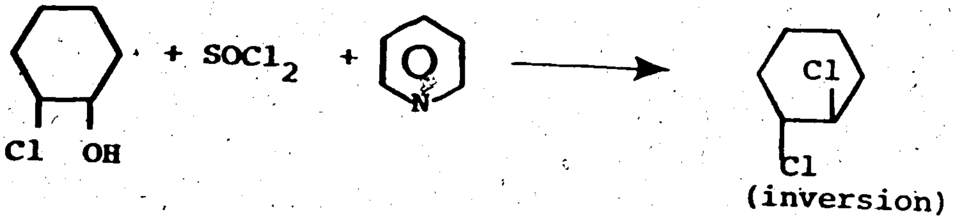
(S_Ni)

The study of the stereochemistry of the alkyl chlorides formed from the reaction of optically active alcohols with thionyl chloride sheds a great deal of light upon the mechanism of the decomposition of the intermediate alkyl chlorosulfite. Kenyon and Phillips (13) demonstrated the effect of pyridine on the steric course of the reaction. When ethyl mandelate was allowed to react with neat thionyl chloride, the resultant chloride formed with 100% retention of configuration (equation (1), Scheme 1). However, when the same reaction was carried out with an added equivalent of pyridine, complete inversion of configuration resulted (equation (2) and (3), Scheme 1).



SCHEME 1

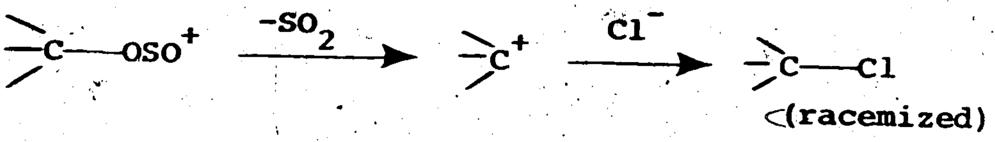
Hughes and Ingold (4) postulated that the pyridine can transform the hydrogen chloride, formed during the reaction of the alcohol with thionyl chloride, into the pyridinium hydrochloride salt ($C_5H_5\overset{+}{N}H\overset{-}{Cl}$), whose chloride ions may attack the chlorosulfite by an S_N2 process as illustrated in Scheme 1. Stevens and Grummitt (14) also proposed the S_N2 mechanism to explain the isolation of *trans*-1,2-dichlorocyclohexane from the reaction of *cis*-2-chlorocyclohexanol with thionyl chloride and added pyridine:



The stereochemical result was attributed to a catalysis of the decomposition of the alkyl chlorosulfite by chloride anion arising from the pyridine hydrochloride.

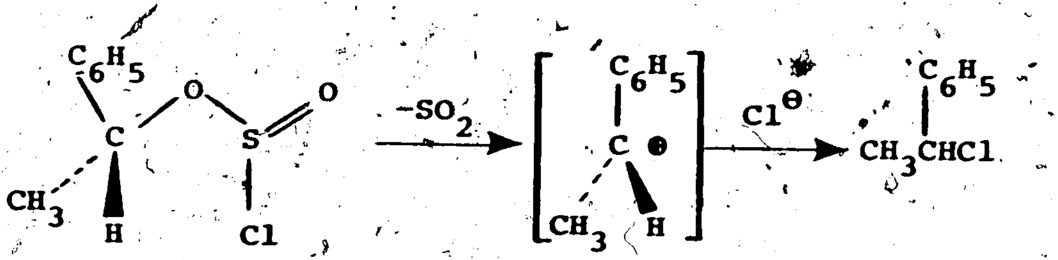
Lewis and Boozer (8b) showed that dilute solutions of pyridine hydrochloride in dioxane gave, from optically active *sec*-butyl chlorosulfite, extensively inverted *sec*-butyl chloride, although configuration is retained in the absence of this salt. Lewis and Boozer (8d) studied the kinetics of the decomposition of *iso*-propyl chlorosulfite in dioxane with added tertiary amines or their hydrochlorides. They showed that the reaction follows a first-order course, with the apparent first-order rate constants increasing linearly with the concentration of the catalyst. Both the stereochemical outcome of this base catalyzed reaction, and the kinetics are consistent with a bimolecular displacement of the S_N2 type between chloride ion and the chlorosulfite.

Hughes, Ingold and co-workers (4), suggested that the decomposition of alkyl chlorosulfite by the S_N1 mechanism can proceed <u>via</u> the route depicted in Scheme 2.



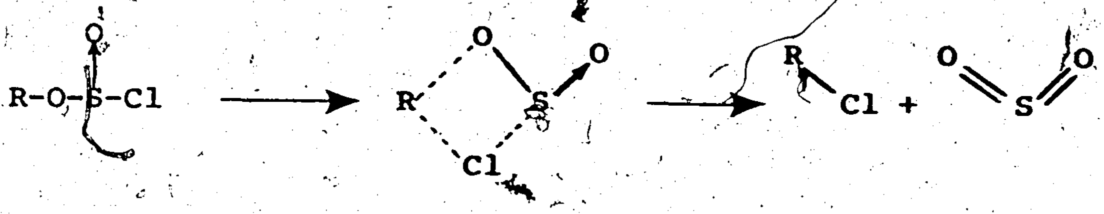
SCHEME 2

The initial step is the ionization of the S-Cl bond. Carbonium ion formation should be favored by strongly ionizing solvents and by electron-releasing groups attached to the carbon undergoing substitution. If the carbonium ion becomes really free, or if it is solvated symmetrically on both sides, the chloride ion may attack from either side with equal facility and an inactive racemic mixture results. Hughes and Ingold attributed the formation of racemized 1-chloro-1-phenylethane in the reaction of α-phenylethanol with neat thionyl chloride, to the ability of the phenyl group to aid in the ionization of the C-O bond of the ester-halide by stabilization of the incipient carbonium ion.

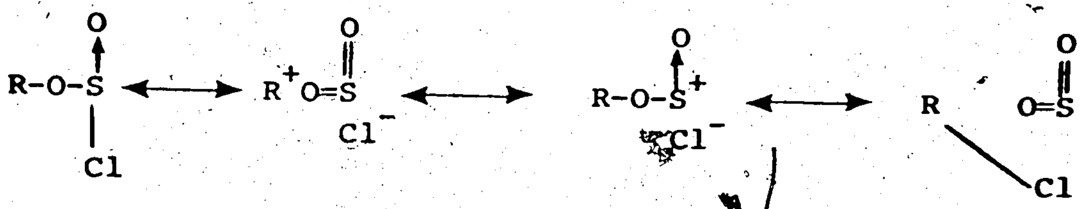


Cram (5) found that racemization increased considerably when the reaction of optically active 3-phenyl-2-butanol with thionyl chloride was carried out in a strongly ionizing solvent such as formic acid. The reaction of the above alcohol with neat thionyl chloride gave an alkyl chloride product with almost complete retention of configuration. However, the reaction of the same alcohol with thionyl chloride in formic acid resulted in totally racemized product. Similarly, Lewis and Boozer (8b) observed that in solvents with fairly high dielectric constants (dioxolane, ethylene chloride), the mechanism of the decomposition of the secondary alkyl chlorosulfites (2-butyl, 2-pentyl and 2-octyl) which led to racemic product was the one which dominated.

The decomposition of an alkyl chlorosulfite which leads to alkyl chloride with inversion of configuration can be rationalized on the basis of the S_N2 mechanism, or it may come about from an ion-pair where the front side is protected by the gegen ion. Decomposition leading to racemization was explained on the basis of the S_N1 mechanism. However, a somewhat different reaction path, termed by Hughes, Ingold and coworkers, the S_Ni mechanism (substitution, nucleophilic internal) was proposed to be necessary to explain retention of the chloride product. They proposed that formation of alkyl chloride product with retention of configuration results from an internal displacement with chlorine of the chlorosulfite acting as the nucleophile. Thus, the decomposition of the alkyl chlorosulfite via the S_Ni mechanism, according to Hughes and Ingold, is a one-step process, which involves the simultaneous loss of sulfur dioxide and the formation of a carbon-chlorine bond at the point where the oxygen had previously been attached by way of a cyclic transition state:

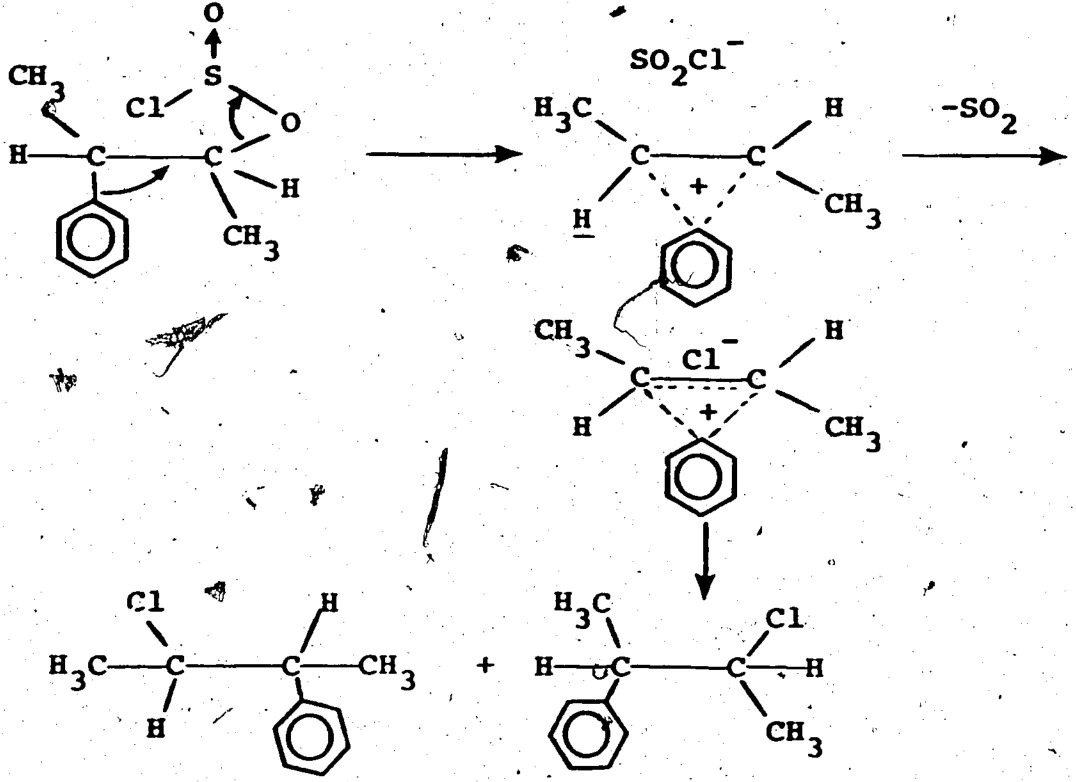


This originally proposed mechanism required extensive modification, since it was subsequently demonstrated (5, 8,11,15) that the decomposition of alkyl chlorosulfites leading to retention of configuration involved intermediates which exhibited considerable ionic character. Lewis and Boozer (8a) studied the kinetics of the thermal decomposition of 2-butyl, 2-pentyl and 2-octyl chlorosulfites in dioxane and isooctane. In dioxane the reaction was found to be first-order and the chloride had the same configuration as the alcohol from which it was derived. The decomposition in isooctane was much slower but the reaction was still apparently first-order. The chloride had the opposite configuration from the alcohol. Lewis and Boozer proposed that if the reaction did proceed by the classical S_Ni mechanism, then the reduction in rate on changing to a less polar solvent implies that the transition state has a higher dipole moment than the normal chlorosulfite, and contributions to the transition state from structures 10 and 11 as well as 9 and 12 should be considered:



9 10 11 12.

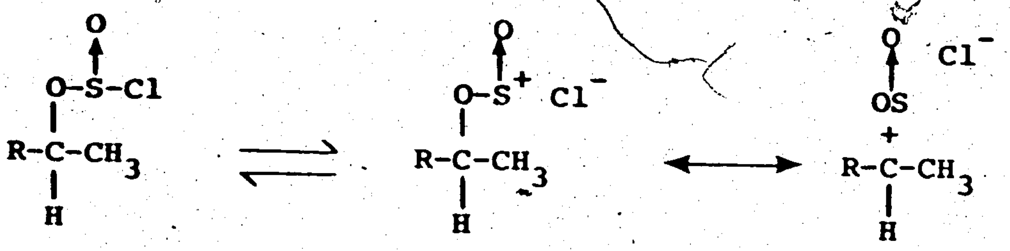
Cram (5) pointed out that the mechanism for producing chloride with retention is closely related to the S_N1 mechanism, since the mechanism leading to retention of configuration best competes with other reaction paths when a relatively stable carbonium ion can be formed and that the reaction proceeds more rapidly in better ion-solvating media. Further, Cram, in the study of the reaction of 3-phenyl-2-butanol with thionyl chloride, makes the plausible postulate that the reaction begins like a typical S_N1 reaction, with the formation of an ion-pair. However, in the case of a chlorosulfite the anion formed is SO_2Cl^- which may rapidly decompose to sulfur dioxide and a chloride ion. Recombination of the ion-pair then gives the chloride with the same configuration as the original alcohol (Scheme 3).



SCHEME 3

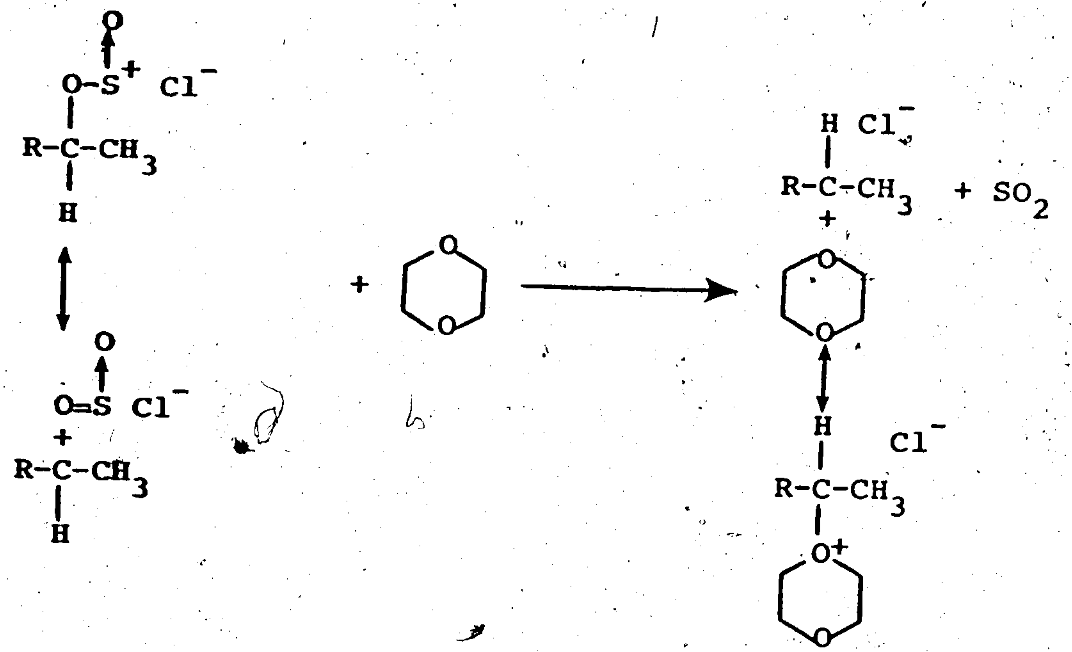
Thus, Cram demonstrated that for the reaction of thionyl chloride with 3-phenyl-2-butanol the classical S_Ni reaction proceeds by a multi-stage mechanism in which open ion-pairs intervene as discrete intermediates between the starting alcohol and the chloride product. The decomposition of chlorosulfite via the process illustrated by Scheme 3, which leads to retention of configuration, should be promoted by the strongly ionizing character of dioxane, the solvent employed in Cram's study.

Lewis and Boozer (8b) carried out a study of the reaction of alcohols with thionyl chloride to demonstrate further the strong influence of solvent upon the stereochemical course of the reaction. Until their investigation, no chlorosulfites had been prepared of any of the alcohols which gave retention of configuration of the products upon reaction with thionyl chloride (8a). The decompositions of the active chlorosulfites of 2-butyl, 2-pentyl, and 2-octyl alcohols were studied in various solvents. It was found that in dioxane there was complete retention and in toluene complete inversion. Tetrahydrofuran, dioxolane, ethylene chloride, and ethylene bromide gave in this order decreasing degrees of retention of configuration. For the reaction leading to retention of configuration the following three-step process was suggested. The first step is ionization of the chlorine-sulfur bond and consequent weakening of the carbon-oxygen bond.



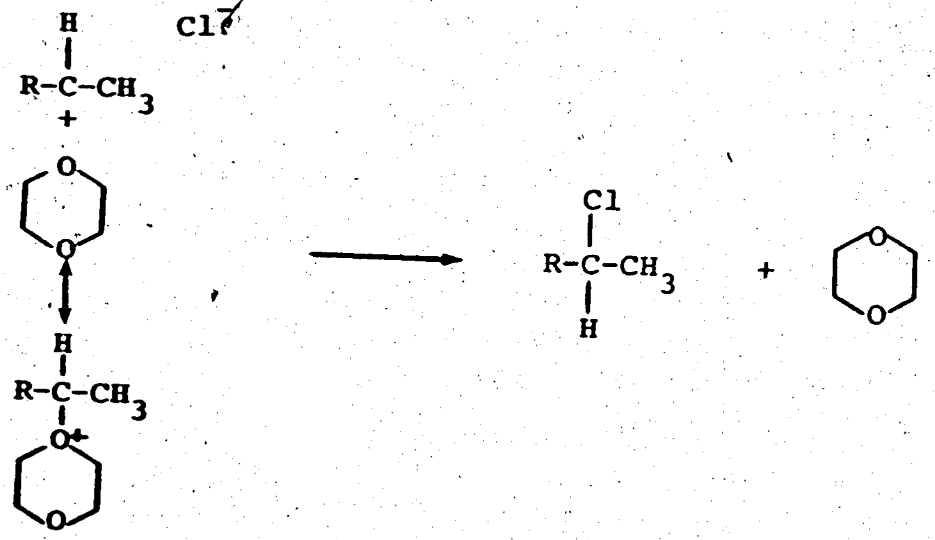
(1)

The second step is the solvation of the incipient carbonium ion by the solvent, in this example dioxane, and loss of sulfur dioxide.


(2)

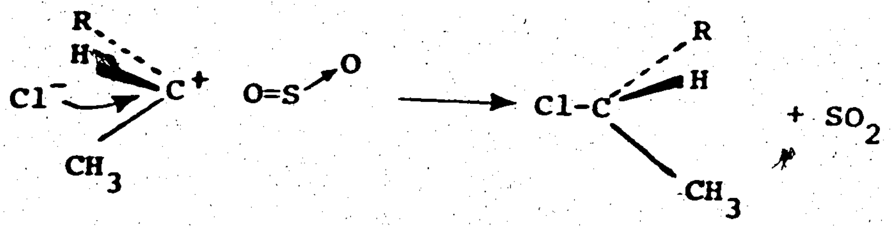
Lewis and Boozer postulated that these carbonium ions, in many respects carbonium ions "solvated" with sulfur dioxide or with dioxane, do not necessarily result in racemization because the solvation can maintain the asymmetry which was initially present in the chlorosulfite.

The final step of the mechanism is the carbonium-ion-pair collapse to yield the alkyl halide. It is plausible


(3)

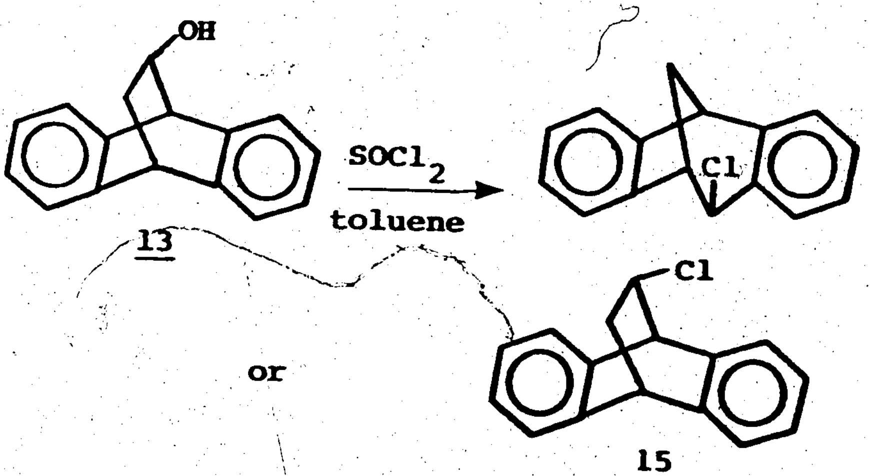
to postulate in the above mechanism that the chlorine becomes attached to the carbon on the same side from which sulfur dioxide has left; on the side opposite to, that at which the dioxane molecule had been associated. This then serves to rationalize the retention of configuration in the reaction performed in dioxane as solvent.

Accordingly, Lewis and Boozer proposed that in toluene a different mechanism must be operative. The reversible reaction in the first step (1) can, however, still occur in toluene. The second step of the above mechanism for dioxane cannot take place in toluene since toluene is neither nucleophilic nor a good solvating agent for carbonium ions. Thus, the loss of sulfur dioxide from the carbonium ion cannot take place and attack of the chloride ion on that side opposite to the sulfur dioxide takes place. A slower ionization reaction may explain the retardation of the second step in the reaction in toluene. The reaction analogous to an S_N2 reaction, could now take place to yield the inverted chloride.



The evidence presented thus far has provided support for the ionic nature of the transition state in the decomposition of alkyl chlorosulfites. Indeed, ion-pairs can be formed as discrete intermediates in the decomposition of the chlorosulfites.

The reaction of thionyl chloride with alcohols, in which the generation of cationic centers led to skeletal rearrangement, provided good evidence for this [illegible]thesis (15). The first evidence of skeletal rearrangement in the reaction of bicyclic alcohols with thionyl chloride was provided by Cristol and Tanner (16). The reaction of dibenzobicyclo[2.2.2]octadien-2-ol (13) with thionyl chloride in toluene led to the isolation of 49% of the skeletally rearranged 4-exo-[3.2.1]chloride, 14. This reaction which was used synthetically for the preparation of 14, gave inconsistent results, since under similar reaction conditions numerous repetitions of the reaction led to unrearranged chloride, 15, in quantitative yields (17). It was believed that the reaction leading to [2.2.2]chloride



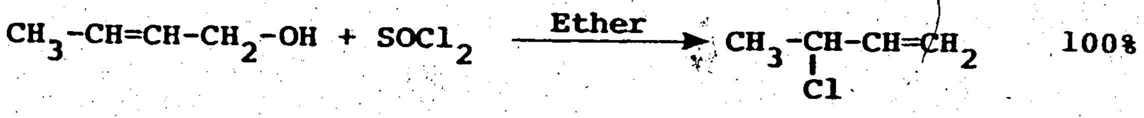
13

14

15

occurred by a scheme which did not involve the formation of the [2.2.2] cation (18) and the possibility existed that its formation could be accounted for by the S_N2 displacement of Cl^- on the alkyl chlorosulfite, or by the postulated S_Ni reaction.

The formation of the rearranged chloride, *14*, could not have occurred if the classical S_Ni mechanism, as proposed by Hughes and Ingold (4) were operating. However, the possibility existed that the *exo*-4-[3.2.1] chloride, *14*, could have come about by an S_Ni' reaction. Such a reaction was used to explain the rearrangement reaction found when 2-buten-1-ol or 3-buten-2-ol were allowed to react with thionyl chloride in ether (19):



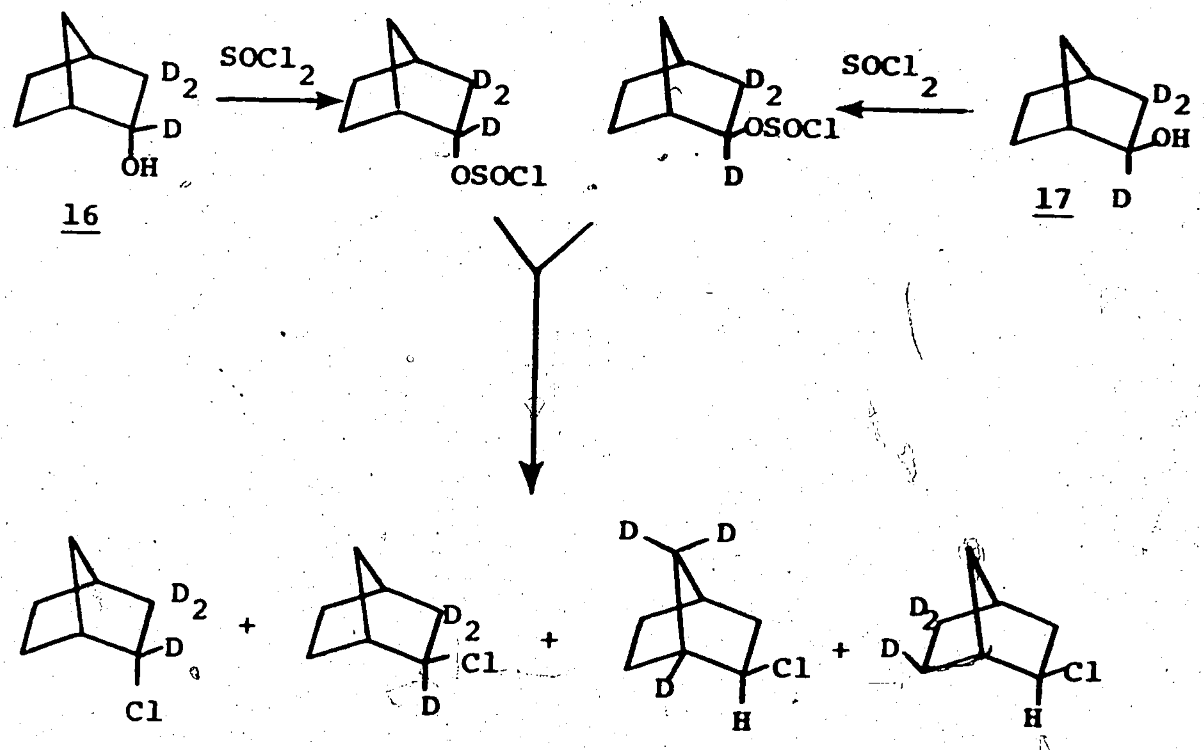
$$CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}OH + SOCl_2 \xrightarrow{\text{Ether}} CH_3\text{-}\underset{Cl}{CH}\text{-}CH{=}CH_2 \quad 100\%$$

$$CH_3\text{-}\underset{OH}{CH}\text{-}CH{=}CH_2 + SOCl_2 \xrightarrow{\text{Ether}} CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}Cl \quad 100\%$$

This rationalization was attractive since the [3.2.1] cation gives *exo* and *endo* products. However, in this reaction only *exo*-[3.2.1] chloride, *14*, was reported.

At the start of the investigation, Stille and Sonnenberg (11) demonstrated skeletal rearrangement in the reaction of bicyclo[2.2.1] heptanols with thionyl chloride. Treatment of *endo*-2-norborneol-2,3,3-*d*$_3$ (*16*) or *exo*-2-norborneol-2,3,3-*d*$_3$ (*17*) led to skeletally transformed chlorides *via* a 6,2-hydride shift and a Wagner-

Meerwein rearrangement. This is illustrated in Scheme 4.



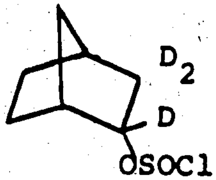
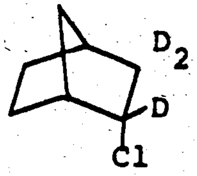
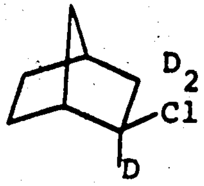
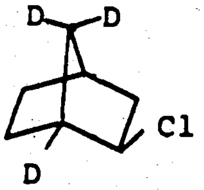
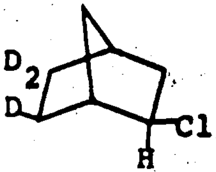
SCHEME 4

The yields of the products arising from the reaction of the two bicyclo[2.2.1]heptanols, 16 and 17, under various reaction conditions, are summarized in Table 1.

It can be deduced from the results of Stille and Sonnenberg, that the reaction of alcohol with thionyl chloride involves cationic intermediates. They observed skeletal rearrangement even under those reaction conditions which have been postulated to be most favorable for the $S_N i$ reaction, namely dioxane (5,8a). Another

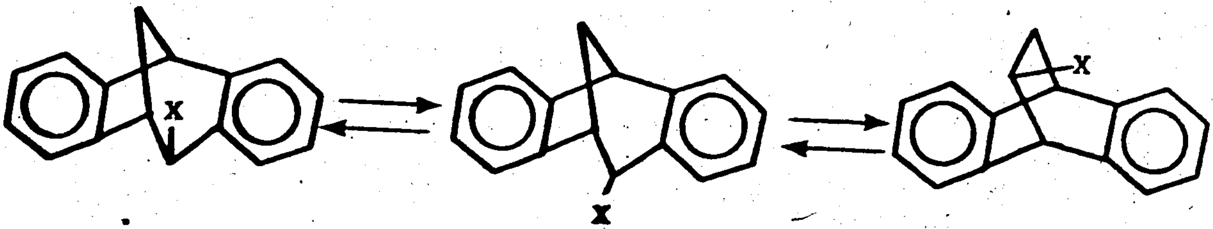
TABLE I

Reactions of endo- and exo-2-Norborneol-2,3,3-d_3 (16 and 17) with Thionyl Chloride

Substrate Alcohol	Reaction Conditions					
16	$SOCl_2/Et_2O$ -20°, 2 hrs	40	<1	2.8	1.3	6.9
	$SOCl_2$/dioxane reflux, 2 hrs	-	<1	15.2	3.4	19.4
	$SOCl_2/Et_2O$ Pyridine reflux, 2 hrs	-	<1	43.3	3.4	10.3
	$SOCl_2$/pyridine reflux, 1 hr	-	<1	42.8	4.8	21.4
17	$SOCl_2$/dioxane reflux, 2 hrs	-	<1	24.4	9.2	12.4
	$SOCl_2/Et_2O$ pyridine reflux 2 hrs	-	<1	32.6	12.2	9.54
	$SOCl_2$/pyridine reflux, 1 hr	-	<1	23.0	4.7	11.3

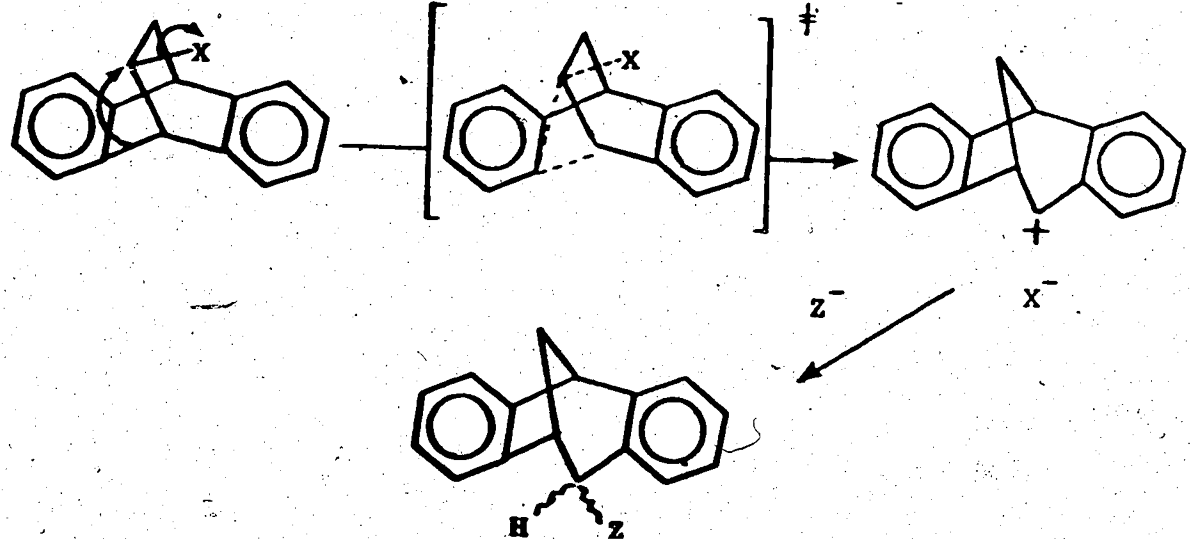
interesting feature which evolves from their study is the observation that skeletal rearrangement occurred when the reaction of alcohol with thionyl chloride was carried out in pyridine as a solvent or catalyst. These are the reaction conditions which have been postulated to be most favorable for the S_N2 mechanism (3,4,8a). On the basis of their results, Stille and Sonnenberg rule out the possibility of the classical S_Ni and S_N2 mechanism. However, the investigation does not shed a great deal of light upon the nature of the stereochemical course of the reaction of alcohols with thionyl chloride, or the solvent dependency of this stereochemistry, since the cationic intermediates which are formed here, can undergo hydride shifts or may lead to non-classical carbonium ions. Thus, a great deal of knowledge about the stereochemical course of the reaction is lost, due to these complications. In addition, the usefulness of the information about the mechanism derivable from this investigation, is diminished in view of the low yields of chloride product obtained (See Table 1).

Distinctive cationic intermediates produced by solvolysis of dibenzobicyclo[2.2.2]octadienyl substrates, 20 invariably led to rearranged exo- and endo-[3.2.1] products, 18, and 19, through kinetic control, and any attempt to generate the [2.2.2] cation under kinetic conditions leads to [3.2.1] product. The [3.2.1] ring system could be converted back to the [2.2.2] ring system under thermodynamic conditions, where it was shown that the usual order of thermodynamic stability is [3.2.1] exo C-2 derivative, 18, < [3.2.1] endo C-2 derivative, 19, < [2.2.2] derivative, 20, (18d).

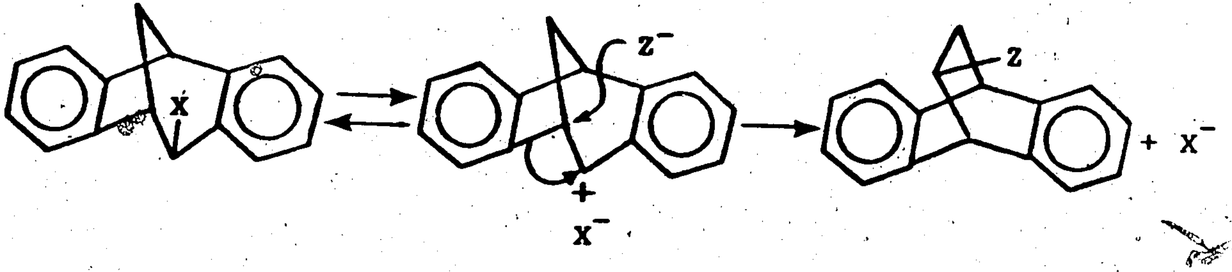


18 19 20

The solvolysis rearrangement reactions demonstrated that the stereochemical outcome corresponded to migration of the bond anti to the leaving group. Thus, from the substituted dibenzobicyclo[2.2.2] octadienyl substrate ionization of the C-X bond is accompanied by anti bond migration to yield a stable benzylic cation:



Under equilibrium conditions, the reverse reaction can occur to yield the product of thermodynamic control:

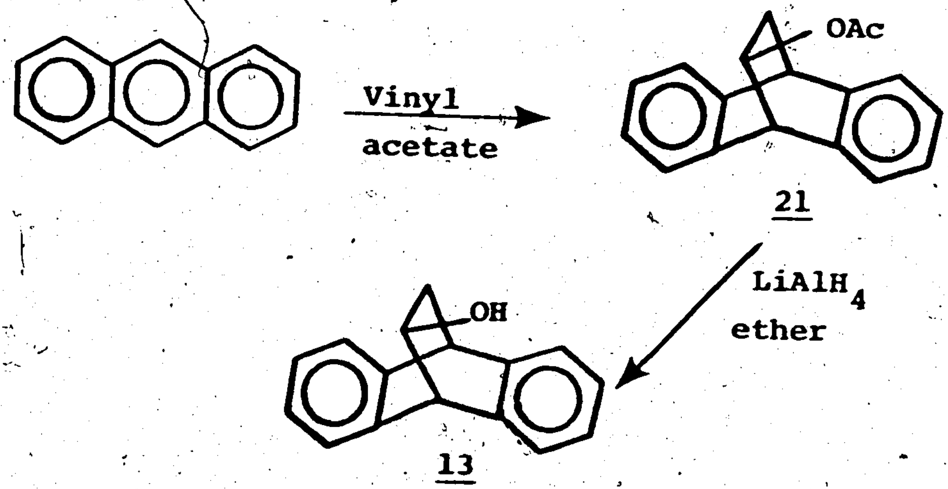


The advantage of employing this system in the study of the decomposition of alkyl chlorosulfite is that the yield of chloride product is quantitative; no olefin by-product is formed, since if the [2.2.2] cation is not present an elimination reaction to yield olefin is not possible. For the dibenzobicyclo[2.2.2] and [3.2.1] octadienyl system, skeletal transformations have been shown to be stereospecific, and the stereochemistry of the reactants and products are known (18d,f,g,20).

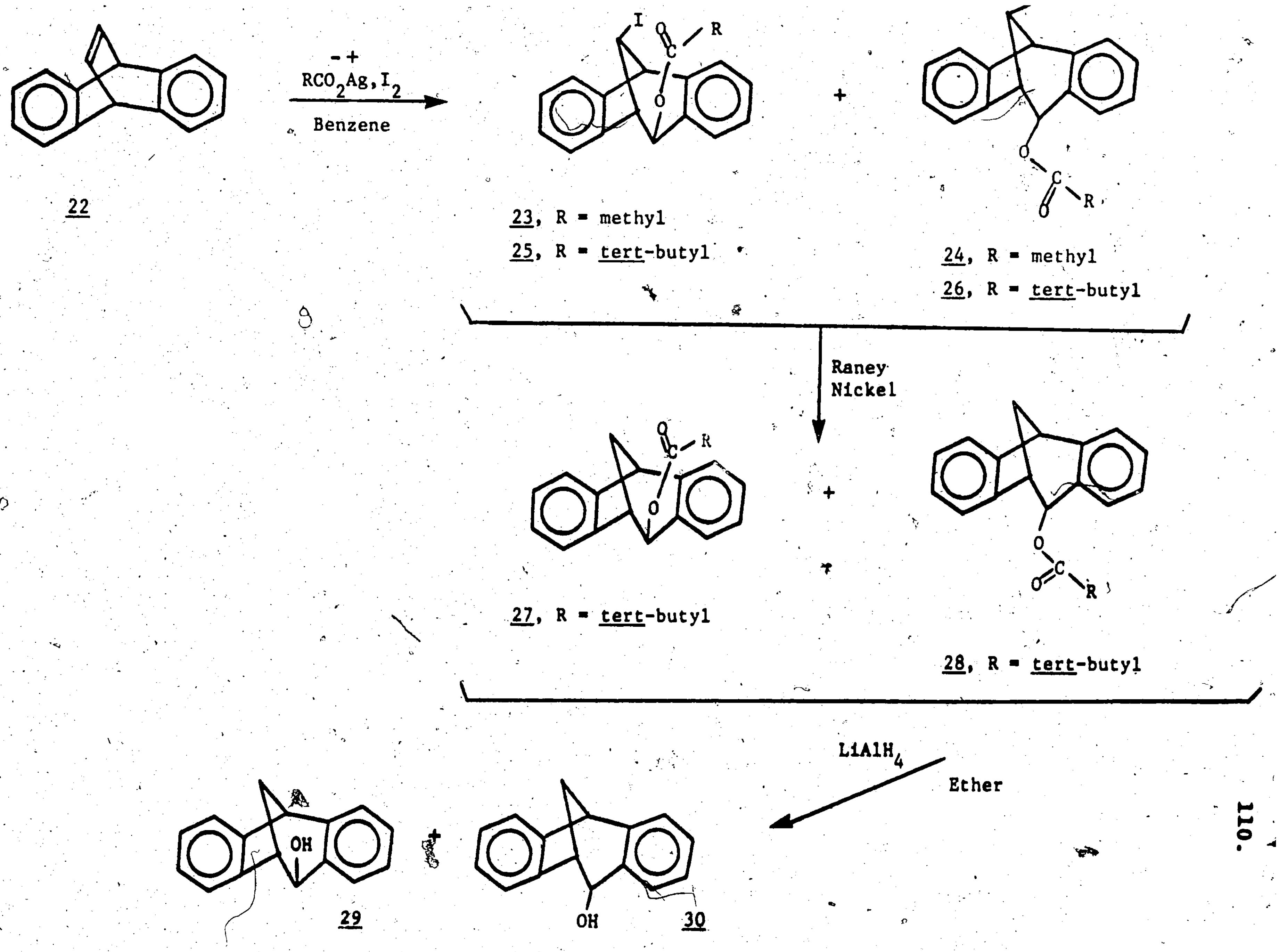
RESULTS

Preparation of Starting Dibenzobicyclic Alcohols

The starting alcohols used in this study were prepared in the following ways as outlined. Dibenzobicyclo[2.2.2]octadien-2-ol, 13, was synthesized by a Diels-Alder reaction of anthracene and vinyl acetate, and the resultant adduct was subsequently reduced with lithium aluminum hydride:

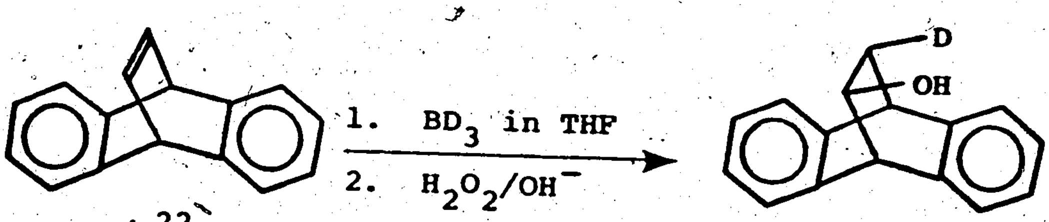


Dibenzobicyclo[2.3.1]octadien-*exo*- and *endo*-2-ol 29 and 30, were synthesized in the following manner: dibenzobicyclo[2.2.2]octatriene (22) was allowed to react with iodine and either silver acetate or silver pivalate in benzene, to yield a 75/25 mixture of *syn*-8-iododibenzobicyclo[3.2.1]octadien-*exo*- and *endo*-2-ol acetate (23 and 24), or a 60/40 mixture of *syn*-8-iododibenzobicyclo[3.2.1]octadien-*exo*- and *endo*-2-ol pivalate (25 and 26). The *exo* and *endo* isomers were


22
$\overset{-\,+}{RCO_2Ag}, I_2$
Benzene
I
R
O
C
O
+
R
C
O
O
23, R = methyl
25, R = tert-butyl
24, R = methyl
26, R = tert-butyl
Raney Nickel
27, R = tert-butyl
+
28, R = tert-butyl
LiAlH$_4$
Ether
OH
29
+
OH
30

separated by column chromatography. Silver pivalate was preferentially employed in the Prevost reaction since the larger tert-butyl group resulted in a higher ratio of endo product. Hydrogenolysis of 25 and 26 led to dibenzobicyclo[3.2.1]octadien-exo- and endo-2-ol pivalate (27 and 28). A lithium aluminum hydride reduction of 27 and 28 gave the desired alcohols, dibenzobicyclo-[3.2.1]octadien-exo- and endo-2-ol (29 and 30).

cis-3-Deuteriodibenzobicyclo[2.2.2]octadien-2-ol (31), was synthesized by means of the deuterioboration with trideuterioborane of dibenzobicyclo[2.2.2]octatriene (22), followed by oxidation with hydrogen peroxide/sodium hydroxide.



22

31

The stereochemistry of the alcohol and the extent of deuteration (>90%), was established by comparing the nmr spectrum of the deuterated alcohol with that of authentic undeuterated alcohol.

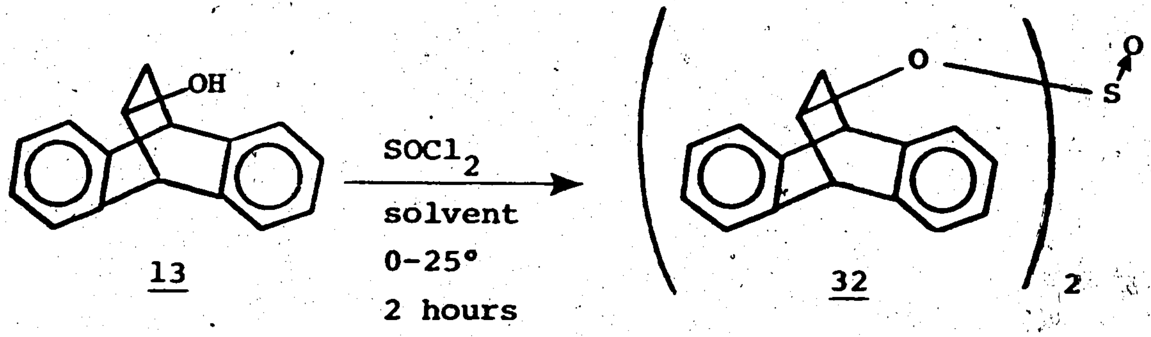
Attempted Preparation of Chlorosulfite Intermediates in the Reaction of Dibenzobicyclic Alcohols with Thionyl Chloride.

In an attempt to prepare the chlorosulfite of dibenzobicyclo[2.2.2]octadien-2-ol (13), the alcohol was allowed to react with thionyl chloride under various reaction conditions. The reactions did not yield a chlorosulfite, but gave instead bis-dibenzobicyclo[2.2.2]octadien-2-yl sulfite (32), in good yield under the following reaction conditions:

(a) Dioxane, 0-25°, 4 hours, 100%

(b) Toluene, 0-25°, 2 hours, 88%

(c) Toluene, equimolar amount of pyridine, 0-25°, 2 hours, 63%

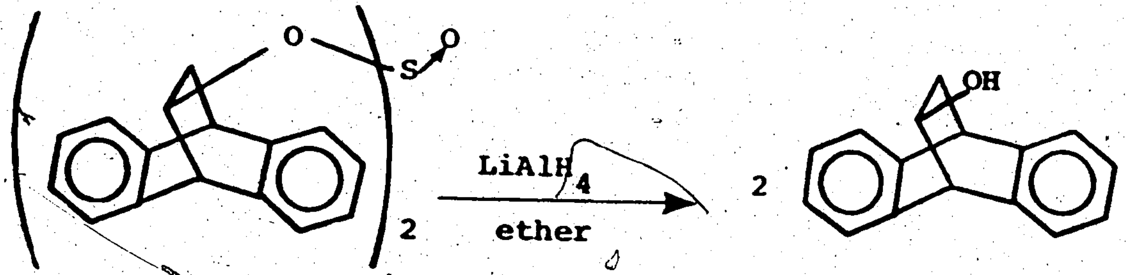


Under similar reaction conditions, the reaction of the [2.2.2] alcohol, 13, with excess thionyl chloride in diethyl ether led to 38% dialkyl sulfite, 32, 46% of exo-4-chlorodibenzobicyclo[3.2.1]octadiene (14) and 15% of endo-4-chlorodibenzobicyclo[3.2.1]octadiene (33). Similarly, when the [2.2.2] alcohol, 13, was allowed to react with neat thionyl chloride, under the same reaction conditions, only 11% yield of the dialkyl sulfite, 32, was realized, the major products being [3.2.1] chloride;

84% of exo-[3.2.1] chloride, 14, formed, and 5% of endo-[3.2.1] chloride, 33.

An attempted synthesis of chlorosulfite or dialkyl sulfite from the reaction of exo-[3.2.1] alcohol, 29, with thionyl chloride in toluene under the reaction conditions described above was unsuccessful; only chloride product was formed under these reaction conditions. In dioxane the reaction of exo-[3,2.1] alcohol, 29, with thionyl chloride at 0-25°, for 2 hours, gave rise to 21% of exo-4-chlorodibenzobicyclo[3.2.1]octadiene (14), 6% of endo-4-chlorodibenzobicyclo[3.2.1]octadiene (33) and 73% of the unreacted alcohol, dibenzobicyclo[3.2.1]-octadien-exo-2-ol (29). When the same alcohol was allowed to react with thionyl chloride in diethyl ether under similar reaction conditions, only chloride product was obtained: exo-[3.2.1] chloride, 14, 89% and endo-[3.2.1] chloride, 33, 11%.

A lithium aluminum hydride reduction of bis-dibenzobicyclo[2.2.2]octadien-2-yl sulfite (32), led to a quantitative amount of dibenzobicyclo[2.2.2]octadien-2-ol.



32

13

Similarly, an attempted column chromatography purification (Woelm neutral alumina, chloroform) resulted in the hydrolysis of the sulfite to the [2.2.2] alcohol, 13.

The dialkyl sulfite, 32, was stable to heating in refluxing toluene. Furthermore, no decomposition of the dialkyl sulfite occurred when it was heated in toluene in the presence of hydrogen chloride. However, when the dialkyl sulfite, 32, was allowed to stir in neat thionyl chloride for 2 hours at 0-25°, a reaction of thionyl chloride with the dialkyl sulfite was observed to yield a mixture of *exo*-[3.2.1] chloride, 14, 40%, *endo*-[3.2.1] chloride, 33, 10% and unreacted *bis*-dibenzobicyclo[2.2.2]-octadien-2-yl sulfite (32), 50%. When this reaction mixture was heated in neat thionyl chloride at refluxing temperatures for 0.5 hours, it gave rise to 54% of *exo*-[3.2.1] chloride, 14, 13% of *endo*-[3.2.1] chloride, 33, and 33% of dialkyl sulfite, 32.

Reaction of Dibenzobicyclic Alcohols with Excess Thionyl Chloride in Toluene

The three alcohols, 13, 29, and 30 were allowed to react with thionyl chloride in toluene. A mixture of an alcohol and thionyl chloride in toluene was stirred for 12 hours at 25° and heated at reflux for 1.5 hours. The volatile compounds were removed by distillation, and the residue was analyzed by nmr to ascertain the reaction products, and the distribution of those products. The error in this method of analysis was shown to be less than 5%. The [2.2.2] chloride, 15, could be isolated by column chromatography. However, the [3.2.1] chlorides frequently hydrolyzed to the corresponding alcohols on the chromatography column. Generally, conversion to chloride products was quantitative. Three chlorides, 7-chlorodibenzobicyclo[2.2.2]-octadiene (15), *exo*-4-chlorodibenzobicyclo[3.2.1] octadiene (14) and *endo*-4-chlorodibenzobicyclo[3.2.1]octadiene (33), were formed from the reaction of the three alcohols, 13, 29 and 30. The major product from each of the alcohols was the [2.2.2] chloride, 15. The *exo*/*endo* ratio of the [3.2.1] chlorides which formed in the reaction, was 3:1. The results of these reactions are summarized in Table 2.

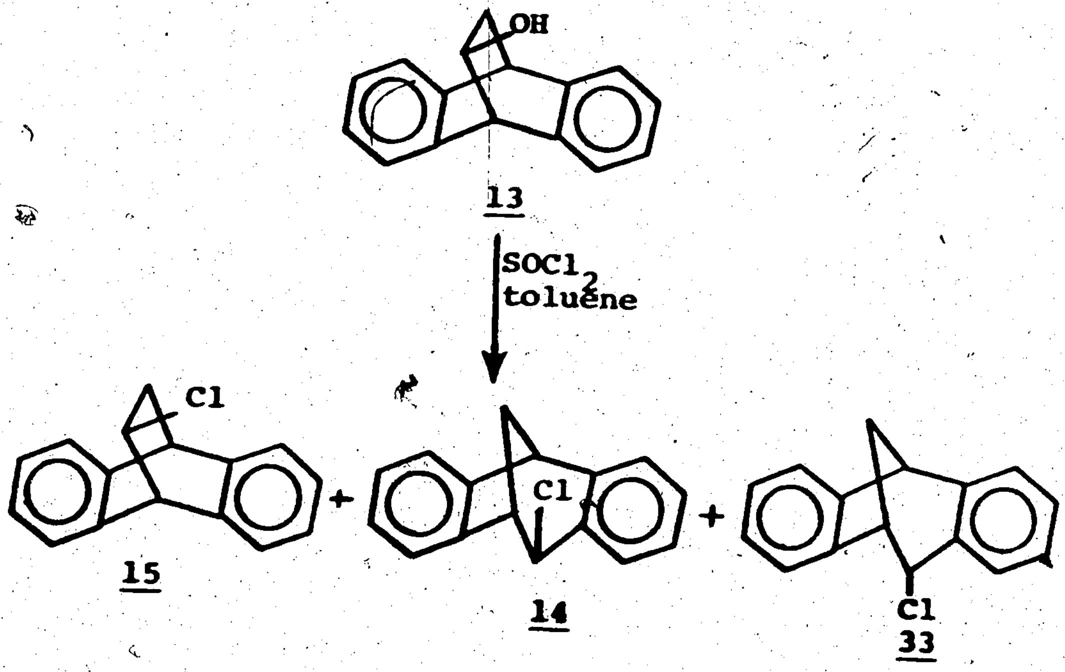
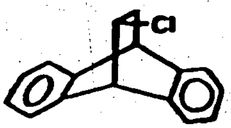
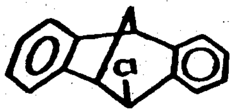
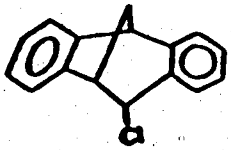
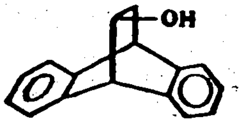
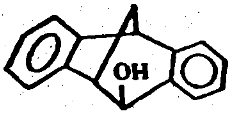
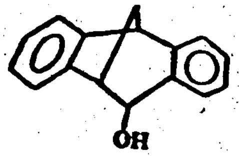


TABLE 2

Reaction of Dibenzobicyclo[2.2.2] and [3.2.1]octadienyl Alcohols with a 10 Molar Excess of Thionyl Chloride, in Toluene

Substrate	Product Distribution %[a,b]		
			
	88 ± 6	9 ± 4	3 ± 2
	74 ± 6	19 ± 4	7 ± 3
	79 ± 14	15 ± 10	6 ± 3

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[a] Percentages determined by nmr integration ratios of characteristic protons of each chloride

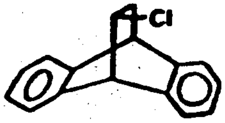
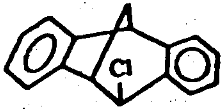
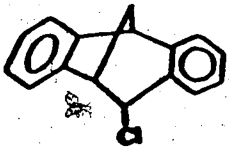
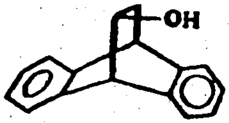
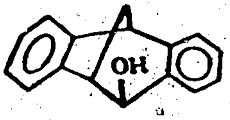
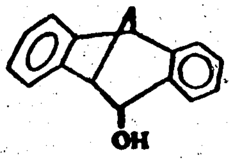
[b] The percentages stated represent a mean of several runs.

Reaction of Dibenzobicyclic Alchols with Excess Thionyl Chloride in Dioxane

The three alcohols, 13, 29 and 30 were allowed to react with thionyl chloride in dioxane. The procedure for these reactions was essentially the same as that for the reaction in toluene. Conversion of alcohol to chloride was nearly quantitative, and the reaction mixture was analyzed in the same manner as the mixture of the products from the reactions carried out in toluene. The chloride product distribution changed considerably in dioxane, giving exo- and endo-[3.2.1] chlorides, 14 and 33, as the major products. For the reaction of both exo- and endo-[3.2.1] alcohols, 29 and 30, with thionyl chloride under these reaction conditions, no detectable amount of [2.2.2] chloride was observed. However, for all the reactions carried out with alcohol 13, some [2.2.2] chloride was formed. In the case of the [2.2.2] alcohol, 13, with thionyl chloride in dioxane, the ratio of exo/endo-[3.2.1] chloride was found to 4.2:1; from exo-[3.2.1] alcohol, 29, the ratio was 3:1 and from endo-[3.2.1] alcohol, 30, the ratio was 2:1. The results of the reaction of these three alcohols with thionyl chloride in dioxane are outlined in Table 3.

TABLE 3

Reaction of Dibenzobicyclo[2.2.2] and [3.2.1]octadienyl Alcohols with a 10 Molar Excess of Thionyl Chloride, in Dioxane

Substrate	Product Distribution % [a,b,c]		
			
	16 ± 11	68 ± 9	16 ± 3
	—	73	27
	—	67	33

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[a] Percentages determined by nmr integration ratios of characteristic protons of each chloride.

[b] The percentages stated for the [2.2.2] alcohol represent a mean of multiple runs.

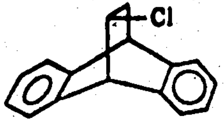
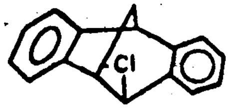
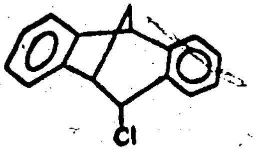
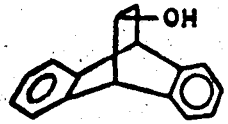
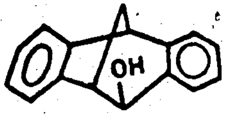
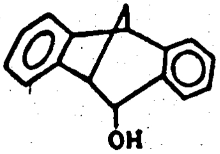
[c] Duplicate experiments were carried out with the [3.2.1] bicyclic alcohols and the product ratios, as determined by nmr, were the same within the limits of experimental error.

Reaction of Dibenzobicyclic Alcohols with Excess Thionyl Chloride in Toluene and a Molar Amount of Added Amine Base

It was believed that the difference in the product distribution for the reaction in toluene and dioxane may be related to the presence or absence of the hydrogen chloride formed during the reaction of alcohol with thionyl chloride. To test this hypothesis, the reaction of the three alcohols 13, 29 and 30, with thionyl chloride, was carried out with molar amounts of added organic amines. Three amine bases were employed for this purpose: pyridine, Huenig's Base (N,N-diisopropylethylamine), and Proton Sponge (1,8-bis(dimethylamino) naphthalene). The latter two bases have been shown to possess extremely poor nucleophilic character (21). However, they are excellent bases for reaction with hydrogen chloride (21). The reactions with molar amounts of added amine were carried out in the same manner as the reactions in toluene, and the products were analyzed as previously outlined. Under these reaction conditions it was found that from all of the three alcohols, the [3.2.1] chlorides formed exclusively. The ratio of exo/endo-[3.2.1] chloride was 4:1 in all cases except for the reaction of endo-[3.2.1] alcohol, 30, with thionyl chloride in pyridine, for which case the exo/endo ratio was 3:1. The results of these reactions are summarized in Table 4.

TABLE 4

Reaction of Dibenzobicyclo[2.2.2] and [3.2.1]octadienyl Alcohols with a 10 Molar Excess of Thionyl Chloride and an Equimolar Amount of Added Amine Base, in Toluene

Substrate	Base	Product Distribution % [a,b]		
				
	Pyridine	—	81	19
	Huenig's Base		80	20
	Proton Sponge	—	80	20
	Pyridine	—	83	17
	Proton Sponge	—	83	17
	Pyridine	—	76	24
	Proton Sponge	—	80	20

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[a] Percentage determined by nmr integration ratios of characteristic protons of each chloride.

[b] Duplicate runs of each reaction were made and they were the same within the limits of experimental error.

Reaction of Dibenzobicyclic Alcohols with (a) Neat Thionyl Chloride with Added Water (0.0024 mole), (b) Neat Thionyl Chloride and a Molar Amount of Added Base, and (c) Neat Thionyl Chloride.

For the reaction with neat thionyl chloride and 0.0024 moles of added water, it was found that appreciable amounts of [2.2.2] chloride, 15, had formed from all of the three alcohols 13, 29 and 30. The reaction of the three alcohols in neat thionyl chloride with added amine base, gave exclusively [3.2.1] chloride product. When the alcohols were allowed to react in neat thionyl chloride virtually quantitative amounts of [3.2.1] chlorides were observed (0-5% [2.2.2] chloride, 15). The results of these reactions are summarized in Table 5.

Reaction of *cis*-3-Deuteriodibenzobicyclo[2.2.2]octadien-2-ol (31), with Thionyl Chloride in Toluene, Thionyl Chloride in Dioxane and Neat Thionyl Chloride.

The stereochemistry of the [2.2.2] - [3.2.1] rearrangement was investigated by carrying out the reaction of *cis*-3-deuteriodibenzobicyclo[2.2.2]octadien-2-ol (31) with thionyl chloride. When the deuterium-labelled alcohol was allowed to react with thionyl chloride in toluene, the major product was the unrearranged [2.2.2] chloride, 34. Similarly, as was the

TABLE 5

Reaction of Dibenzobicyclo[2.2.2] and [3.2.1]octadienyl Alcohols with Neat Thionyl Chloride, Thionyl Chloride with Added Water (0.0024 Mole) and Thionyl Chloride with Molar Amount of Amine Added

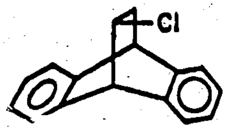
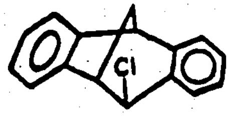
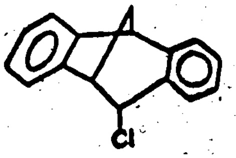
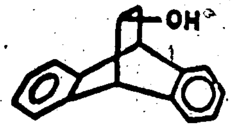
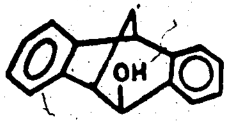
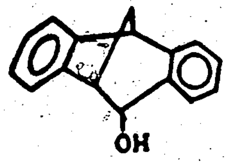
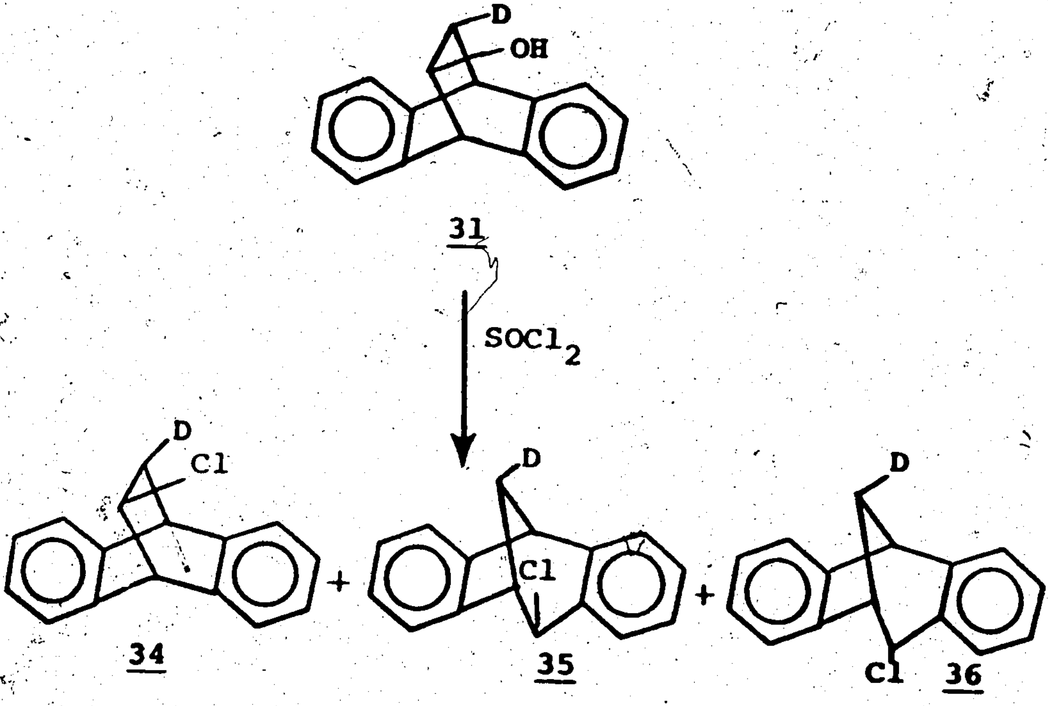
Substrate	Reaction Condition	Product Distribution % [a,b]		
				
	Neat Thionyl Chloride [b]	5	73	22
	Added Water	30	50	20
	Added Pyridine	--	90	10
	Added Huenig's Base	--	82	18
	Added Proton Sponge	--	87	13
	Neat Thionyl Chloride	2	66	32
	Added Water	26	53	21
	Added Pyridine	--	85	15
	Added Proton Sponge	--	90	10
	Neat Thionyl Chloride	--	83	17
	Added Water	25	64	11
	Added Pyridine	--	78	22
	Added Proton Sponge	--	80	20

TABLE 5 (continued)

[a] Percentages determined by nmr integration ratios of characteristic protons of each chloride.

[b] The percentages stated represent a mean of duplicate runs, except for those reactions of the [3.2.1] alcohols with added water. The values of the % product distribution of each duplicated reaction were the same within the limits of experimental error.

case for the undeuterated alcohol when the reaction with thionyl chloride was carried out in dioxane, the major products were rearranged [3.2.1] chlorides. The reaction of the deuterated alcohol, 31, in neat thionyl chloride gave exclusively [3.2.1] chloride product. As in all other reactions of alcohol with thionyl chloride, the product distributions were determined by nmr analysis. Decoupled spectra (see Discussion p. 144) of the deuterated chlorides, revealed that for the unrearranged chloride the deuterium was placed cis to the chlorine; cis-7-deuteriodibenzobicyclo[2.2.2]-octadiene (34), was formed as the only [2.2.2] chloride. In both the exo- and endo-[3.2.1] chlorides, 35 and 36, the deuterium occupied the syn-8-position. The results of these reactions are summarized in Table 6.

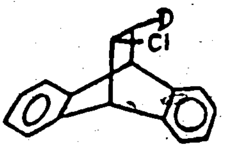
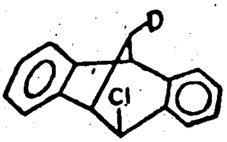
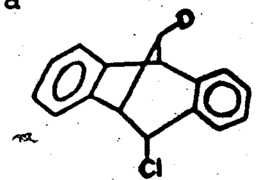
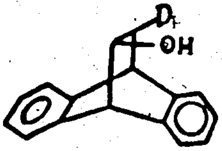


31

34 + 35 + 36

TABLE 6

Reaction of cis-3-Deuteriodibenzobicyclo[2.2.2]octadien-2-ol with a 10 Molar Excess of Thionyl Chloride in both Toluene and Dioxane, and in Neat Thionyl Chloride

Substrate	Reaction Conditions	Product Distribution %[a]		
				
	Thionyl Chloride in Toluene	60	30	10
	Thionyl Chloride in Dioxane	16	68	16
	Neat Thionyl Chloride	+	86	14

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[a] Percentages determined by nmr integration ratios of characteristic protons of each chloride.

Examination of the Stability of the Chlorides 14, 15 and 33 under Various Reaction Conditions.

It was necessary to obtain information about the stability of the various dibenzobicyclic chlorides to the conditions used for the reaction, the isolation and the analysis employed in the investigation of the reaction of the alcohols used. The stability of the [3.2.1] chlorides was examined under those reaction conditions which led to unrearranged [2.2.2] chloride, 15, as the major product, namely the reaction of alcohol with thionyl chloride in toluene. n-Propyl alcohol was allowed to react with thionyl chloride in toluene with an added molar amount of an authentic mixture of exo- and endo-[3.2.1] chlorides. The reaction conditions were the same as those normally employed in the reaction of alcohol with thionyl chloride in toluene. Nmr analysis and quantitative infrared spectroscopy analysis of the reaction mixture revealed that 18-20% rearrangement of the [3.2.1] chloride mixture to [2.2.2] chloride had occurred.

In an attempt to reproduce more closely the reaction conditions in the reaction of the dibenzobicyclic alcohols with thionyl chloride in toluene, it was decided to test the stability of the [3.2.1] chlorides during the reaction of tert-butyl alcohol with thionyl chloride in toluene. However, the results obtained were not consistent. For reactions which were carried out according to the procedure for the reaction of the dibenzobicyclic alcohols with thionyl chloride in toluene, it was found that rearrangement of [3.2.1] chloride to [2.2.2] chloride occurred from 15% to 56%. When dibenzobicyclo[3.2.1]octadien-<u>exo</u>-2-ol, (<u>29</u>) was allowed to react with thionyl chloride in toluene, with a molar amount of a mixture of <u>exo</u>- and <u>endo</u>-[3.2.1] chloride, under the exact reaction conditions employed in the reaction of alcohol with thionyl chloride in toluene, the following product distribution was observed: endo-[3.2.1] chloride, <u>33</u>, 6%; <u>exo</u>-[3.2.1] chloride, <u>14</u>, 18% and 7-chlorodibenzobicyclo[2.2.2]octadiene (<u>15</u>) 76%.

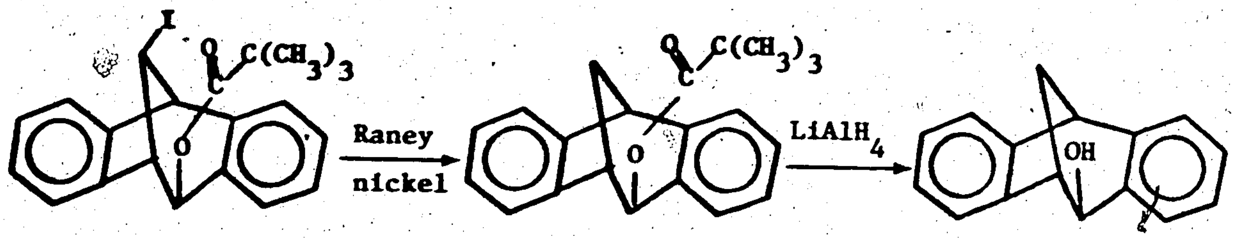
The stability of the [3.2.1] chlorides to the reaction conditions of the reaction of alcohol with thionyl chloride in dioxane was also examined. The reaction of <u>tert</u>-butyl alcohol with thionyl chloride in dioxane and a molar amount of [3.2.1] chlorides, led to quantitative reisolation of unchanged [3.2.1] chlorides. Similarly, 7-chlorodibenzobicyclo[2.2.2]-octadiene was found to be stable to the reaction conditions of the reaction of alcohol with thionyl chloride in dioxane. Both [3.2.1] chlorides and [2.2.2] chloride were found to be stable to the reaction conditions for the reaction of alcohols with neat thionyl chloride.

Reaction of Dibenzobicyclo[3.2.1]octadien-*exo*-2-ol (*29*), and Dibenzobicyclo[2.2.2]octadien-2-ol (*13*) with 50 Mole Percent Thionyl Chloride in Toluene.

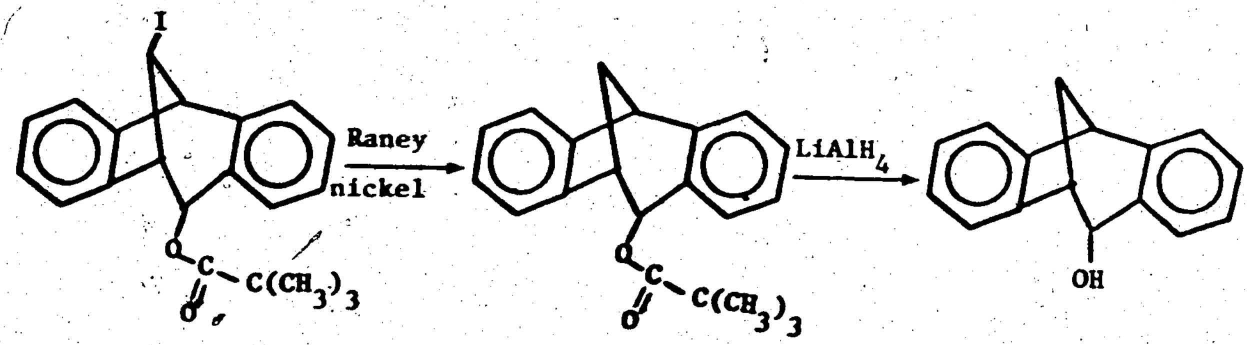
The stability of the alcohols to the reaction conditions which led to unrearranged chloride product was investigated. Both alcohols, *13* and *29*, were allowed to react with 50 mole percent of thionyl chloride in toluene. In each case the reisolated alcohol was the starting alcohol. The nmr spectrum, in carbon tetrachloride, of the crude reaction mixture showed that only the [2.2.2] chloride, *15*, had formed in the reaction of the *exo*-[3.2.1] alcohol, *29*. For the case of the [2.2.2] alcohol, some [3.2.1] chloride product and dialkyl sulfite, *32*, had formed.

DISCUSSION

A study of the reaction of thionyl chloride with various [2.2.2] and [3.2.1] bicyclic alcohols was carried out. Dibenzobicyclo[2.2.2]octadien-2-ol was synthesized according to the method of Alder and Rickert (32), and its structure confirmed by both spectral and chemical means. The assignment of the stereochemistry of cis-3-deuteriodibenzobicyclo[2.2.2]octadien-2-ol was accomplished by comparing its nmr spectrum with that of the undeuterated analog. The assignment of the structure of the [3.2.1] alcohols, 29 and 30 was also accomplished by both chemical and spectral means. Alcohols 29 and 30

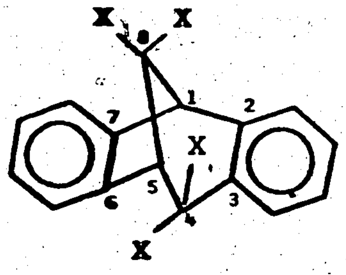


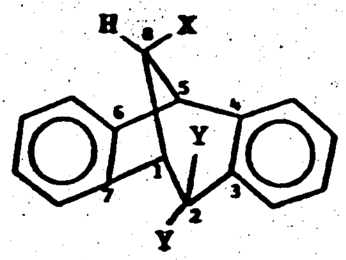
25 27 29



26 28 30

were synthesized by the reduction of <u>25</u> and <u>26</u>. The structure of the [3.2.1] ring system and stereochemistry at C-2 is known since after the reduction reactions, known compounds were isolated. The stereochemistry at the 8 position of <u>25</u> and <u>26</u> was established by comparing the nmr spectra of <u>25</u> and <u>26</u> with those reported for the corresponding iodoacetates, <u>23</u> and <u>24</u> (20,22). Tanner reported the absorption of the <u>anti</u>-8 proton of <u>syn</u>-<u>exo</u>-[3.2.1]iodo acetate, <u>23</u>, at τ 5.16, and of <u>syn</u>-<u>endo</u>-[3.2.1]iodoacetate at τ 5.01. One coupling constant due to the H_8 and H_1 protons was reported: <u>anti</u>-$J_{1,8}$ = 4.4 cps for the <u>exo</u>-[3.2.1]iodoacetate, <u>23</u>, and <u>anti</u>-$J_{1,8}$ = 3.5 cps for the <u>endo</u>-[3.2.1]iodoacetate, <u>24</u>. On the basis of the "Karplus Plot" (23) these coupling constants are consistent with the dihedral angles H_1, <u>anti</u>-H_8 = 45°, H_1, <u>syn</u>-H_8 = 75°, for the 4,8-dichlorodibenzobicyclo[3.2.1]octadienes, predicted by Tanner and Gilman (24).





X = H or halogen

Y = H, acetate, pivalate, OH
X = halogen, H

Dihedral angles:

H_1, <u>anti</u>-H_8 = H_5, <u>anti</u>-H_8 = 45°
H_1, <u>syn</u>-H_8 = H_5, <u>syn</u>-H_8 = 75°

The absorption band for the H_8 proton of the exo-[3.2.1]-iodo pivalate, 25, occurred at τ 5.29 ($J_{1,8}$ = 5 cps), and the absorption band for the H_8 proton of the endo-[3.2.1]iodo pivalate, 26, occurred at τ 5.24 ($J_{1,8}$ = 4.8 cps). These observations were consistent with the anti assignment of the H_8 proton of the [3.2.1]iodo pivalates, 25 and 26. The other distinguishing feature of the nmr spectra of these two compounds is the different spectral frequencies of the acetate groups. By analogy with the reported spectra for these two compounds, the stereochemistry of syn-8-iododibenzobicyclo[3.2.1]octadien-exo- and endo-2-ol pivalate was assigned: exo-H_2, τ 3.82, $J_{1,2}$ = 6.0 cps and endo-H_2, 4.35, $J_{1,2}$ = 1.8 cps.

The reaction of thionyl chloride with alcohols consists of two discrete steps, the formation of the alkyl chlorosulfite, and its decomposition. The intermediacy of the chlorosulfite has been widely confirmed, since it was first postulated by pioneer workers of the reaction of alcohols with thionyl chloride. In some cases the reaction of a molecule of alcohol with the initially formed alkyl chlorosulfite can occur to yield only dialkyl sulfite at an early stage of the reaction:

$$ROH + SOCl_2 \longrightarrow HCl + ROSOCl$$

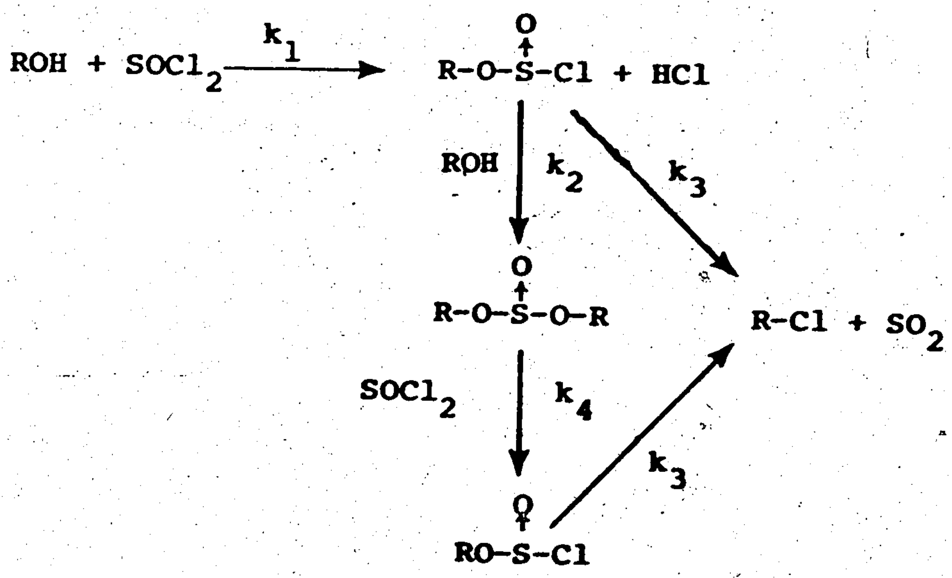
$$ROH + ROSOCl \longrightarrow HCl + (RO)_2SO$$

Subsequently, however, a reaction between dialkyl sulfite and thionyl chloride takes place, eventually producing alkyl chlorosulfite:

$$(RO)_2SO + SOCl_2 \longrightarrow 2ROSOCl$$

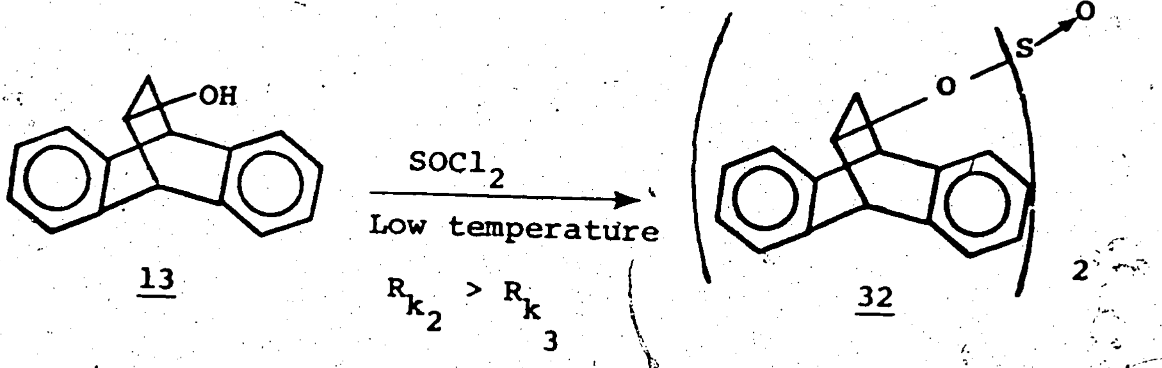
The attempted isolation of an intermediate alkyl chlorosulfite in the reaction of the [2.2.2] alcohol, 13, with thionyl chloride in toluene failed; instead, a quantitative amount of the dialkyl sulfite, 32, was isolated. This sulfite was observed to be stable to heating in refluxing toluene, and refluxing toluene with added hydrogen chloride. Thus, chloride product did not come about by an acid-catalyzed decomposition of the dialkyl sulfite. However, the sulfite did react with thionyl chloride to yield chloride product.

The various routes to the intermediate chlorosulfite can be summarized as in Scheme 5.



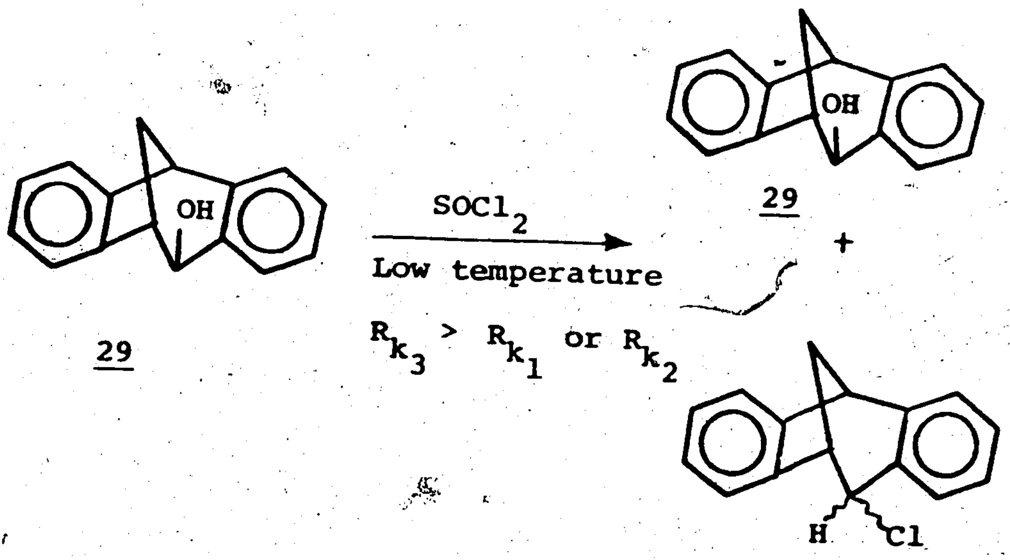
SCHEME 5

At low temperatures (0-25°, 2 hours) good yields of the dialkyl sulfite, 32, could be isolated from the reaction of the [2.2.2] alcohol, 13, with thionyl chloride in various solvents.



For this case, the rate for the process whose rate constant is k_2, R_{k_2}, must be greater than R_{k_3}, and therefore the reaction of another molecule of alcohol with the initially formed alkyl chlorosulfite can occur to form the dialkyl sulfite, 32. Presumably this dialkyl sulfite reacts with thionyl chloride at elevated temperatures to form the [2.2.2] alkyl chlorosulfite, 43, which finally de[illegible] yield alkyl chloride product.

The attempted isolation of dialkyl sulfite or alkyl chlorosulfite from the reaction of exo-[3.2.1] alcohol with thionyl chloride in various solvents at low temperatures (0-25°, 2 hours) was unsuccessful (Table 8). Even under these mild reaction conditions only unreacted exo-[3.2.1] alcohol, 29, and a mixture of [3.2.1] chlorides, 14 and 33 was observed.



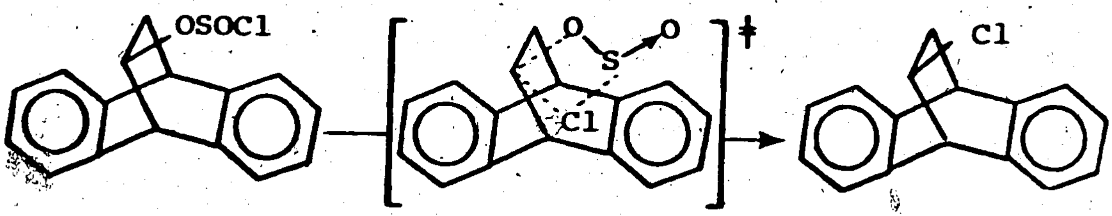
14 and 33

Since only unreacted alcohol and alkyl chloride were formed from the reaction of exo-[3.2.1] alcohol, 29, with thionyl chloride at low temperatures, it can be postulated that in this case $R_{k_3} > R_{k_1}$ or R_{k_2}. The magnitude of R_{k_3} is presumably dependent upon the nature of R. The greater the ability of the R group to stabilize the incipient positive charge during the ionization of the R-O bond, the more facile should be the decomposition of the initially formed alkyl chlorosulfite. It is proposed that due to the increased stability of the benzylic [3.2.1] cation, formed during the ionization of the C-O bond of a [3.2.1] alkyl chlorosulfite, no dialkyl sulfite was realized. For this case R_{k_3} is larger than R_{k_2}. An alkyl chlorosulfite could not be isolated even at low temperatures, presumably due to the facile decomposition of the [3.2.1] alkyl chlorosulfite.

At elevated temperatures no dialkyl sulfite or chlorosulfite was isolated from the reaction of the dibenzobicyclic alcohols with thionyl chloride. Under these reaction conditions the decomposition of the alkyl chlorosulfite predominates, since the decomposition of the alkyl chlorosulfite or the decomposition of the dialkyl sulfite are accelerated.

The mechanism of the reaction of alcohol with thionyl chloride is concerned with the mode of decomposition of the intermediate alkyl chlorosulfite. In the case of the intermediate dibenzobicyclco[2.2.2]octadienyl chlorosulfite, decomposition could occur by at least four mechanistically conceivable processes: S_Ni, S_Ni', S_N2. and S_N1. These mechanisms are depicted in Schemes 6 to 9.

Before any discussion about the relative importance of the above mechanisms can proceed it is necessary to establish the structure and stereochemistry of the various bicyclic chlorides formed in this reaction. The reaction of the three bicyclic alcohols, <u>13</u>, 29 and <u>30</u>, with thionyl chloride under various reaction conditions could conceivably give rise to any of the following <u>mono</u>-chlorides:



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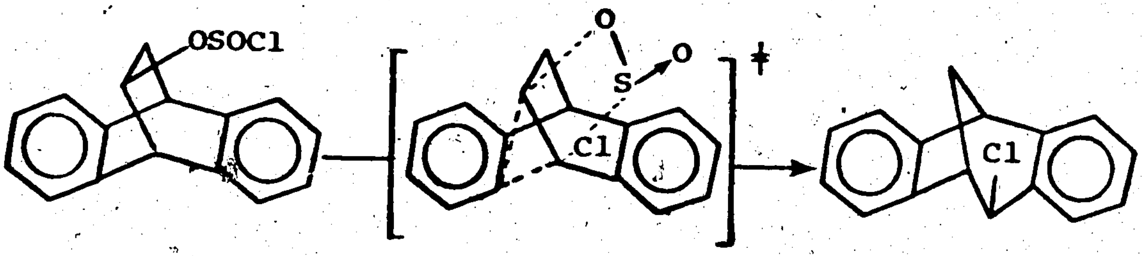
SCHEME 6 (S_Ni Mechanism)

retention



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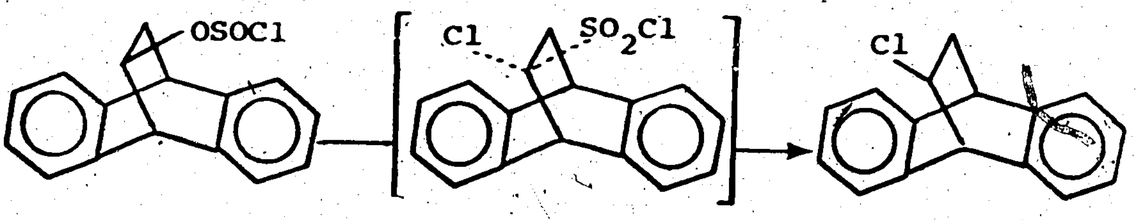
SCHEME 7 (S_Ni′ Mechanism)

rearrangement



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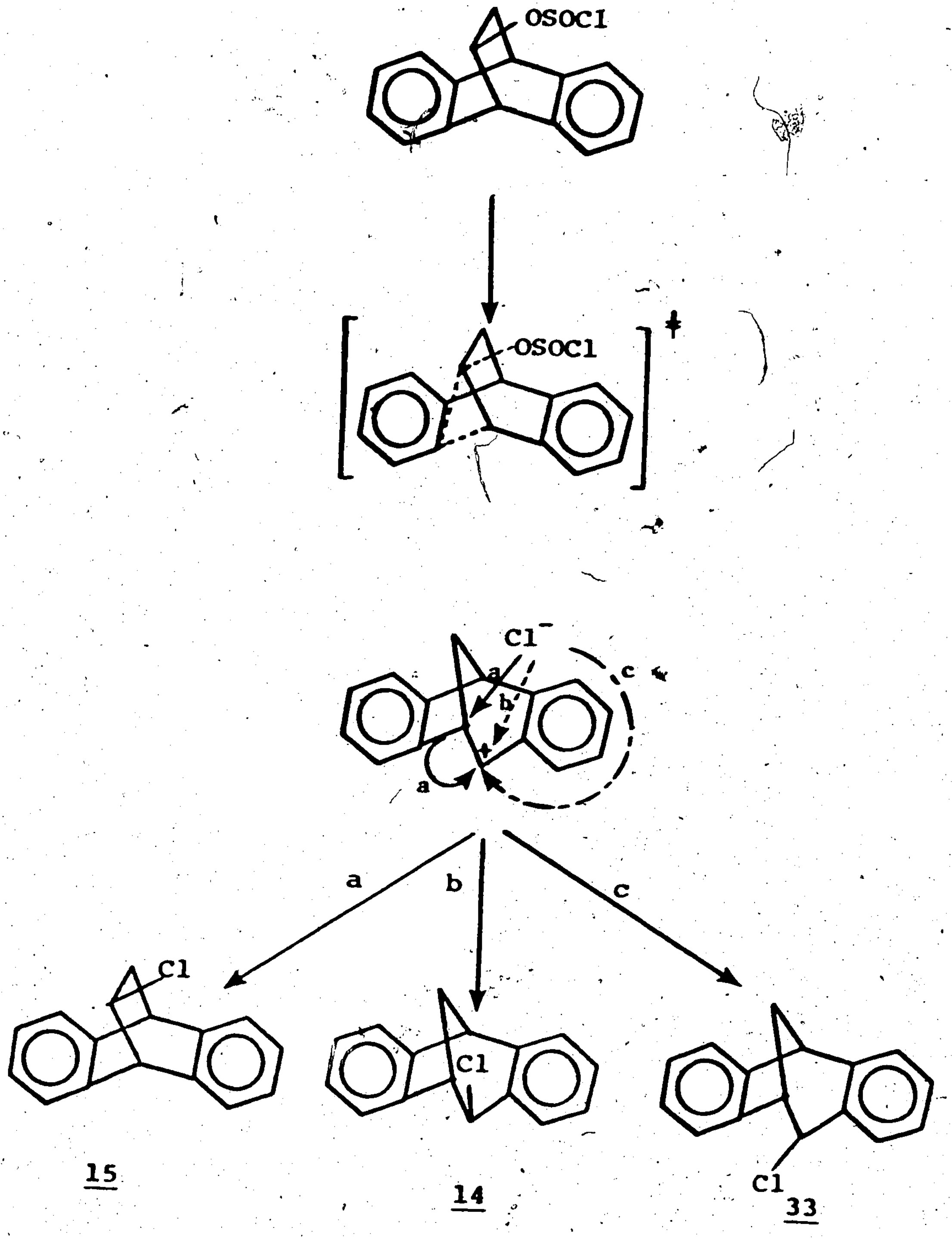
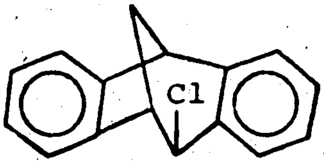
SCHEME 8 (S_N2 Mechanism)

inversion



SCHEME 9 (S_N1 Mechanism)



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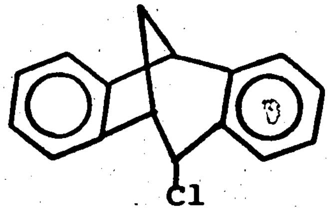

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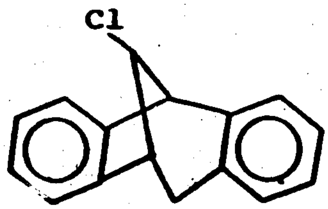

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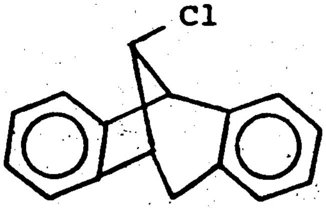

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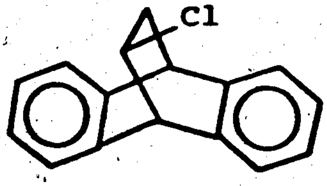

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The nmr spectra of the chlorides 14, 15, 37 and 38 have been reported by Cristol (22,25). The nmr spectrum of a mixture of [3.2.1] chlorides, obtained from the reaction of the three bicyclic alcohols, 13, 29 and 30 with thionyl chloride under the appropriate reaction conditions (see Figures 1-5), showed that two mono-[3.2.1] chlorides were present in the reaction mixture; the sum of the integration of the absorption bands at τ 4.68 and 5.00 was equal to one proton on the basis of one-eighth of the integration of the 8 aromatic protons. The absorption band at τ 5.00 was that of endo-H_4 of exo-[3.2.1] chloride, 14, as reported by Cristol. The chemical shift of the spectral frequencies of the aliphatic protons of 15, 37 and 38 are sufficiently dif-

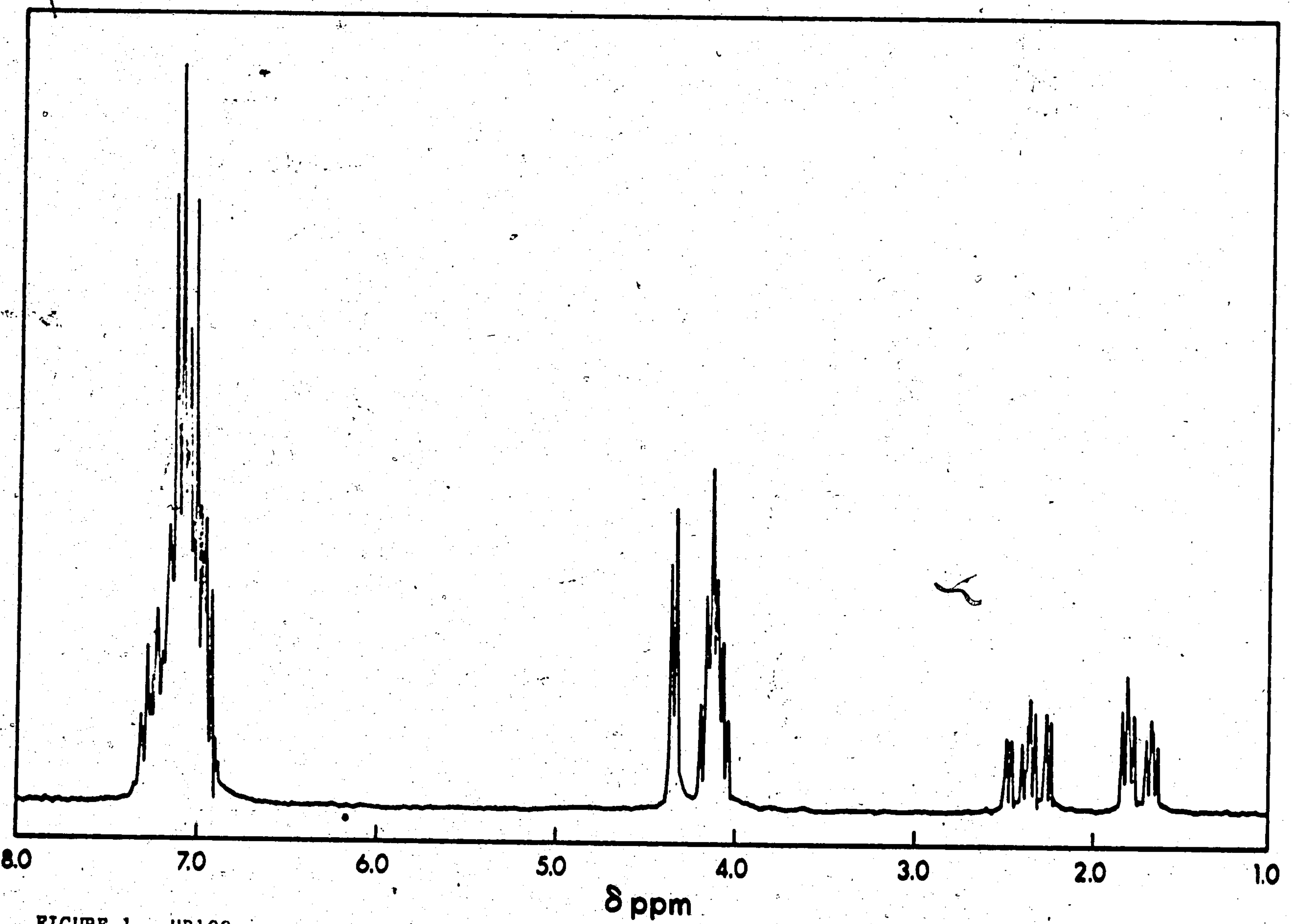


FIGURE 1. HR100 nmr spectrum (CCl_4) of 7-chlorodibenzobicyclo[2.2.2]octadiene.

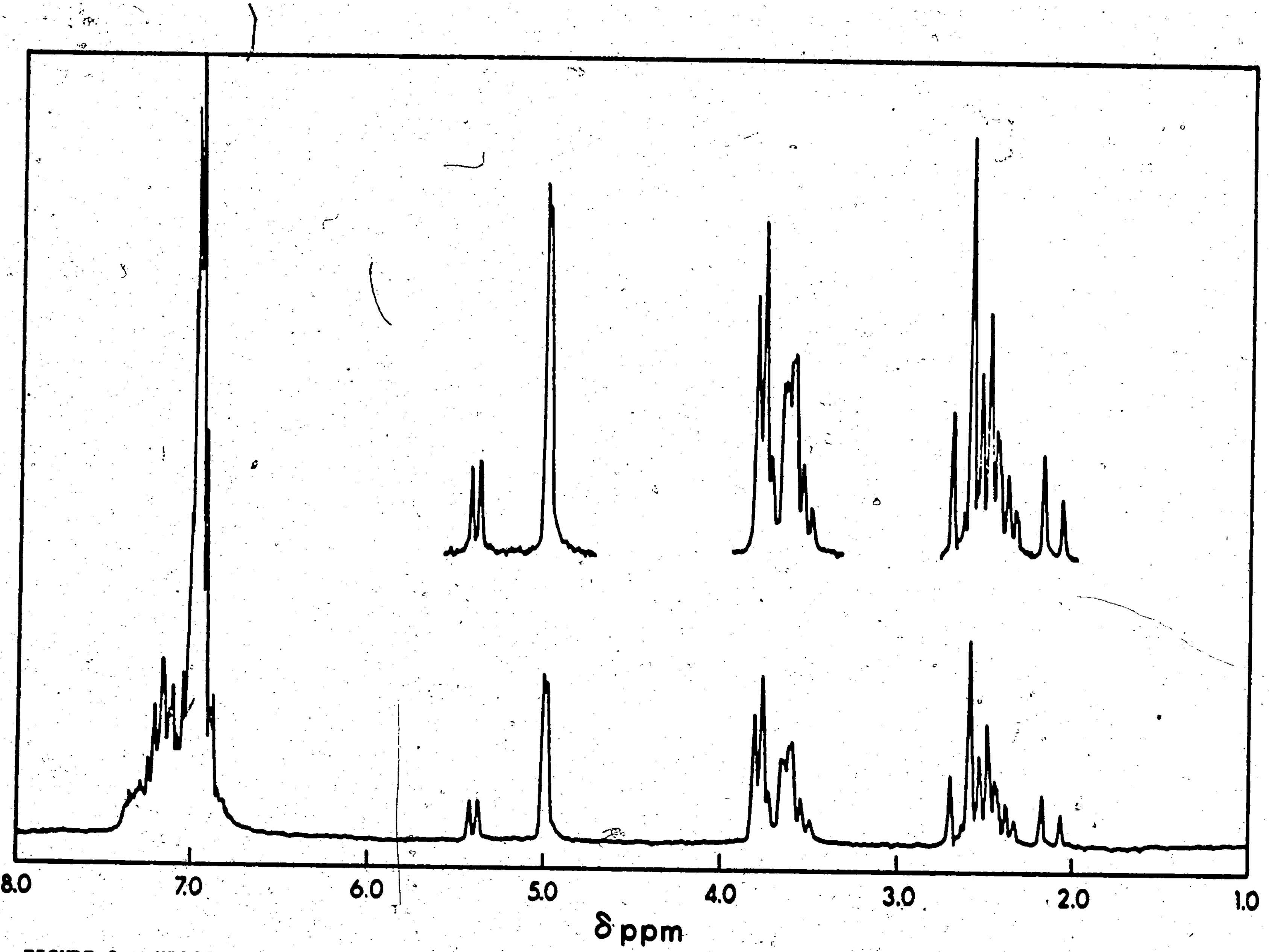


FIGURE 2. HR100 nmr spectrum (CCl_4) of a mixture of exo-and endo-4-chlorodibenzobicyclo[3.2.1]octadiene

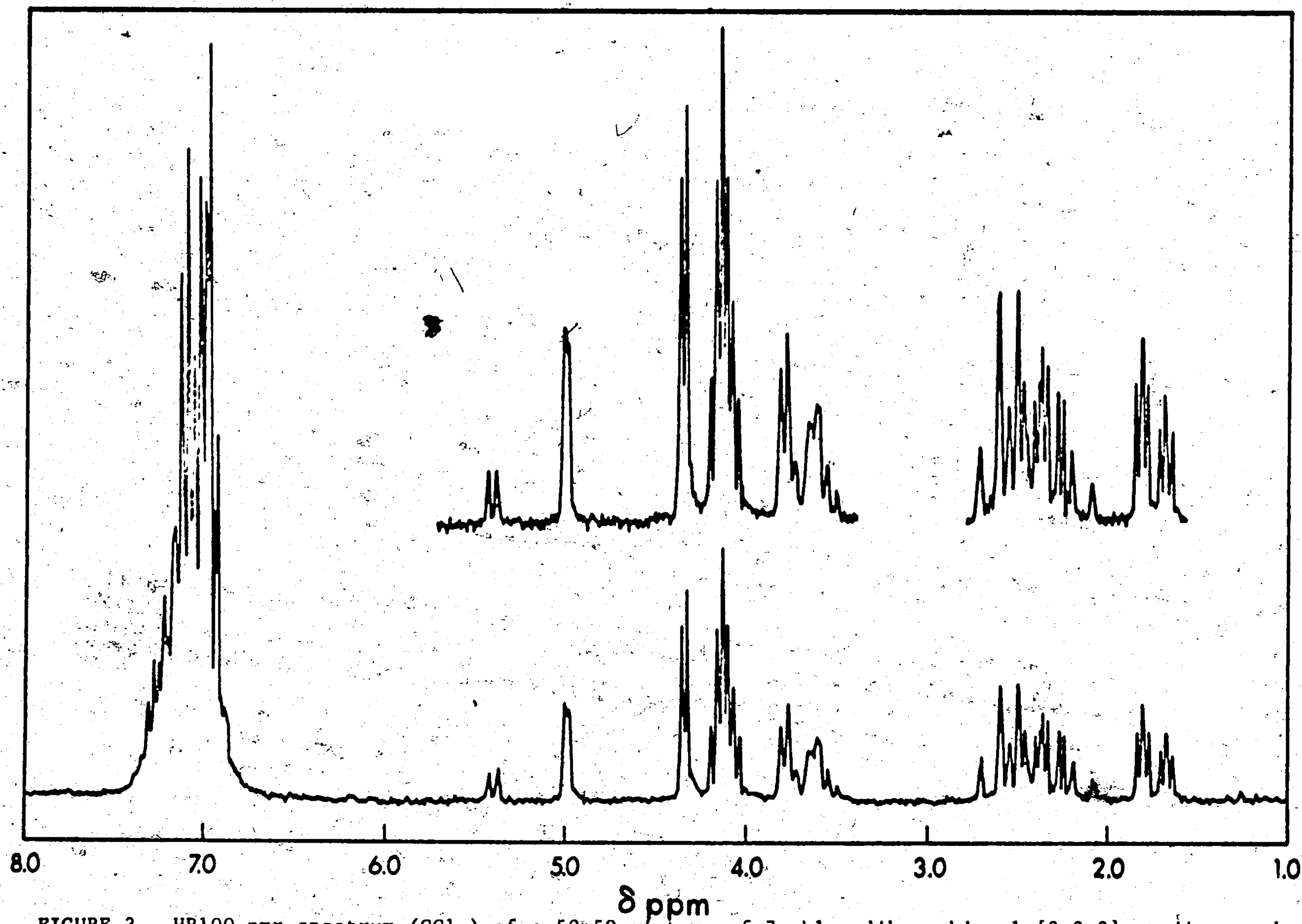


FIGURE 3. HR100 nmr spectrum (CCl_4) of a 50:50 mixture of 7-chlorodibenzobicyclo[2.2.2]octadiene and a mixture of *exo*- and *endo*-4-chlorodibenzobicyclo[3.2.1]octadiene.

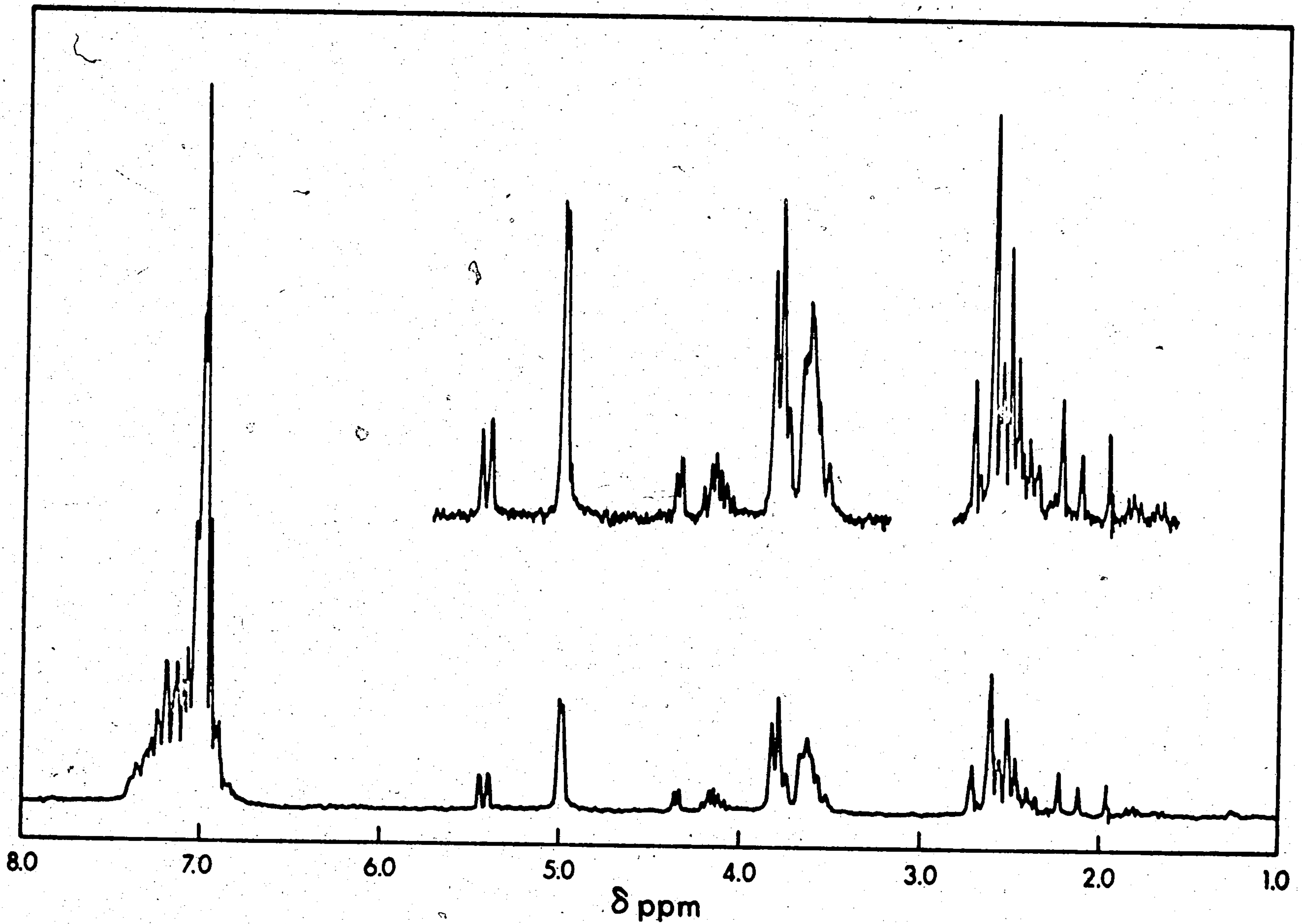


FIGURE 4. HR100 nmr spectrum (CCl_4) of a 95:5 mixture of exo- and endo-4-chlorodibenzobicyclo[3.2.1]-octadiene and 7-chlorodibenzobicyclo[2.2.2]octadiene

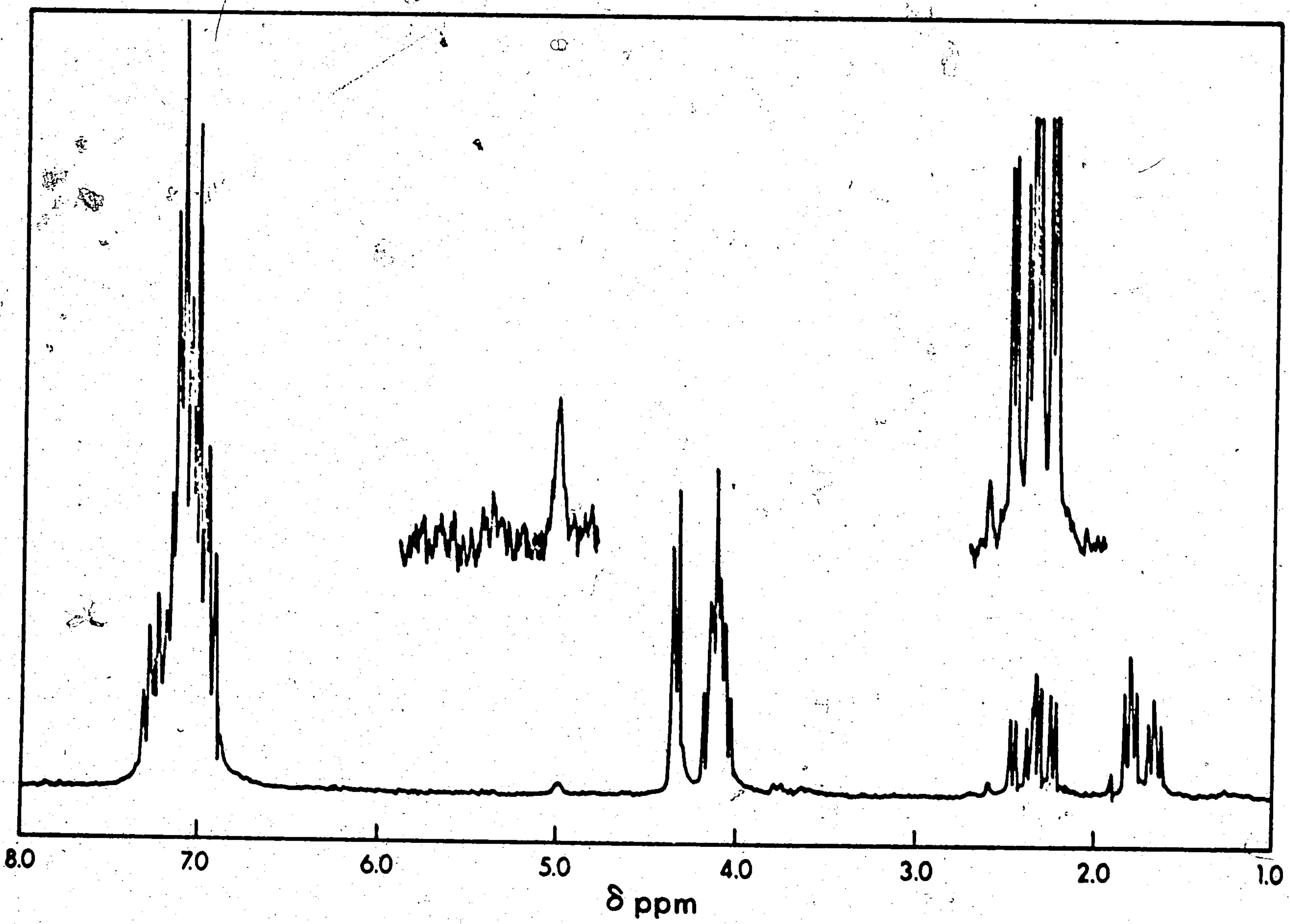
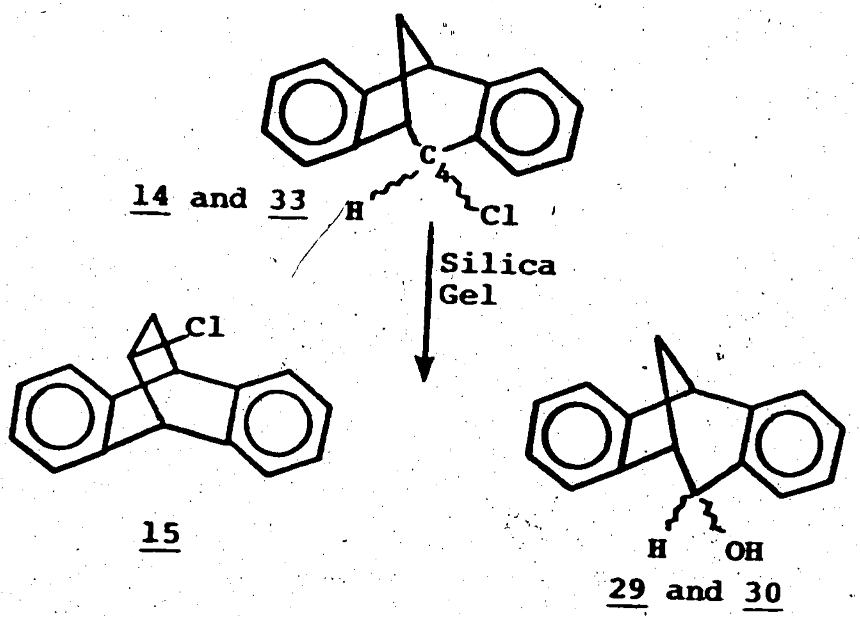


FIGURE 5. HR100 nmr spectrum (CCl_4) of a 95:5 mixture of 7-chlorodibenzobicyclo[3.2.1]octadiene and a mixture of exo- and endo-4-chlorodibenzobicyclo[3.2.1]octadiene.

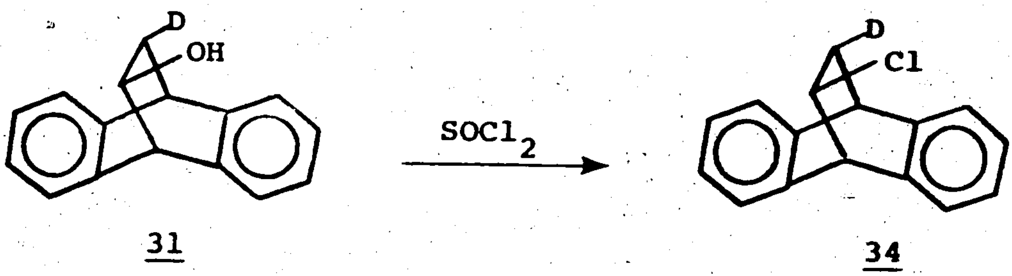
ferent from those of exo-[3.2.1] chloride, 14, to allow the detection of their presence by examination of the nmr spectrum of the reaction mixture. Furthermore, the signal at τ 4.68 was assigned to exo-H_4 of endo-4-chlorodibenzobicyclo[3.2.1]octadiene, on the basis of the chemical shift and coupling constant ($J_{4,5}$ = 5.0 cps), for this proton.

The stereochemical assignments of the two mono-[3.2.1] chlorides was substantiated by chemical means. A purified mixture of the [3.2.1] chlorides gave analyses for the elements C, H and Cl which were consistent with those calculated for the compounds. Further, an attempted purification of a mixture of the [3.2.1] chlorides by column chromatography (Silica Gel packed in carbon tetrachloride), gave rise to two fractions, 83% of 7-chlorodibenzobicyclo[2.2.2]octadiene (15), and 13% of a mixture of exo- and endo-[3.2.1] alcohols, 29 and 30. These products isolated from the chromatography column could only have arisen from [3.2.1] chlorides in which the chloride is bonded to C-4 in either exo or endo position, since the [2.2.2] chloride, 15, was shown to be stable to chromatographic treatment:

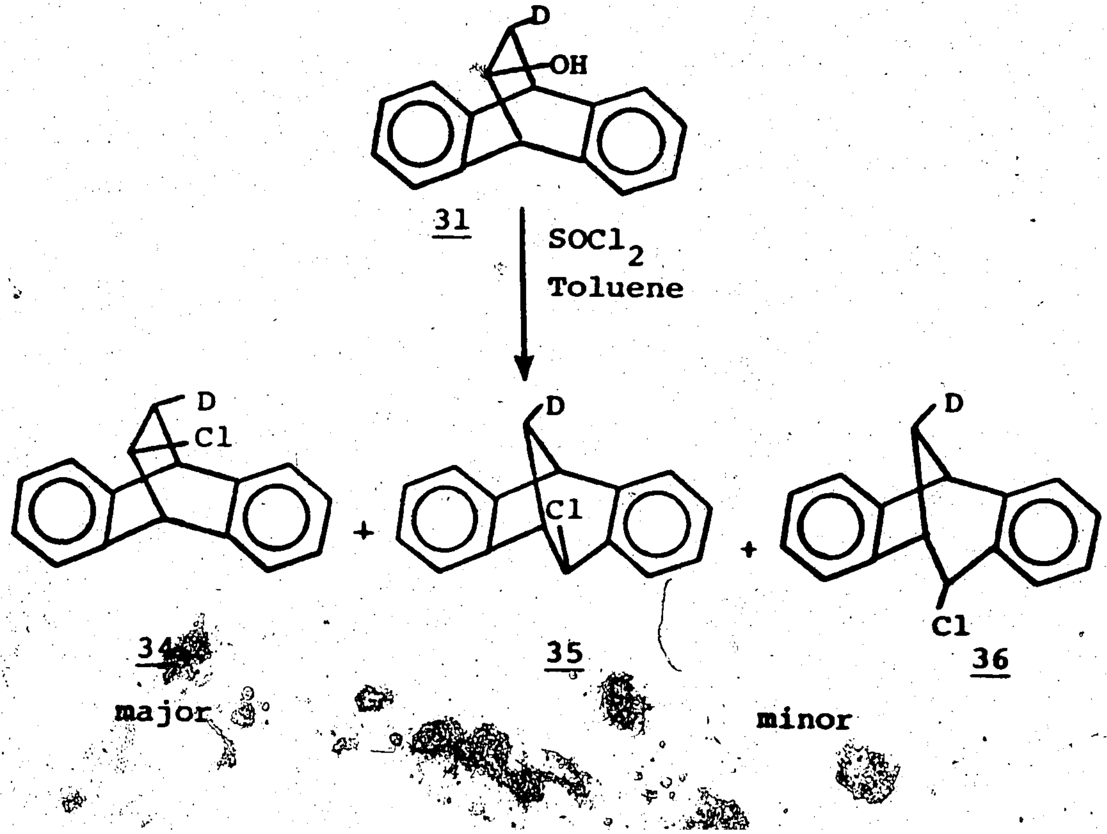


a) <u>Possibility of the Classical S_Ni Mechanism</u> - The classical S_Ni mechanism as outlined in Scheme 6, illustrates that the carbon-oxygen bond breaking and the carbon-chlorine bond formation are concerted processes. This intramolecular nucleophilic change results in retention of configuration; the carbon-chlorine bond forms on the same side as the carbon-oxygen of the original alkyl chlorosulfite. If the S_Ni mechanism as defined in the classical sense, were operating in the reaction of thionyl chloride with the alcohols under investigation, then each alcohol should lead to the chloride of the same skeletal structure and same stereochemistry. Dibenzobicyclo[2.2.2]octadien-2-ol (<u>13</u>), should yield only 7-chlorodibenzobicyclo[2.2.2]octadiene (<u>15</u>). More specifically, the deuterated [2.2.2] alcohol, <u>31</u>, should lead exclusively to <u>cis</u>-7-chloro-8-deuteriodi-

Benzobicyclo[2.2.2]octadiene (34):

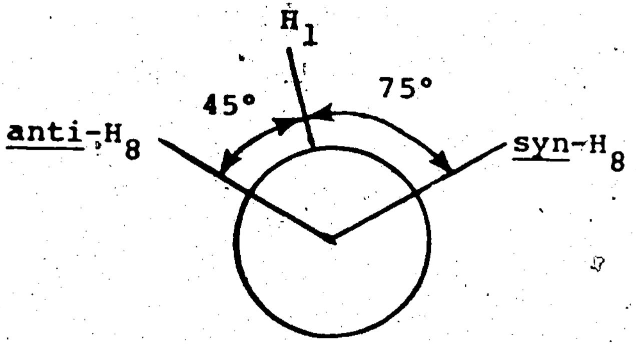


The results obtained from the reaction of the deuterated alcohol, 31, with thionyl chloride in toluene did agree with the S_Ni mechanism. The major product under these reaction conditions was the [2.2.2] chloride, 34. A mixture of [3.2.1] chlorides was also formed:

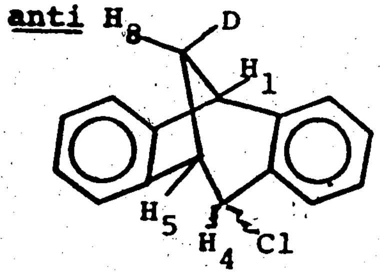


However, the possibility existed that the [2.2.2] chloride, 34, could have come about by a geitonodesmic rearrangement (18d) of the mixture of the [3.2.1] chlorides, 35 and 36. Indeed this was found to be the case, and will be discussed later.

The stereochemistry of the chlorides 34 - 36 was established by nmr. Information concerning the exact position of the deuterium relative to the chlorine could be obtained by examining which absorption peak of the deuterated chloride was absent when the spectrum was compared to that of the nondeuterated analog. Cristol (22) has reported two coupling constants for the H_8 protons with H_1 proton, for exo-4-chlorodibenzobicyclo[3.2.1]-octadiene: $J_{1,8} = 4.0, 1.1$ cps. The coupling between protons on vicinal carbon atoms in rigid systems depends primarily on the dihedral angle θ between the H-C-C' and C-C-H' planes (23). These angles, which have been estimated by Tanner and Gilman (24), can be visualized by an end-on view of the bond between the vicinal carbon atoms, C-8 and C-1:



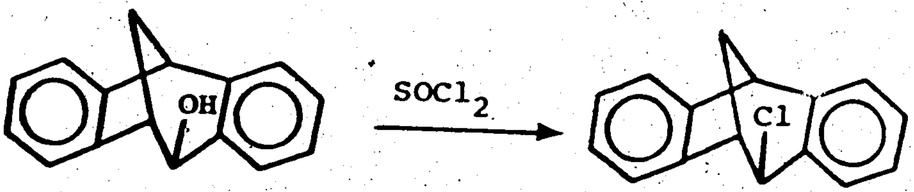
A plot of the calculated relationship between the dihedral angles and vicinal coupling constants, has been made (23). On the basis of the "Karplus Plot", the estimated coupling constants of the H_8 protons with the H_1 proton are as follows: <u>anti</u> $J_{1,8}$ = 3.8 cps, and <u>syn</u> $J_{1,8}$ = 0.2 cps. To measure the coupling constant between the H_8 and H_1 protons in the [3.2.1] chloride product, the absorption band due to the H_5 proton was irradiated.



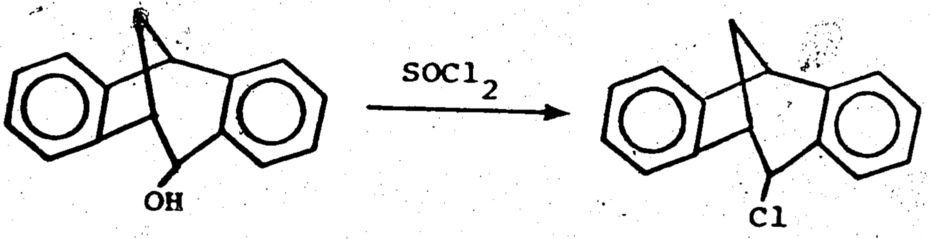
Only one coupling constant of $J_{1,8}$ = 4 cps was observed. Therefore, it was the <u>anti</u>-H_8 proton which was coupled to the H_1 proton, in the <u>exo</u>- and <u>endo</u>-4-chloro-syn-8-deuteriodibenzobicyclo[3.2.1]octadienes. The irradiation of the H_1 proton allowed a determination to be made of the $J_{8,5}$ coupling constant. The dihedral angle between <u>anti</u>-H_8 and H_5 is the same as that of <u>anti</u>-H_8 and H_1 (24). A coupling constant of 4 cps was found for these two protons ($J_{8,5}$ = 4.0 cps). This large coupling constant is further corroboration for the deuterium assignment.

In the analysis of 7-chloro-*cis*-8-deuteriodibenzobicyclo[2.2.2]octadiene (34), it was established that the proton absorption for *cis*-H_8 at τ 8.25 was absent in the nmr spectrum. Further, Cristol (25) reported three coupling constants for the H_7 proton of 7-chlorodibenzobicyclo[2.2.2]octadiene: $J_{1,7}$ = *trans* $J_{7,8}$ = 2.5 and *cis* $J_{7,8}$ = 8.0. Irradiation of the H_1 proton resulted in a doublet for H_7 with a coupling constant of 8 cps.

For the reaction of the [3.2.1] alcohols, 29 and 30, the S_Ni mechanism predicts that the *exo*-[3.2.1] alcohol, 29, should lead to *exo*-[3.2.1] chloride, 14, and *endo*-[3.2.1] alcohol, 30, should lead to *endo*-[3.2.1] chloride, 33.



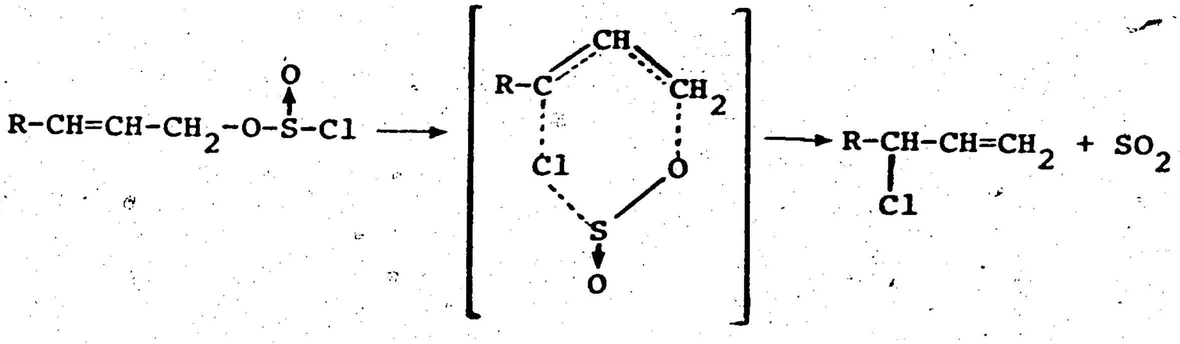
29 14



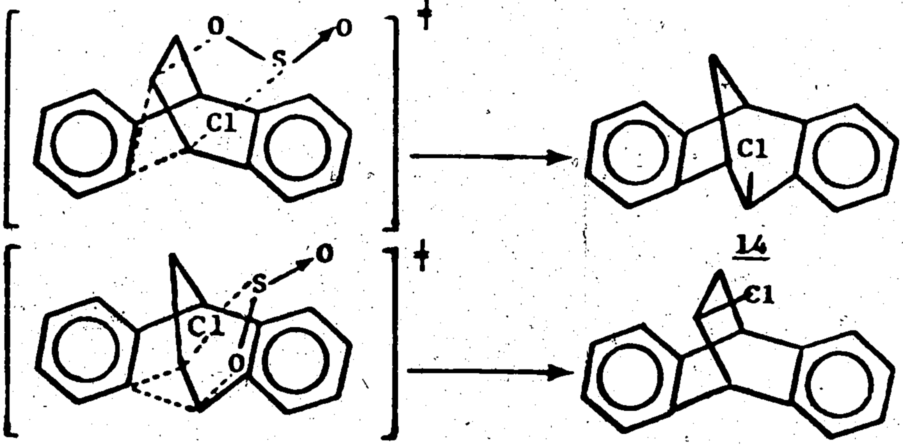
30 33

The best opportunity for the S_Ni mechanism to occur is when a polar solvent such as dioxane is used in the reaction of alcohols with thionyl chloride (5, 8b). The reaction of the three bicyclic alcohols with thionyl chloride in dioxane did not lead to a quantitative amount of a chloride of the same stereochemistry as the alcohol from which it was derived. Instead, the same chloride product ratio was obtained from each of the alcohols investigated, when the reaction was carried out in dioxane, with the major product being a mixture of exo- and endo-[3.2.1] chlorides, 14, and 33. It could be argued that the reaction of each of the alcohols with thionyl chloride in dioxane initially gave rise to the chloride with the same sterochemistry as the starting alcohols, and that the final, common, chloride product ratio was due to subsequent rearrangement of the initially formed chloride product. It was found that in dioxane, all of the dibenzobicyclic chlorides were stable to the reaction conditions employed for this reaction. Further, the rearrangement of the [2.2.2] chloride to [3.2.1] chloride would not occur since it has been shown that the [2.2.2] octadienyl derivatives are the thermodynamically most stable ones (18d). Thus, even under those reaction conditions claimed to be the most favourable for reactions whose stereochemical outcome has been rationalized by the S_Ni, the results from the reaction of these alcohols are not compatible with this mechanism.

b) *The S_Ni' Mechanism* - The S_Ni' mechanism as depicted in Scheme 7 is different from the S_Ni mechanism only in the sense that the intramolecular nucleophilic change accompanies bond migration. Thus, when an allylic alcohol is allowed to react with thionyl chloride, the product obtained exclusively is the one in which allylic rearrangement has occu



Both the [2.2.2] alcohol, *13*, and *exo*-[3.2.1] alcohol, *29*, could conceivably give rise to chlori[illegible]roduct *via* the S_Ni' mechanism:

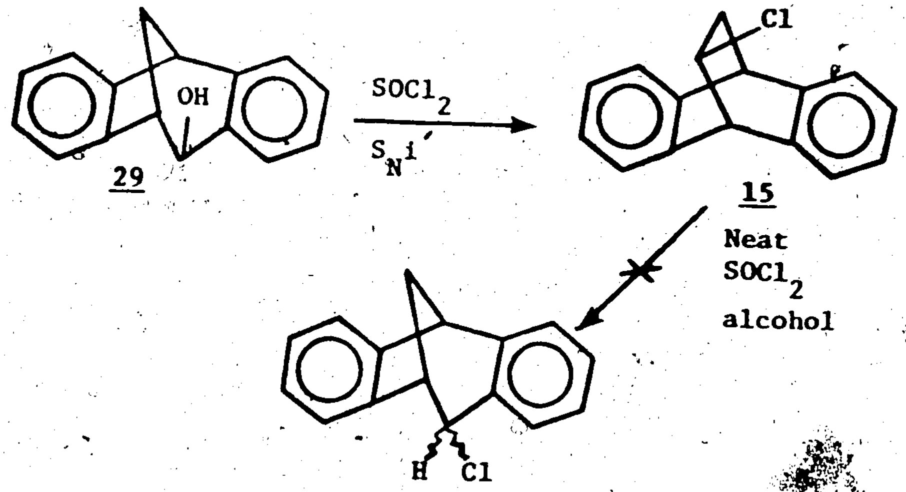


14

The reaction of the [2.2.2] alcohol, 13, should lead exclusively to exo-[3.2.1] chloride, 14, and exo-[3.2.1] alcohol, 29, should lead exclusively to [2.2.2] chloride, 15. The decomposition of the chlorosulfite of the endo-[3.2.1] alcohol, 30, cannot occur via the S_Ni' mechanism. Since each of the three alcohols (13, 29 and 30), gave rise to the same chloride product ratios, it is unlikely that the decomposition of the bicyclic chlorosulfites proceeds via the S_Ni' mechanism.

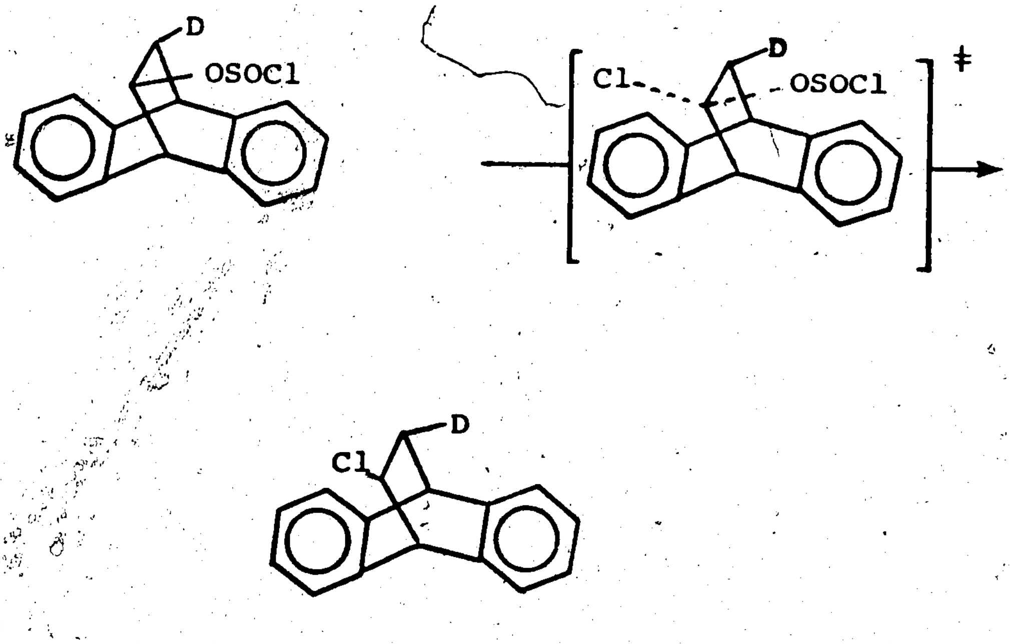
The S_Ni' mechanism has been most extensively demonstrated for reactions of allylic alcohols with thionyl chloride with diethyl ether as the solvent, or in neat thionyl chloride (19). When the two alcohols, 13, and 29, whose chlorosulfites could conceivably decompose via the S_Ni' pathway, were allowed to react with thionyl chloride in dry diethyl ether, only rearranged [3.2.1] chloride product was realized. Similarly, both of these alcohols gave rise to virtually quantitative amounts of [3.2.1] chlorides when they were allowed to react with neat thionyl chloride. If it is argued, as previously stated, that the final product ratios arise from rearrangements of the initially formed chlorides, then it is necessary that the [2.2.2] chloride, 15, the initial product predicted by the S_Ni mechanism from the reaction of exo-[3.2.1] alcohol, 29, with thionyl chloride, must rearrange to the [3.2.1] chloride products.

It was found as in dioxane that the [2.2.2] chloride, 15, was completely stable under the reaction conditions of the bicyclic alcohols with neat thionyl chloride:



14 and 33

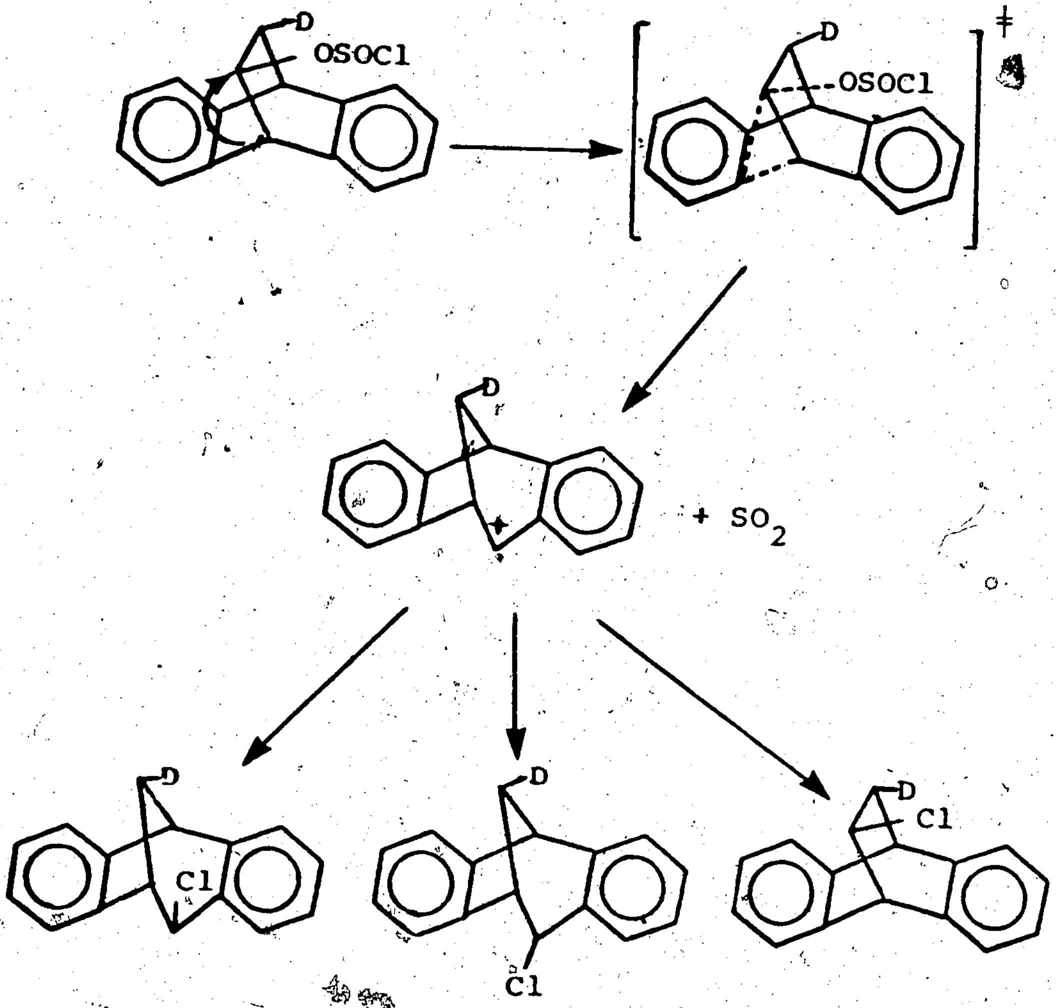
c) The S_N2 Mechanism - The reaction of cis-3-deuteriodibenzobicyclo[3.2.1]octadien-2-ol (31), with thionyl chloride was carried out to obtain some information about the stereochemistry of this reaction and to assess the importance of the S_N2 mechanism. The S_N2 reaction process implies that the chloride in the product must be attached to the side opposite from which the sulfur dioxide molecule departed. Clearly, cis-3-deuteriodibenzobicyclo[3.2.1]octadien-2-ol (31), when allowed to react with thionyl chloride must yield trans-7-chloro-8-deuteriodibenzobicyclo[2.2.2]octadiene, if the S_N2 mechanism were operative.



34

Lewis and Boozer (8b) found that the decomposition of a variety of optically active secondary alkyl chlorosulfites in toluene led to alkyl halides with complete inversion of configuration. They concluded that toluene was a solvent extremely conducive to the S_N2 pathway, where the chloride anion can approach the alkyl chlorosulfite from the backside, giving rise to inverted chloride product. When the deuterated alcohol, 31, was allowed to react with thionyl chloride in toluene, the major product formed was cis-7-chloro-8-deuteriodibenzobicyclo[2.2.2]octadiene (34). Thus, the stereochemistry of the deuterated chloride formed was not consistent with the S_N2 pathway.

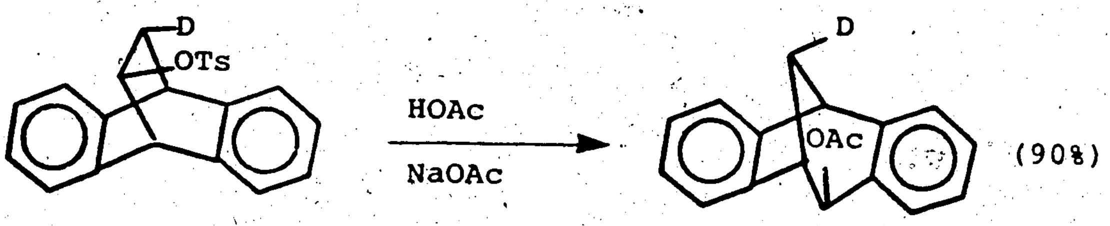
The deuterated alcohol, 31, was also allowed to react with thionyl chloride in dioxane and in neat thionyl chloride. Under both of these reaction conditions the major products were a mixture of *exo*- and *endo*-4-chloro-*syn*-8-deuteriodibenzobicyclo[3.2.1]octadiene (*35* and *36*). The *syn*-8 position of the deuterium is consistent with the well documented stereospecific *anti*-bond migration between the [2.2.2] and the [3.2.1] system (18c).



35 *36* *34*

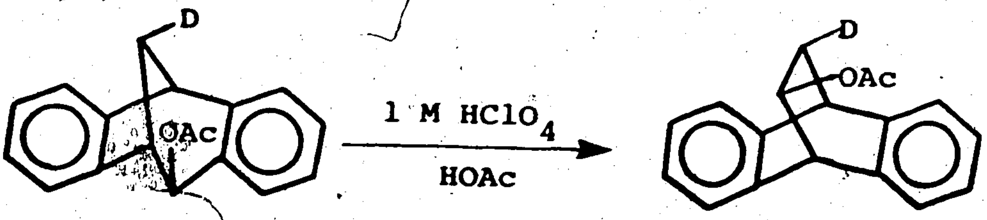
On the basis of these results the possibility of the S_N2 mechanism could be ruled out.

d) *The S_N1 Mechanism* - It has been shown that a [2.2.2] carbonium ion does not intervene as an intermediate in both solvolysis and addition reactions of 7-substituted dibenzobicyclo[2.2.2]octadienyl derivatives (18b, c, d, f, g). Solvolyses of dibenzobicyclo[2.2.2]octadien-7-yl derivatives are known to give exclusively or preponderantly dibenzobicyclo[3.2.1]octadien-*exo*-2-yl derivatives (18a, c, d, g), and the reactions which occurred were generally stereospecific with respect to the skeletal migration (18c, d, f, g). For example (18f), acetolysis of the *cis*-deuterio *p*-toluenesulfonate, 39, gave *syn*-8-deuteriodibenzobicyclo[3.2.1]octadien-2-ol acetate (40):



39 40

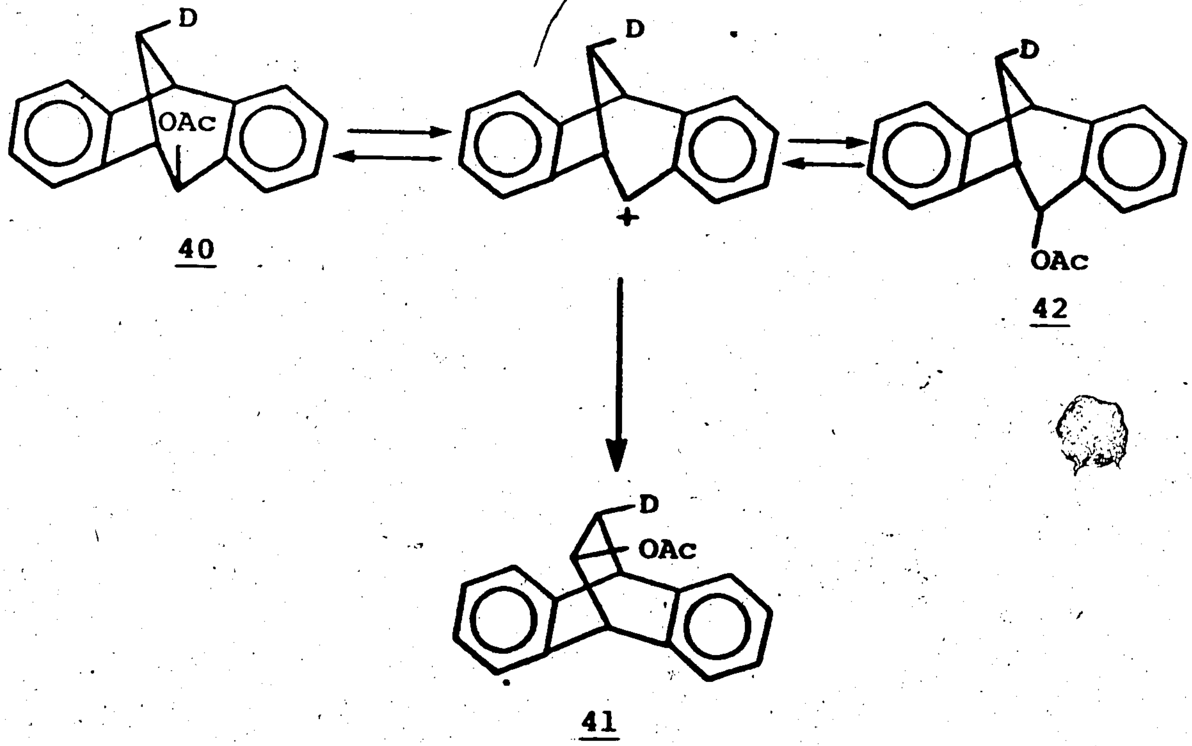
When 40 was treated with 1 M perchloric acid in acetic acid at room temperature for 160 minutes, it rearranged to the thermodynamically more stable [2.2.2] acetate, 41:



40

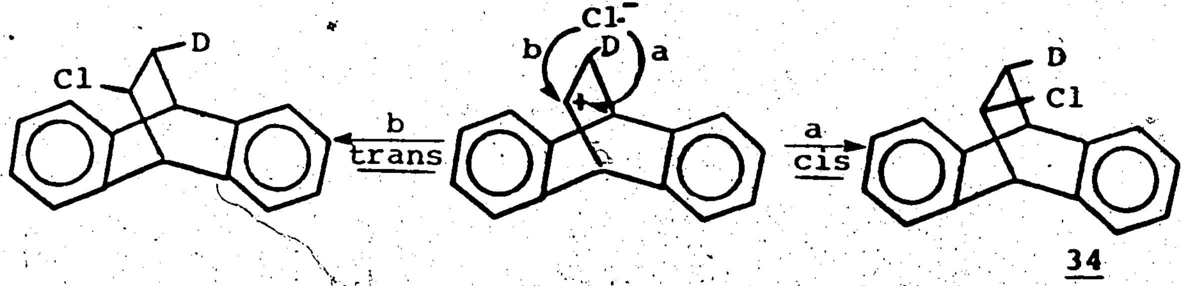
41

Thus the acid catalyzed rearrangement from the [3.2.1] system to the [2.2.2] system was also stereospecific. In 1 M perchloric acid in acetic acid the *exo* acetate, 40, was found to equilibrate rapidly (<5 min) to a 58:42 mixture of *exo* and *endo* acetates, 40 and 42, respectively, before any substantial rearrangement to the [2.2.2] system had taken place. Thus, *exo*-[3.2.1] product is produced by kinetic control, and with stereospecific *anti* bond migration from the [2.2.2] system. This is then rapidly converted into the equilibrium mixture of *exo*- and *endo*-[3.2.1] isomers, and more slowly converted, again stereospecifically, into the [2.2.2] isomer. Intervention of a classical [2.2.2] cation is interdicted by the clean stereospecificity of the [3.2.1] $\rightleftarrows$ [2.2.2] rearrangements. Cristol (18f) suggested that the acid catalyzed rearrangement of the [3.2.1] system to the [2.2.2] system followed the path of Scheme 10.



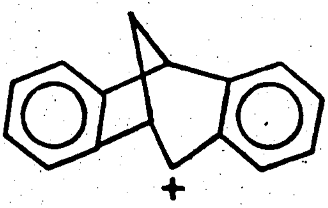
SCHEME 10

The reaction of the deuterated alcohol, 31, with thionyl chloride provided results which were consistent with the hypothesis that the [2.2.2] cation does not form as an intermediate, since if it had formed then both *cis* and *trans* deuterio-[2.2.2] chloride should have been obtained as products:

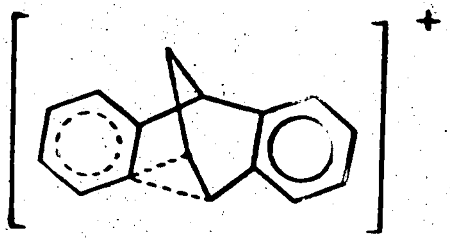


Product analysis of the deuterated chloride had shown that only the *cis*-[2.2.2] isomer, *34*, had formed in the reaction of the deuterated alcohol, *31*, with thionyl chloride. The stereochemical result that only *syn*-8-deuterio-[3.2.1] chlorides were formed in the reaction of the bicyclic alcohols with thionyl chloride implies that the [2.2.2] carbonium ion cannot be an intermediate in the decomposition of the bicyclic chlorosulfites. If it were, such an intermediate would give both *syn*- and *anti*-8-deuterio-[3.2.1] chlorides.

The above results indicate that migration must accompany ionization of the carbon-oxygen bond of the alkyl chlorosulfite. If migration occurs at the time of ionization the cationic intermediate can be envisaged as either a "classical" benzylic ion, I, with only ordinary delocalization into the vicinal aromatic ring, or as the "nonclassical" intermediate, II:



I



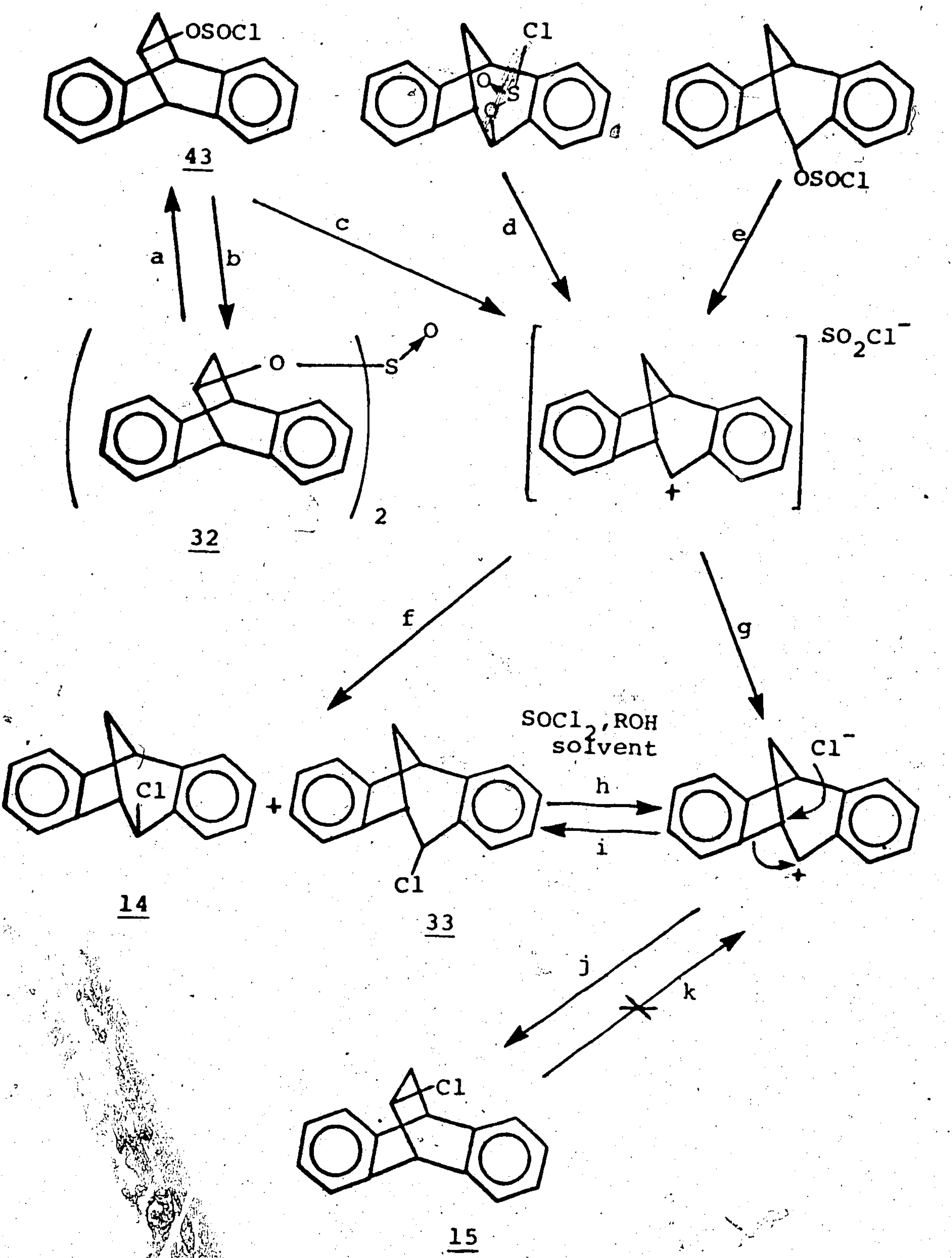
II

Cristol (18d) has ruled out the possibility of the cationic intermediate II on the basis of the observation that exo-endo isomerism of various [3.2.1]-octadienyl derivatives occurs rapidly compared with [3.2.1] $\rightleftarrows$ [2.2.2] isomerization.

MECHANISTIC CONCLUSIONS

Each of the above mechanistic pathways is inadequate to explain the results obtained from the reaction of the various bicyclic alcohols with thionyl chloride. However, experimental results obtained during the course of this investigation indicate strongly that the decomposition of the alkyl chlorosulfite occurs by an ionic mechanism, in which the "classical" [3.2.1] cation, stabilized by benzylic resonance, can be the sole cationic intermediate. The stereochemical results and the product distributions observed in the reaction of the bicyclic alcohols with thionyl chloride, can best be accommodated by Scheme 11.

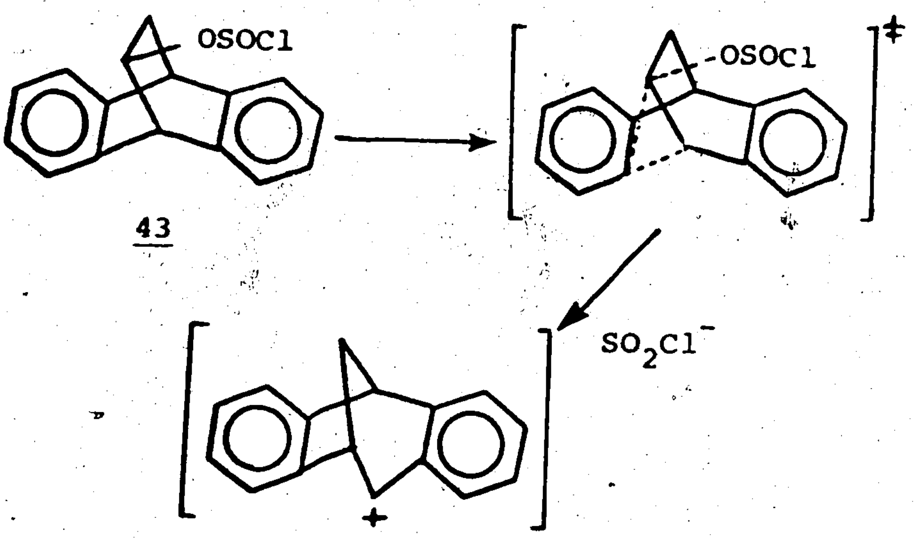
As shown in Scheme 11, it is assumed that no [2.2.2] cation intervenes in the decomposition of the bicyclic chlorosulfites irrespective of the solvent employed in the study of the reaction of alcohol with thionyl chloride. Lewis and Boozer (8b) attributed the stereochemical outcome from the reaction of secondary optically active alcohols with thionyl chloride, to differences in the solvating power of various solvents. For the bicyclic alcohols, no such special effect for the


OSOCl
43
Cl
O
S
O
OSOCl
a
b
c
d
e
O
S
O
2
32
SO$_2$Cl$^-$
+
f
g
SOCl$_2$,ROH
solvent
h
i
Cl$^-$
+
Cl
14
+
Cl
33
j
k
Cl
15

SCHEME 11

solvation of the cation needs to be postulated. It is proposed that in all the solvents the [3.2.1] cation is formed from the decomposition of the bicyclic chlorosulfite, while only the position of the "gegen ion" is different.

For the [2.2.2] chlorosulfite the formation of the [3.2.1] cation involves the migration of a carbon-carbon bond coincident with and anti to the departure of the SO_2Cl^- leaving group:



43

I

The resultant benzylic carbonium ion is then trapped by chloride anion to yield a mixture of exo- and endo-[3.2.1] chlorides, 14 and 33, with a preponderance of the exo isomer. The larger percentage of exo product (quasi-axial attack), over endo product (quasi-equatorial attack) has been rationalized (18b). Preferential exo attack occurs since the p-π overlap of the benzylic carbonium ion with the benzene ring will be lost less rapidly if the chloride coordinates from the quasi-axial (exo) position than from the quasi-equatorial (endo) position. Thus, the transition state for bonding from the exo side is of lower energy than that for the bonding from the endo side.

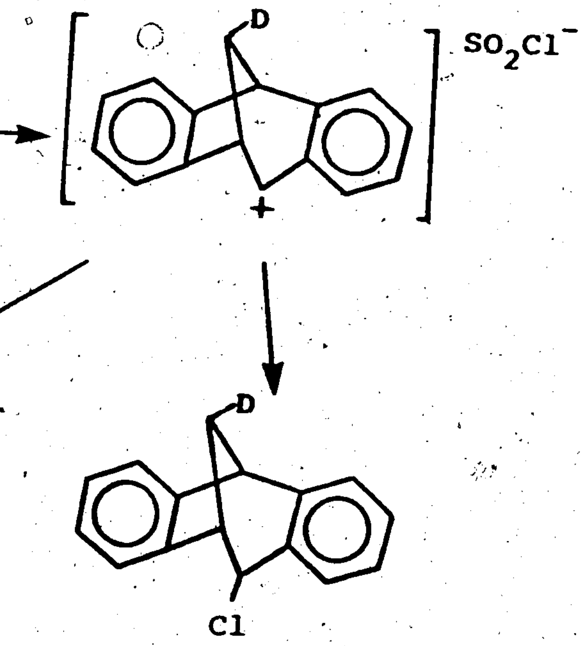
The major product from the reaction of the bicyclic alcohols with thionyl chloride in toluene, is the [2.2.2] chloride, 15. Scheme 11 illustrates that the unrearranged chloride arises from the rearrangement of an initially formed mixture of [3.2.1] chlorides. The initial evidence for this [3.2.1] to [2.2.2] rearrangement arose during the attempted preparation of the chlorosulfite or dialkyl sulfite of exo-[3.2.1] alcohol, 29. When this alcohol was allowed to react with thionyl chloride in toluene under the reaction conditions employed for the preparation of dialkyl sulfite, 32, (0-25°, 2 hours), only [3.2.1] chloride product was realized. It was observed that at this early stage of chlorosulfite formation in the reaction of alcohol with thionyl chloride, the first-formed chloride product was a 4:1 mixture of exo- and endo-[3.2.1] chlorides, 14 and 33. This was contrary to the formation of [2.2.2] chloride as the major product when the bicyclic alcohols were allowed to react with thionyl chloride in toluene under the normal reaction conditions.

It is postulated that toluene, which is a poor ionizing solvent, should result in the hydrogen chloride formed in the reaction, to be largely undissociated. Thus, the hydrogen chloride dissolved in the toluene is able to catalyze the rearrangement of the mixture of [3.2.1] chlorides to [2.2.2] chloride. Control experiments in which n-propanol, tert-butanol or allyl alcohol were allowed to react with thionyl chloride in toluene, with a molar amount of a mixture of [3.2.1] chlorides added, did not give consistent results; the extent of [3.2.1] to [2.2.2] rearrangement varied from about 20% to about 56%. However, when dibenzobicyclo[3.2.1]octadien-exo-2-ol (29) was allowed to react with thionyl chloride in toluene with a molar amount of a mixture of [3.2.1] chlorides added, the nmr spectrum revealed the presence of 76% of the [2.2.2] chloride, 15, in the reaction mixture.

To demonstrate the catalytic effect of hydrogen chloride in the rearrangement, the bicyclic alcohols were allowed to react with thionyl chloride in toluene with a molar amount of an amine base added. Under these reaction conditions quantitative amounts of [3.2.1] chloride product were isolated. It is postulated that the bases employed for this purpose (pyridine, Huenig's Base and Proton Sponge) are extremely effective in taking up the hydrogen chloride formed during the reaction (21), thus totally inhibiting the acid-catalyzed rearrangement of the [3.2.1] chlorides to the [2.2.2] chloride.

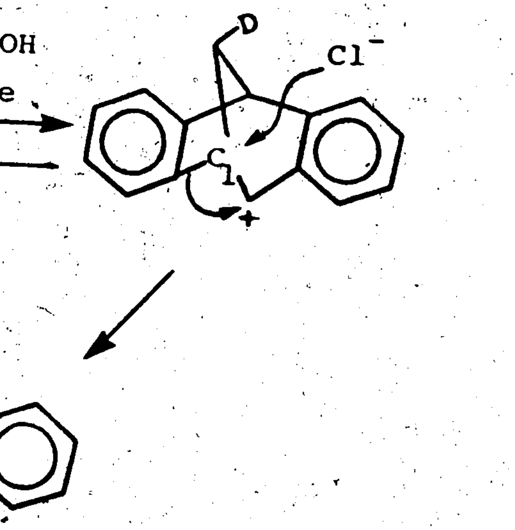
Further, the stability of the [3.2.1] chlorides under these reaction conditions was examined when n-propanol was allowed to react with thionyl chloride in toluene, with molar amounts of both an amine base and a mixture of [3.2.1] chlorides. The only chloride product re-isolated quantitatively was the original starting mixture of [3.2.1] chlorides. It was concluded, therefore that the [2.2.2] chloride, formed as the major product in the reaction of [2.2.2] alcohol, 13, with thionyl chloride in toluene, came about by a hydrogen chloride catalyzed rearrangement of the initially formed mixture of [3.2.1] chlorides.

The stereospecificity of the [3.2.1] $\rightleftarrows$ [2.2.2] rearrangement, under these reaction conditions, was demonstrated by the reaction of the deuterated [2.2.2] alcohol, 31, with thionyl chloride. The only [2.2.2] chloride obtained was the one which had the deuterium in a position cis to the chlorine, 34. According to Scheme 11 this necessitates that ionization of the C-O bond of the alkyl chlorosulfite is accompanied by migration of the bond anti to the leaving group to yield the [3.2.1] cation, in which the deuterium is in the syn-8 position. Attack by chloride anion at the benzylic position then leads to the initial mixture of [3.2.1] chlorides, 35 and 36:



<u>36</u>

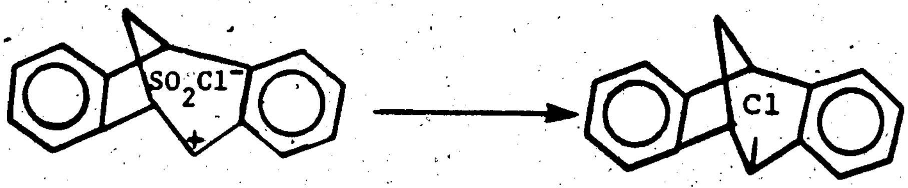
under the reaction condi-
cation again, and <u>cis</u>-7-
.o[2.2.2]octadiene (<u>34</u>)
chloride anion at C_1 with
:



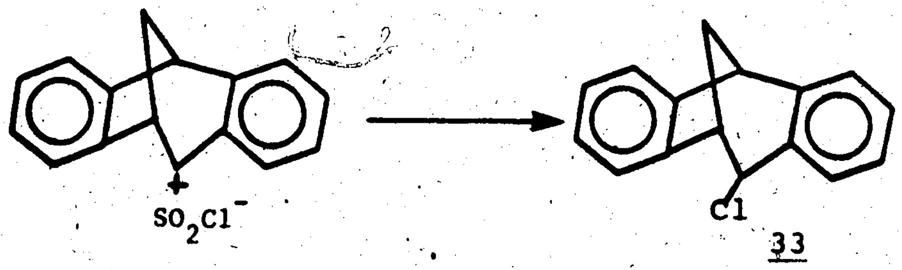
The final products obs
the bicyclic alcohols with n
thionyl chloride in dioxane
of [3.2.1] chlorides. It is
the hydrogen chloride formed
with thionyl chloride, is lar
which may act as a Lewis base
stantially higher concentrati
toluene. The chloride anion
trap the benzylic carbonium i
dioxane by hydrogen chloride
hydrogen chloride to catalyze
initially formed mixture of [
ely inhibits the rearrangement
to [2.2.2] chloride. When the
was increased by the addition
amine base to both the reactio
chloride and thionyl chloride/
case with toluene, the formati
was inhibited completely.

An interesting aspect of
observed in the reaction of the
thionyl chloride in dioxane war
It was found that the reaction
octadien-2-ol (<u>13</u>) with thionyl
rise to an <u>exo</u>/<u>endo</u> [3.2.1] chlo

For the same reaction with dibenzobicyclo[3.2.1]octadien-*exo*-2-ol (29) an *exo*/*endo* ratio of 3:1 was obtained, and for the reaction of dibenzobicyclo[3.2.1]octadien-*endo*-2-ol (30), the ratio of *exo*/*endo* was 2:1. The differences observed in the *exo*/*endo* ratio for the three alcohols can be rationalized by assuming that some chloride product comes about by collapse of an intimate ion-pair; *endo*-[3.2.1] alcohol, 30, gave rise to a higher percentage of *endo*-[3.2.1] chloride, 33, than either *exo*-[3.2.1] alcohol, 29, or [2.2.2] alcohol, 13.

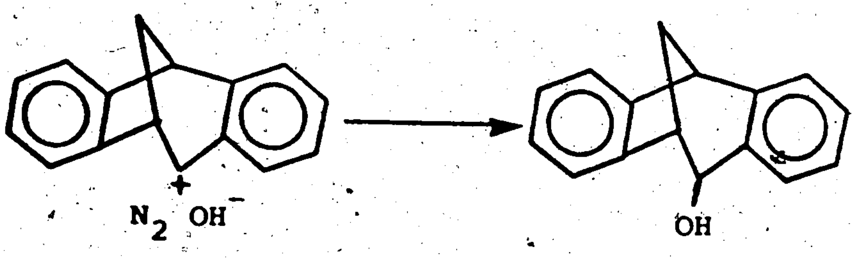


14

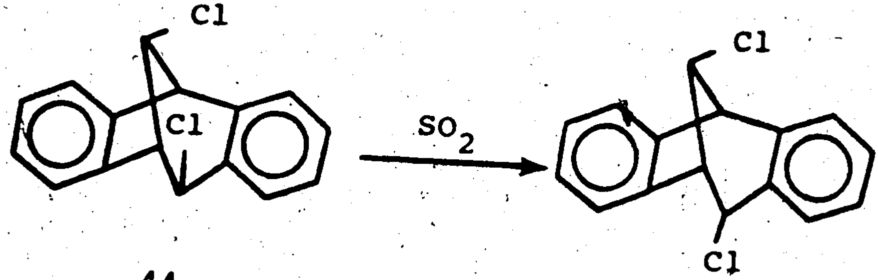


33

The initially formed *endo* chlorosulfite ion-pair has chlorine at a position favourable for attack at the *endo* side of the carbonium ion, and some coordination from this side may occur before chloride anion reacts at the usual preferred *exo* direction on the dibenzobicyclo[3.2.1]octadienyl cation. Product formation by an ion-pair pathway has recently been postulated (18g) for the formation of *endo*-[3.2.1] alcohol, *30*, in the deamination reaction of dibenzobicyclo[3.2.1]octadien-*endo*-2-yl ammonium *p*-toluenesulfonate. No *endo*-[3.2.1] alcohol was realized from the deamination reaction of the corresponding [2.2.2] and *exo*- [3.2.1] *p*-toluenesulfonate amine salts. It was postulated (18g) that hydroxide ion in the initially formed benzyl cation-hydroxide ion-pair can attack from the *endo* side before it migrates to the *exo* side:



The product distribution in the reaction of the bicyclic alcohols with neat thionyl chloride could be altered appreciably by the addition of a catalytic amount of water to the reaction mixture. Under these reaction conditions, 25-30% of the [2.2.2] chloride, *15*, was formed which compares to less than 10% for the reaction without water added. The result may be rationalized by proposing that the water in the reaction mixture reacts with thionyl chloride resulting in a higher concentration of hydrogen chloride, which is then available to catalyze the [3.2.1] to [2.2.2] chloride rearrangement. Alternatively, water may react with thionyl chloride to form sulfur dioxide which could catalyze a [3.2.1] to [2.2.2] rearrangement. Cristol, Arganbright and Tanner (18b) demonstrated the epimerization of 44 to 45 with liquid sulfur dioxide:



44 45

CONCLUSIONS

The study of the reaction of thionyl chloride with the bicyclic alcohols 13, 29 and 30 has demonstrated that the reaction mechanism for the decomposition of the intermediate bicyclic chlorosulfites is largely ionic in nature, proceeding through the "classical" benzylic [3.2.1] cation (I). Attack at the benzylic cation leads to an initial mixture of exo- and endo-[3.2.1] chlorides. The final product distribution is determined by the amount of undissociated hydrogen chloride present in the solvent. In toluene, the hydrogen chloride is largely undissociated resulting in an acid catalyzed rearrangement of the initial kinetically controlled [3.2.1] chloride product mixture to the thermodynamically more stable [2.2.2] chloride. To a lesser extent this rearrangement occurred under the reaction conditions, neat thionyl chloride with water added. In neat thionyl chloride and in the solvent dioxane the hydrogen chloride is presumably largely dissociated preventing the acid catalyzed rearrangement from occurring to any large extent. When the basicity of the various solvents was increased by the addition of tertiary amine bases, the hydrogen chloride catalyzed rearrangement was inhibited completely.

EXPERIMENTAL

Materials

Blue-violet fluorescent anthracene was obtained from Aldrich Chemical Company and was used without further purification. Purification of benzene, toluene and p-xylene was accomplished by washing with concentrated sulfuric acid followed by refluxing over sodium for 24 hours and distillation. Benzene and xylene were stored over molecular sieve (4A), and the purified toluene was stored in degassed and sealed ampoules. Diethyl ether and tetrahydrofuran were purified by refluxing over lithium aluminum hydride for 12 hours followed by fractional distillation.

Commercial dioxane was passed through a chromatography column (80 g of activated alumina for 100 ml of dioxane), to remove peroxides, and then purified according to the method of Fieser (26). The pure dioxane, $n_D^{20} = 1.4226$, was stored in 35 ml aliquots in degassed sealed ampoules. Pyridine was purified by distillation from barium oxide and stored over molecular sieve (4A). Diglyme (diethylene glycol dimethyl ether) was obtained from Matheson Coleman and Bell Co. Ltd. and purified by refluxing over sodium metal for four hours followed by distillation. Commercial thionyl chloride was purified according to the method of Fieser (27).

The pure thionyl chloride was stored in degassed, sealed ampoules.

Boron trifluoride etherate obtained from Eastman Kodak Co. was purified by distillation under reduced pressure from calcium hydride. Huenig's Base (N,N-diisopropylethylamine) was purchased from Aldrich Chemical Co., and purified by distillation at atmospheric pressure (bp 126°). Proton Sponge (1,8-bis (dimethylamine) naphthalene) available from Aldrich Chemical Co. was dried in a vacuum desiccator and employed without further purification (mp 49-50°). Sodium borodeuteride was purchased from Alfa Inorganics Inc. and used directly.

Silver pivalate was prepared in a similar manner to that described by Eliel and Haber (28) for the preparation of silver benzoate. To a stirred solution of 20.4 g (0.20 mole) of pivalic acid in 100 ml of 2 M aqueous sodium hydroxide was added dropwise 2 ml of nitric acid followed by a few drops of 2 M sodium hydroxide solution. Silver nitrate (0.22 mole in 30 ml water) was then added slowly. The silver salt which precipitated was collected by filtration, washed successively with water and carbon tetrachloride and dried in a vacuum oven for 24 hours before use. The purity of the material was checked in the following manner. To 2.00 g of the dry silver salt was added

30 ml carbon tetrachloride, the solution was heated and filtered. To the filtrate was added 30 ml water, the mixture was stirred and 2 drops of phenolphthalein was added. The solution was immediately titrated with 0.04 M sodium hydroxide. Addition of 1 drop of base turned the mixture pink and thus, it was assumed that the silver pivalate was acid-free.

Lead tetraacetate (LTA) was obtained from Alfa Inorganics and recrystallized from acetic acid/acetic anhydride prior to use. Raney nickel catalyst was prepared by the procedure of Vogel (29).

Preparation of Substrates and Authentic Samples

trans-7,8-Dichlorodibenzobicyclo[2.2.2]octadiene - This compound was synthesized according to the procedure of Cristol (30) from trans-1,2-dichloroethylene and anthracene in 64% yield: mp 113.5 - 114.5° (lit. 113.5 - 114°). The infrared and nmr spectra, in carbon tetrachloride, of pure trans-7,8-dichlorodibenzobicyclo[2.2.2]-octadiene were compatible with those reported for this compound (25).

Dibenzobicyclo[2.2.2]octatriene (22) - The olefin, 22, was prepared from trans-7,8-dichlorodibenzobicyclo-[2.2.2]octadiene according to the method of Cristol (18c) in 75% yield. The crude product was purified by column chromatography (Woelm neutral alumina, pentane/carbon tetrachloride), and recrystallized from 95% ethyl alcohol: mp 116 - 117° (lit. 118.5 - 119°). The infrared spectrum of this olefin was compatible with the assigned structure, and the nmr spectrum in carbon tetrachloride was the same as that reported for this compound (25). The compound, 22, could also be prepared from the oxidative decarboxylation of trans-7,8-dibenzobicyclo[2.2.2]octadienedicarboxylic acid with lead tetraacetate in dioxane by the method of Walsh and Bradly (31). The yield of dibenzobicyclo[2.2.2]-octatriene prepared by this method was 43%: mp 115 - 118°.

Dibenzobicyclo[2.2.2]octadien-2-ol acetate (21) - The ester, 21, was prepared according to the method of Alder and Rickert (32), from the reaction of vinyl acetate and anthracene in p-xylene. After recrystallization from aqueous ethyl alcohol, white crystals (81%) were isolated: mp 99 - 100° (lit. 100 - 101°); $\nu_{C=O}$ 1740 cm^{-1}; nmr spectrum was identical to that reported (25).

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.64; H, 6.20.

Dibenzobicyclo[2.2.2]octadien-2-ol (13) - The alcohol, 13, was obtained in 88% yield from the lithium aluminum hydride reduction of dibenzobicyclo[2.2.2]-

octadien-2-ol acetate (21), according to the procedure of Cristol, Arganbright and Tanner (18b): mp 140 - 142° (lit. 140 - 142°); ir(CCl_4) ν_{O-H} 3570 cm^{-1}; nmr ($CDCl_3$) was identical with that reported (25).

Anal. Calcd for $C_{16}H_{14}O$: C, 86.54; H, 6.35. Found: C, 86.21; H, 6.44.

cis-3-Deuteriodibenzobicyclo[2.2.2]octadien-2-ol (31) -- One hundred and fifty ml of tetrahydrofuran were placed into a 300 ml three-necked round-bottomed flask fitted with a dropping funnel stoppered with a serum cap, a capillary tube for introduction of nitrogen and a trap containing acetone. Under a rapid stream of nitrogen, 2.09 g (0.01 mole) of ethenoanthracene (22) and 0.59 g (0.014 mole) of sodium borodeuteride were added. Under a slow stream of nitrogen 5.58 g (0.043 mole) of freshly distilled boron trifluoride etherate was injected through the serum stopper into the dropping funnel. The slow nitrogen stream was maintained while the boron trifluoride etherate was slowly added to the solution and stirred. When an atmosphere of deuterioborane gas had built up, the nitrogen gas flow was interrupted. The mixture was stirred for an hour after which time the excess sodium borodeuteride was destroyed by the cautious addition of water. The subsequent oxidation was carried out by the slow addition of 27 ml of 30% hydrogen peroxide and stirring for one hour. The reaction product was extracted with ether and the ethereal layer was dried over anhydrous magnesium sulfate. After removal of the solvent using a rotary vacuum evaporator 2.23 g (98%) of a white crystalline product remained: mp 143 - 144° (lit. 142 - 143° (18f)); nmr ($CDCl_3$) τ 2.58 - 3.25 (multiplet, 8H, aromatic), 5.69 (doublet, 1H, J = 3.0 Hz, bridgehead H_1), 5.82 (doublet, 1H, J = 3.0 Hz, bridgehead H_4), 5.92 (doublet of doublet, 1H, J = 3.0 Hz and 8.6 Hz, H_5), 6.65 (broad doublet, 1H, H_3 trans to OH) and 8.39 (singlet, 1H, OH). The cis stereochemistry of this alcohol was assigned on the basis of the absence of the cis-H_3 absorption band at τ 8.82 assigned by Cristol (25) for the non-deuterated alcohol, 13. Integration of the nmr spectrum showed that deuteration had occurred to the extent of >90%.

Anal. Calcd for $C_{16}H_{13}DO$: C, 86.06; H(D), 6.73. Found: C, 85.70; H(D), 6.49.

syn-8-Iododibenzobicyclo[3.2.1]octadien-exo-2-ol acetate (23) - Cristol and coworkers (18c) synthesized the compound, 23, by the Prevost method in which the olefin, 22, silver acetate and the iodine in benzene were heated under reflux for 26 hours. They reported that the only products isolated were unreacted olefin, 22, and syn-8-iododibenzobicyclo[3.2.1]octadien-exo-2-ol acetate. However, under the reaction conditions employed here, it was found that a substantial amount of the endo isomer formed in addition to the exo isomer. To a vigorously stirred suspension of 0.526 g (0.0034 mole) of silver acetate in 25 ml of dry benzene was added 0.874 g (0.0034 mole) of sublimed iodine in 10 ml benzene and the mixture was stirred vigorously for five minutes. Then a solution of 0.678 g (0.0033 mole) of ethenoanthracene in 10 ml of dry benzene was added to the silver acetate solution by means of a dropping funnel. After stirring for 20 minutes the silver salt was filtered and washed with benzene. The filtrate was washed with 1 M solution of sodium carbonate and water, and dried over anhydrous magnesium sulfate. The solvent was removed using a rotary vacuum evaporator, leaving 1.1 g (87%) of a colorless oil. An nmr spectrum in carbon tetrachloride was taken to ascertain the relative ratios of the products formed: ethenoanthracene (22), (17%), syn-8-iododibenzobicyclo[3.2.1]octadien-exo-2-ol acetate (62%), and syn-8-iododibenzobicyclo[3.2.1]octadien-endo-2-ol acetate (21%) were the products present. The reaction mixture was subjected to column chromatography using Woelm neutral alumina packed in Skelly B, with 50/50 pentane/carbon tetrachloride as the eluting solvent. Two fractions were collected. The first fraction contained 0.180 g (16%) of the unreacted ethenoanthracene (22). The second fraction gave 0.080 g

(73%) of a white crystalline material which did not possess a sharp melting point. An nmr spectrum in carbon tetrachloride showed two characteristic peaks at τ 3.78 (H_2 of syn-8-iododibenzobicyclo[3.2.1]octadien-endo-2-ol acetate (27%) (20)), and 4.43 (H_2 of syn-8-iododibenzobicyclo[3.2.1]octadien-exo-2-ol acetate (73%)).

exo and endo-syn-8-Iododibenzobicyclo[3.2.1]octadien-2-ol pivalate (25) and (26) - Silver pivalate, rather than silver acetate was used in the Prevost reaction, since the bulkier tert-butyl group was anticipated to result in the formation of a greater percentage of the endo isomer. To a vigorously stirred suspension of 31.4 g (0.015 mole) of dry silver pivalate in 200 ml of dry benzene was added 38.1 g (0.15 mole) of freshly sublimed iodine and the mixture was stirred vigorously for 5 minutes. Then a solution of 30.0 g (0.147 mole) of dibenzobicyclo[2.2.2]octatriene (22) in 100 ml dry benzene was slowly added from a dropping funnel. The mixture was stirred for 12 hours and the silver salts were filtered and washed with benzene. The filtrate was washed with 1 M sodium carbonate, followed by water and then dried over anhydrous magnesium sulfate. After the removal of the organic solvent using a rotary vacuum evaporator, 56 g (89%) of a solid residue remained.

A total of 11 g of this crude product was subjected to column chromatography on Fisher Adsorption Alumina packed in Skelly B, with 50/50 pentane/carbon tetrachloride as the eluting solvent. The progress of the chromatography was followed by thin layer chromatography (TLC). Fractions 1-3 consisted of unreacted olefinic starting material (mp 118 - 119°). A total of 1.05 g (9.5%) of this compound was isolated. Fractions 4-6, 1.85 g (16%), mp 170 - 172°, was that of pure syn-8-iododibenzobicyclo[3.2.1]octadien-exo-2-ol pivalate. Fractions 7 and 8, 1.19 g (11%), showed two products by TLC and an nmr (CCl_4) revealed these to be a mixture of the exo-(75%) and endo-(25%) isomers. Fractions 9-15, 2.57 g (23%) was a mixture of the two isomers but now the ratios had changed; exo-(20%), endo-(80%). Fractions 16-21, 2.93 g (27%), were shown to be a mixture of exo-(10%) and endo-(90%) isomers again. Fractions 22-25, 0.811 g (7%), mp 164 - 166°, was that of pure syn-8-iododibenzobicyclo[3.2.1]octadien-endo-2-ol pivalate (26).

The two isomers thus isolated were recrystallized from carbon tetrachloride: syn-8-iododibenzobicyclo[3.2.1]octadien-exo-2-ol pivalate; mp 171.5 - 173°; ir (CCl_4) $\nu_{C=O}$ 1718, ν_{C-I} 698 cm^{-1}; nmr (CCl_4) τ 2.55 - 3.05 (multiplet, 8H, aromatic), 4.35 (doublet, 1H, endo-H_2), 5.29 (doublet of doublet, 1H, anti-H_8), 6.05

(doublet, 1H, H_5), 6.45 (doublet of doublet, 1H, H_1) and 8.75 (singlet, 9H, pivalate, *tert*-butyl).

Anal. Calcd for $C_{21}H_{21}IO_2$: C, 58.35; H, 4.90. Found: C, 58.58; H, 4.76. *syn*-8-Iododibenzobicyclo[3.2.1]octadien-*endo*-2-ol pivalate; mp 164 - 165°; ir (CCl_4) $\nu_{C=O}$ 1725, ν_{C-I} 700 cm^{-1}; nmr (CCl_4) τ 2.50 - 3.17 (multiplet, 8H, aromatic), 3.82 (doublet, 1H, *exo*-H_2), 5.24 (doublet of doublet, 1H, *anti*-H_8), 5.98 (doublet, 1H, H_5), 6.33 (doublet of doublet, 1H, H_1) and 8.83 (singlet, 9H, pivalate *tert*-butyl).

Anal. Calcd for $C_{21}H_{21}IO_2$: C, 58.35; H, 4.90. Found: C, 58.60; H, 4.81.

Dibenzobicyclo[3.2.1]octadien-*exo*-2-ol pivalate (27) -- Into a one liter round-bottomed flask was added 5.3 g (0.012 mole) of pure *syn*-8-iododibenzobicyclo-[3.2.1]octadien-*exo*-2-ol pivalate in 300 ml absolute ethyl alcohol. To this solution were added 1.20 g (0.012 mole) of triethylamine and 5 ml of freshly prepared Raney nickel. The resulting mixture was shaken under 1 atm of hydrogen at room temperature for 12 hours. The catalyst was filtered and the flask rinsed several times with absolute ethyl alcohol. The solvent was removed by rotary evaporation and the crude residue was dissolved in carbon tetrachloride. The organic solution was washed with 10% hydrochloric acid and with distilled water, and dried over anhydrous magnesium sulfate. After removal of solvent by rotary evaporation, 3.70 g (100%) of a colorless, oily residue remained which solidified on standing. The reaction product was dissolved in 30/70 pentane/carbon tetrachloride and filtered through alumina. Recrystallization from cold n-pentane gave a white crystalline solid: mp 75 - 76°; ir(CCl_4) $\nu_{C=O}$ 1714 cm^{-1} (no absorption band at 698 cm^{-1} as for the starting material, 25); nmr (CCl_4) τ 2.58 - 3.16 (multiplet, 8H, aromatic) 4.38 (doublet, 1H), 6.24 (triplet, 1H), 6.66 (multiplet, 1H), 7.69 (multiplet, 2H) and 8.90 (singlet, 9H, pivalate tert-butyl).

Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.06; H, 7.50.

Dibenzobicyclo[3.2.1]octadien-endo-2-ol pivalate (28) - This compound was obtained by the Raney nickel reduction of syn-8-iododibenzobicyclo[3.2.1]octadien-endo-2-ol pivalate according to the method described for the exo isomer. A total of 3.2 g (0.0074 mole) of the endo isomer was allowed to react, and 2.1 g (93%) of a colorless oily residue was isolated. The reaction product was purified by column chromatography according to the procedure described for the exo isomer. Compound 28 is a colorless waxy oil: ir(CCl_4) $\nu_{C=O}$ 1724 cm^{-1} (no absorption band at 700 cm^{-1} as found for the starting material, 26); nmr (CCl_4) τ 2.83 - 3.29 (multiplet, 8H, aromatic), 3.98 (doublet, 1H), 6.43 (multiplet, 2H), 7.82 (multiplet, 2H) and 8.94 (singlet, 9H, pivalate *tert*-butyl).

Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.17; H, 7.41.

Dibenzobicyclo[3.2.1]octadien-*exo*-2-ol (29) - Compound 29 (2.87 g, 0.009 mole) was reduced with lithium aluminum hydride according to the method described for the reduction of dibenzobicyclo[2.2.2]octadien-2-ol acetate (21) to yield 1.9 g (91%) of a white crystalline material. The compound was recrystallized from cold carbon tetrachloride: mp 119.5 - 120.5° (lit. 117 - 119° (17)); ir(CCl_4) ν_{O-H} 3619, 3336 cm^{-1}, ν_{C-O} 1005 cm^{-1}; nmr ($CDCl_3$) was identical to that reported for this compound (22).

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.58; H, 6.21.

Dibenzobicyco[3.2.1]octadien-*endo*-2-ol (30) - The reduction of dibenzobicyclo[3.2.1]octadien-*endo*-2-ol pivalate (28) with lithium aluminum hydride to give the *endo* alcohol, was carried out in an analogous manner to that described for alcohol 29. A total of 1.22 g (0.0045 mole) of compound 28 was reduced to yield a white crystalline product (0.81 g, 95%). Recrystallization from cold carbon tetrachloride gave pure dibenzobicyclo[3.2.1]octadien-*endo*-2-ol: mp 143 - 144° (lit. 145.0 - 145.6 (17)); ir (CCl_4) ν_{O-H} 3422, 3600 cm^{-1}; nmr ($CDCl_3$) τ 2.60 - 3.20 (multiplet, 8H, aromatic), 5.52 (doublet, 1H, *exo*-H_2), 6.24 (multiplet, 1H, H_5), 6.55 (multiplet, 1H, H_1), 7.60 (multiplet, 2H, *syn*-H_8 and *anti*-H_8) and 8.59 (singlet, 1H, OH).

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.63; H, 6.36.

Proton Magnetic Resonance Analysis of Reaction Mix[illegible] from the Reaction of Dibenzobicyclic Alcohols with Thionyl Chloride.

The products from the reaction of the dibenzobicyclic alcohols are all known compounds except *endo*-4-chlorodibenzobicyclo[3.2.1]octadiene (33). The nmr spectra for the [2.2.2] chloride, 15, and the *exo*-[3.2.1] chloride, 14, have been reported (22,25). Integration ratios of three characteristic protons were ascertained to establish the ratios of the three chlorides: τ 4.48, *exo*-H_4 of *endo*-4-chlorodibenzobicyclo[3.2.1] (33) (see discussion p.144 for structure assignment), τ 5.00 *endo*-H_4 of *exo*-4-chlorodibenzobicyclo[3.2.1]octadiene (14), and τ 5.70, H_1 of 7-chlorodibenzobicyclo[2.2.2]octadiene (15). In each reaction it was found that the sum of the integration of these protons was equal to one proton based on the magnitude of one-eighth of the integration of the 8 aromatic protons. A spectrum of pure

7-chlorodibenzobicyclo[2.2.2]octadiene (15) is given in Figure 1. *Endo*- and *exo*-4-chlorodibenzobicyclo[3.2.1]-octadiene (33 and 14) could not be separated. A spectrum of a mixture of pure *endo*- and *exo*-[3.2.1] chlorides is also given (Figure 2). Standard solutions of [2.2.2] chloride and [3.2.1] chlorides were prepared and their nmr (CCl_4) spectra taken: Figure 3 shows the spectrum of a 50:50 mixture of [2.2.2] chloride, 15, and a mixture of *exo*- and *endo*-[3.2.1] chlorides, 14 and 33; Figure 4 shows a mixture of 95% *exo*- and *endo*-[3.2.1] chlorides, 14 and 33, and 5% [2.2.2] chloride, 15. Figure 5 shows a mixture of 95% [2.2.2] chloride, 15, and 5% of a mixture of *exo*- and *endo*-[3.2.1] chlorides, 14 and 33. From the spectra of the 95:5 mixtures it could be deduced that it was possible to detect <2% of a mixture of 13 and 33 or <5% of 15, in a mixture of the three monochlorides. The reproducibility of the spectral analysis was estimated as >98% from multiple analysis of the same mixtures.

Reaction of dibenzobicyclo[2.2.2]octadien-2-ol (13) with thionyl chloride in toluene - Into a 100 ml three-necked round-bottomed flask fitted with a dropping funnel, a magnetic stirring bar, a reflux condenser and a drying tube was added a solution of 2.48 g (0.02 mole) of freshly purified thionyl chloride in 25 ml of purified toluene. A solution of 0.706 g (0.0032 mole) of dibenzobicyclo[2.2.2]octadien-2-ol in 20 ml of purified toluene was added slowly from the dropping funnel. The resulting solution was stirred at room temperature for 12 hours and then allowed to reflux for an additional 1.5 hours. The excess thionyl chloride was subsequently distilled from the mixture at atmospheric pressure, and the distillation continued until the volume was reduced to 15 ml. The remaining solution was allowed to cool to room temperature and washed twice with saturated aqueous sodium bicarbonate solution and twice with water. The organic layer was dried over anhydrous magnesium sulfate. After the solvent was removed using a rotary vacuum evaporator 0.77 g (101%) of a faintly yellow oily residue was obtained. The residue was dissolved in carbon tetrachloride and an infrared spectrum was taken to show the absence of unreacted alcohol. An nmr spectrum of the same solution revealed the following characteristic peaks of the chlorides at τ 4.68 (exo-H_4 of 33, 4%), 5.00 (endo-H_4 of 14, 14%) and 5.70 (H_1 of 7-chlorodibenzobicyclo[2.2.2]octadiene (15), 82%). The reaction product was chromatographed using Fisher acid washed alumina/n-pentane. Elution was initially carried out with n-pentane and then the polarity of the solvent was slowly increased. No product was realized until carbon tetrachloride was used as the eluting solvent. Fractions 3-8 contained a total of 0.56 g (73%), of 7-chlorodibenzobicyclo[2.2.2]octadiene; mp 111.5 - 113°, (lit. mp 112 - 113° (17)); ir ν_{C-Cl} 620 cm^{-1} (characteristic band of 7-chlorodibenzobicyclo[2.2.2]-octadiene); nmr (CCl_4), identical with that reported for this compound (25).

Anal. Calcd for $C_{16}H_{13}Cl$: C, 79.82; H, 5.44; Cl, 14.73. Found: C, 79.52; H, 5.31; Cl, 14.84. No further chloride product was isolated. It was found that under certain reaction conditions the [3.2.1] chlorides hydrolyzed to [3.2.1] alcohols on the chromatography column. Elution with chloroform gave fractions 11 and 12 which contained 0.140 g (19%) of a compound (118 - 119°) whose infrared and proton magnetic spectrum was identical to that of authentic dibenzobicyclo[3.2.1]octadien-exo-2-ol.

The three monochlorides 14, 15, and 33 were subjected to the conditions of the isolation and analysis of the reaction mixture and were found to be stable.

Reaction of [2.2.2] alcohol, 13, with thionyl chloride in dioxane - Into a three-necked round-bottomed flask, fitted with a dropping funnel, a magnetic stirring bar, a reflux condenser and a drying tube, was placed a solution of 2.98 g (0.025 mole) of freshly purified thionyl chloride in 25 ml of purified dioxane. A solution of 0.505 g (0.0023 mole) of dibenzobicyclo-[2.2.2]octadien-2-ol in 15 ml purified dioxane was slowly added from the dropping funnel. The resulting solution, after being allowed to stir for 12 hours at room temperature, was heated to reflux for an additional 1.5 hours. The excess thionyl chloride was distilled from the reaction mixture at atmospheric pressure, and the volume reduced to 20 ml by further distillation. The solution was transferred to a separatory funnel and water was added until no more precipitate formed. After extraction with carbon tetrachloride the organic layer was washed twice with saturated sodium bicarbonate and twice with water. The organic layer was dried over anhydrous magnesium sulfate, and after rotary vacuum evaporation of solvent 0.49 g (90%) of a faintly yellow, oily residue remained. The infrared spectrum (CCl_4) showed that no unreacted alcohol was present in the reaction mixture, and that the characteristic absorption band at 620 cm^{-1} of 7-chlorodibenzobicyclo[2.2.2]octadiene, was weak. The nmr spectrum of the same solution revealed the following percentages of chlorides: τ 4.68 (<u>exo</u>-H_4 of <u>endo</u>-4-chlorodibenzobicyclo[3.2.1]octadiene, 15%), 5.00 (<u>endo</u>-H_4 of <u>exo</u>-4-chlorodibenzobicyclo[3.2.1]octadiene, 60%) and 5.70 (H_1 of 7-chlorodibenzobicyclo[2.2.2]octadiene, 25%). The reaction mixture was chromatographed on alumina packed in Skelly B. Elution with 50/50 pentane/carbon tetrachloride (fractions 1-23) yielded a total of 0.136 g (28%) of the [2.2.2] chloride, <u>15</u>.

Elution with chloroform gave 0.211 g (47%) of an alcohol whose infrared spectrum in carbon tetrachloride was identical to that of dibenzobicyclo[3.2.1]octadien-*exo*-2-ol (29).

The three chlorides 14, 15, and 33 were subjected to the work-up and analysis conditions employed in the reaction of the bicyclic alcohols with thionyl chloride in dioxane and were found to be stable.

Reaction of [2.2.2] alcohol, 13, with neat thionyl chloride - Into a 50 ml three-necked round-bottomed flask, fitted with a magnetic stirrer, reflux condenser and a calcium chloride drying tube, was added 10 ml (0.140 mole) of pure thionyl chloride. The flask was cooled in an ice bath to 0°, and 1.50 g (0.0068 mole) of the alcohol, 13, was added. The solution was allowed to stir at room temperature for 12 hours and then heated to reflux for 1.5 hours. Subsequently, the excess thionyl chloride was distilled at reduced pressure and the resultant oily residue was dissolved in 10 ml carbon tetrachloride. The solution was washed with saturated sodium bicarbonate, then with water and subsequently dried over anhydrous magnesium sulfate. After evaporation of the organic solvent at 3 mm Hg, 1.58 g (97%) of a colorless, oily residue remained. An infrared spectrum in carbon tetrachloride showed that there was no unreacted alcohol, and it also showed a small absorption band at 620 cm^{-1}, characteristic for 7-chlorodibenzobicyclo[2.2.2]chloride. The nmr analyzed for the following ratios of the three chlorides: τ 4.68 (exo-H_4 of [3.2.1] chloride, 33, 25%), (endo-H_4 of [3.2.1] chloride, 14, 69%) and 5.70 (H_1 of [2.2.2] chloride, 15, 6%). The reaction mixture was recrystallized from purified n-hexane to yield a white crystalline solid (92%) whose infrared spectrum was the same as that of the crude reaction mixture.

Anal. Calcd for $C_{16}H_{13}Cl$: C, 79.83; H, 5.44; Cl, 14.73. Found: C, 80.01; H, 5.59; Cl, 14.88.

Chlorides 14, 15 and 33 were found to be stable to the work-up and analysis conditions employed in this reaction.

Reaction of dibenzobicyclo[2.2.2]octadien-2-ol with neat thionyl chloride and added water - Into a 50 ml three-necked round-bottomed flask, fitted with a magnetic stirring bar, and a reflux condenser were added 3 ml (0.042 mole) of pure thionyl chloride and 0.043 g (0.0024 mole) of water. The solution was cooled to 0° in an ice bath, and then 0.246 g (0.0011 mole) of the [2.2.2] alcohol, 13, was added. The solution was stirred at room temperature for 12 hours followed by 1.5 hours heating at reflux. After the reaction period the excess thionyl chloride was distilled under reduced pressure. The remaining oily residue was dissolved in

10 ml carbon tetrachloride and the organic solution was washed with saturated sodium bicarbonate and then with water, and dried over anhydrous magnesium sulfate. After removal of the solvent 0.265 (100%) of a colorless oily residue remained. The infrared spectrum in carbon tetrachloride showed no unreacted alcohol, and a moderately strong absorption band at 620 cm^{-1}. The nmr spectrum of the same solution showed three chlorides: τ 4.68 (*exo*-H_4 of 33, 20%), 5.00 (*endo*-H_4 of 14, 50%) and 5.70 (H_1 of 15, 30%).

The chloride products formed in this reaction were shown to be stable to the work-up and analysis conditions employed in this reaction.

Reaction of dibenzobicyclo[2.2.2]octadien-2-ol with neat thionyl chloride and added pyridine - Into a 50 ml three-necked round-bottomed flask, fitted with a magnetic stirring bar, a reflux condenser and drying tube was added 3 ml (0.042 mole) of thionyl chloride and the solution cooled to 0°. Then 0.077 g (0.00097 mole) of purified pyridine, and 0.215 g (0.00097 mole) of alcohol 13 were added in rapid succession. The solution was stirred at room temperature for 12 hours and then heated at reflux for 1.5 hours. After the reaction period the excess thionyl chloride was evaporated at reduced pressure. The oily residue was dissolved in carbon tetrachloride and the organic solution was washed with 10% hydrogen chloride, saturated sodium bicarbonate and finally with water. The organic layer was dried over anhydrous magnesium sulfate and after evaporation of the solvent at reduced pressure, 0.226 g (97%) of a yellow oily residue remained. The infrared spectrum in carbon tetrachloride showed complete reaction of the alcohol and no absorption band at 620 cm^{-1}. The nmr spectrum showed two chlorides: τ 4.68 (exo-H$_4$ of <u>33</u>, 11%) and 5.00 (endo-H$_4$ of <u>14</u>, 89%).

Similar reactions were undertaken with the bases N,N-diisopropylethylamine and 1,8-bis (dimethylamino)-naphthalene, instead of pyridine. The results of these experiments are summarized in Table 5. In each case the chloride products formed were shown to be stable to the conditions of the isolation and analysis used in this reaction.

<u>Reaction of dibenzobicyclo[2.2.2]octadien-2-ol (13) with thionyl chloride in toluene and added pyridine</u> - The procedure for this reaction was analogous to that employed in the reaction of the [2.2.2] alcohol, <u>13</u>, with thionyl chloride in toluene. A solution of 0.217 g (0.00098 mole) of the [2.2.2] alcohol, <u>13</u>, in 20 ml of pure toluene and 0.077 g (0.00098 mole) of dry pyridine was allowed to react with 0.75 ml (0.01 mole) of thionyl chloride. The reaction gave a crude yield of 0.225 g

(96%); ir (CCl_4): no absorption in the hydroxyl region and no absorption band at 620 cm^{-1} was found; nmr (CCl_4) τ 4.68 (exo-H_4 of 33, 19%) and 5.00 (endo-H_4 of 14, 81%).

Both exo and endo-[3.2.1] chlorides, formed in this reaction, were shown to be stable to the conditions of the isolation and analysis used in this reaction.

The results of repeated experiments of dibenzobicyclo[2.2.2]octadien-2-ol with thionyl chloride, under the reaction conditions described above, are listed in Tables 2-5.

Reaction of cis-3-deuteriodibenzobicyclo[2.2.2]octadien-2-ol (31) with thionyl chloride in toluene - The procedure for this reaction of alcohol with thionyl chloride in toluene was the same as that described for the non-deuterated analog. A total of 0.300 g (0.0013 mole) of the alcohol, 31, was allowed to react with 2.98 g (0.0025 mole) of thionyl chloride in 20 ml toluene. A crude yield of 0.28 g (89%) of a faintly yellow oily residue was isolated. The infrared spectrum in carbon tetrachloride showed the absence of unreacted alcohol, and a band at 620 cm^{-1}. An nmr spectrum of the same solution showed absorption at τ 4.68 (exo-H_4 of 36, 10%), 5.00 (endo-H_4 of 35, 30%) and 5.70 (H_1 of 8-deuterio-7-chlorodibenzobicyclo[2.2.2]octadiene (34), 60%)).

Reaction of cis-3-deuteriodibenzobicyclo[2.2.2]-octadien-2-ol (31) with thionyl chloride in dioxane - The procedure for the reaction of compound, 31, with thionyl chloride in dioxane was the same as that described for the non-deuterated analog. The alcohol (1.0 g, 0.0044 mole) was allowed to react with 3.3 g (0.028 mole) of purified thionyl chloride in 60 ml purified dioxane. A total of 1.06 g (100%) of a faintly yellow oily residue was isolated. An infrared spectrum in carbon tetrachloride showed no alcohol absorption and a weak band at 620 cm^{-1}. An nmr spectrum (CCl_4) of the sample showed the following percentages of the three chlorides: τ 4.68 (exo-H_4 of 36, 16%), 5.00 (endo-H_4 of 35, 68%) and 5.70 (H_1 of 34, 16%). The HR-100 nmr spectrum (CCl_4), showed that the deuterium atom was cis to the chlorine in the [2.2.2] chloride, 34, and that it occupied the syn-8-position in exo- and endo-[3.2.1] chlorides, 35 and 36.

Reaction of cis-3-deuteriodibenzobicyclo[2.2.2]-octadien-2-ol (31) with neat thionyl chloride - The procedure for this reaction was analogous to that of the undeuterated alcohol. A total of 0.120 g (0.00054 mole) of cis-3-deuteriodibenzobicyclo[2.2.2]octadien-2-ol was allowed to react with 2 ml (0.03 mole) purified thionyl chloride, to yield 0.121 g (93%) of a colorless oily residue. The infrared spectrum in carbon tetrachloride showed the absence of both the hydroxyl absorption band, and the absorption band at 620 cm^{-1}. The nmr spectrum of the same solution showed that only two chlorides had formed: τ 4.68 (<u>exo</u>-H$_4$ of <u>36</u>, 14%), and 5.00 (<u>endo</u>-H$_4$ of <u>35</u>, 86%). Two coupling constants for the H$_8$ proton were found <u>anti</u> $J_{1,8}$ = 4 cps, <u>anti</u> $J_{5,8}$ = 4 cps. This was consistent with the <u>syn</u> position of the deuterium The reaction mixture was subjected to column chromatography on Woelm neutral alumina/carbon tetrachloride. Elution with carbon tetrachloride gave 35 mg (29%) of the unrearranged chloride <u>cis</u>-7-chloro-8-deuteriodibenzobicyclo[2.2.2]octadiene (<u>34</u>) (as evidenced by ir and nmr). The nmr spectrum in carbon tetrachloride of this compound showed no signal at τ 8.25 due to the <u>cis</u>-H$_8$ proton. Two coupling constants were observed for the <u>trans</u>-H$_8$ proton, $J_{4,8}$ = 2.5 cps and as $J_{7,8}$ = 8.0 cps. This was again consistent with the <u>cis</u> assignment of the deuterium atom. Elution with chloroform yielded 58 mg (52%) of product whose infrared spectrum in deuteriochloroform showed strong absorption in the hydroxyl region. The nmr spectrum of this solution was compatible with a mixture of 8-deuteriodibenzobicyclo[3.2.1]octadien-<u>exo</u>- and <u>endo</u>-2-ol. By analogy with the nmr spectra of the undeuterated [3.2.1] alcohols <u>29</u> and <u>30</u>, reported by Cristol, the following assignments for the compounds of this fraction were made; syn-8-deuteriodibenzobicyclo[3.2.1]octadien-exo-2-ol, 65% and syn-8-deuteriodibenzobicyclo[3.2.1]octadien-endo-2-ol, 35%.

Reaction of exo- and endo-[3.2.1] alcohols, 29 and 30, with thionyl chloride - Both dibenzobicyclo[3.2.1]octadien-exo- and endo-2-ol, 29 and 30, were allowed to react with thionyl chloride under the same reaction conditions used for the reactions of dibenzobicyclo[2.2.2]octadien-2-ol (13). In each reaction of the [3.2.1] alcohols, the product distributions were similar to those obtained from the reactions of the [2.2.2] alcohol, 13, with thionyl chloride. The results of the reaction of exo- and endo-[3.2.1] alcohols, 29 and 30, with a 10 molar excess of purified thionyl chloride in toluene, are listed in Table 2; the results of the same reaction in dioxane are contained in Table 3. The results from the reaction of these two alcohols with a 10 molar excess of thionyl chloride in toluene and an equimolar amount of amine base added are listed in Table 4. The results from the reaction of the [3.2.1] alcohols with neat thionyl chloride, neat thionyl chloride and 0.0024 moles of water added, and neat thionyl chloride with a molar amount of an amine base added, are contained in Table 5.

Reaction of n-propyl alcohol with thionyl chloride in toluene and a molar amount of a mixture of exo- and endo- [3.2.1] chlorides added - A mixture of [3.2.1] chlorides was shown by nmr to consist of 75% exo- [3.2.1] chloride, 14, and 25% endo- [3.2.1] chloride, 33. The amplified spectrum of a carbon tetrachloride solution of these chlorides could not detect the presence of the [2.2.2] chloride, 15. The infrared spectrum of the same solution did not exhibit an absorption band at 620 cm^{-1}. A 2% solution of 7-chlorodibenzobicyclo[2.2.2]octadiene in carbon tetrachloride gave rise to a weak absorption band at 620 cm^{-1}. Into a 50 ml three-necked round-bottomed flask, fitted with a reflux condenser, a magnetic stirring bar, a dropping funnel and a drying tube, were added 10 ml of purified toluene and 0.45 g (0.0038 mole) of purified thionyl chloride. From the dropping funnel was added a solution of n-propyl alcohol (0.0348 g, 0.00047 mole) and 0.112 g (0.00047 mole) of a mixture of exo- and endo- [3.2.1] chlorides, in 5 ml purified toluene. The reaction mixture was allowed to stir at room temperature for 12 hours and then heated at reflux for 1.5 hours. The excess thionyl chloride was removed by distillation at atmospheric pressure, and the total volume of the solution reduced to 10 ml. The organic solution was washed with saturated sodium bicarbonate, twice with water and then dried over anhydrous magnesium sulfate. After evaporation of the solvent at reduced pressure, 0.107 g (94%) of a yellow oily residue remained: nmr (CCl_4); τ 4.68 (<u>exo</u>-H_4 of <u>33</u>, 25%), 5.00 (<u>endo</u>-H_4 of <u>14</u>, 55%) and 5.70 (H_1 of <u>15</u>, 20%).

An authentic mixture of [3.2.1] chlorides when subjected to the same work-up conditions employed in this reaction, gave an nmr spectrum (CCl_4) unchanged from that of the starting mixture.

Quantitative Infrared Analysis of the Reaction Mixture from the Reaction of n-Propyl Alcohol with Thionyl Chloride in Toluene, with a Molar Amount of a Mixture of [3.2.1] Chlorides Added.

The amount of the [2.2.2] chloride, <u>15</u>, formed in this reaction was determined by differential quantitative infrared analysis, according to the method described by Cristol, Arganbright and Tanner (18b). The region between 500 and 700 cm^{-1} of the infrared spectrum was scanned using a Beckmann IR-11 spectrophotometer. Potassium bromide optics were employed to obtain the desired frequency range. A characteristic absorption band at 620 cm^{-1} was observed for the [2.2.2] chloride, <u>15</u>. This absorption band was absent in the infrared spectrum of the mixture of the [3.2.1] chlorides, <u>14</u> and <u>33</u>. The presence of the absorption band at 620 cm^{-1} in the infrared spectrum of the reaction mixture of the rearrangement experiment, indicated that the [2.2.2] chloride, 15, had formed during the course of the reaction.

The experimental rearrangement reaction mixture, 0.134 M in carbon tetrachloride, was compared with authentic mixtures in the following manner: each of a matched pair of 0.5 mm potassium bromide cells was filled with a sample of one of the authentic mixtures and the rearrangement reaction mixture, respectively. The authentic mixture was placed in the sample beam of the spectrophotometer, and the experimental reaction mixture was placed in the reference beam of the spectrophotometer, and the resultant spectrum was taken. This process was repeated until the most nearly straight line (i.e., at constant T, where $T = I/I_o$) was obtained. The authentic mixture containing 20% of the [2.2.2] chloride, 15, and 80% of a mixture of the [3.2.1] chlorides, 14 and 33, when compared in this manner with the experimental rearrangement reaction mixture, gave relatively no deviation from the most nearly straight line. This analytical method could detect the presence of 2% [2.2.2] chloride.

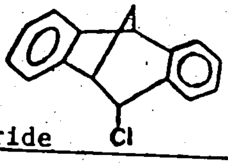
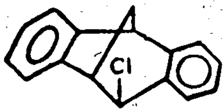
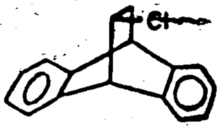
The presence of 20% of the [2.2.2] chloride in the experimental reaction mixture was also confirmed by measurement of the area of the absorption band at 620 cm^{-1}. Both the authentic mixture (20% [2.2.2] chloride), and the experimental reaction mixture were scanned against pure carbon tetrachloride, giving rise to an absorption band at 620 cm^{-1}. The areas of the 620 cm^{-1} absorption band from both solutions were the same within the limits of experimental error.

Similar reactions, as the one described for _n_-propyl alcohol, were carried out with allyl and _tert_-butyl alcohol. The results of these experiments are listed in Table 7.

Reaction of dibenzobicyclo[3.2.1]octadien-exo-2-ol (29) with thionyl chloride in toluene with a molar amount of a mixture of [3.2.1] chlorides added - The _exo_-[3.2.1] alcohol, _29_, (0.082 g, 0.00037 mole) was dried in a vacuum oven for 24 hrs at 90°, and subsequently allowed to react with 0.11 g (0.00092 mole) of freshly purified thionyl chloride in 10 ml purified toluene and 0.089 g (0.00037 mole) of a mixture of _exo_- and _endo_- [3.2.1] chlorides added, according to the procedure normally employed for the reaction of an alcohol with thionyl chloride in toluene. The mixture of [3.2.1] chlorides used in this reaction was shown by nmr to be free of any [2.2.2] chloride, _15_. It consisted of 19% _endo_-[3.2.1] chloride (_33_) and 81% of _exo_- [3.2.1] chloride (_14_). A total of 0.175 g (98%), of reaction product was isolated. An HR-100 amplified spectrum of the reaction mixture revealed the following product distribution: _endo_- [3.2.1] chloride, _33_ , 6%, _exo_- [3.2.1] chloride, _14_ , 18% and [2.2.2] chloride, _15_ , 76%.

TABLE 7

Reaction of Allyl or *tert*-Butyl Alcohol with Thionyl Chloride in Toluene, with a Molar Amount of [3.2.1] chlorides Added.[a]

Alcohol[b] Moles	$SOCl_2$ Moles	[3.2.1] Chlorides Moles *exo*-, *endo*-, %	Yield % of recovered chloride	Product Distribution, % 	 	 
Allyl 0.00069	0.007	0.00069 *exo*-, 79 *endo*-, 21	97	19	66	15
tert-Butyl[c] 0.00026	0.002	0.00026 *exo*-, 79 *endo*-, 21	96	21	64	15
tert-Butyl 0.00033	0.003	0.00033 *exo*-, 79 *endo*-, 21	97	21	59	20
tert-Butyl 0.00026	0.0026	0.00026 *exo*-, 88 *endo*-, 12	97	11	33	56
tert-Butyl 0.00028	0.0028	0.00028 *exo*-, 88 *endo*-, 12	97	13	31	56

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[a] The reaction conditions were the same as those normally employed for the reaction of alcohol with thionyl chloride in toluene (stir at room temperature for 12 hours, reflux for 1.5 hours).

[b] The alcohols were purified by distillation from sodium metal, except where indicated otherwise.

[c] Crude *tert*-butyl alcohol was used.

Reaction of n-propyl alcohol with thionyl chloride in toluene with molar amounts of exo- and endo- [3.2.1] chlorides, 14 and 33, and pyridine - The procedure for this reaction was the same as that of the reaction of alcohols with thionyl chloride in toluene. A mixture of [3.2.1] chlorides was shown by nmr analysis to be a mixture of exo (83%) and endo (17%). The infrared spectrum (CCl_4) and the HR-100 amplified nmr spectrum of the same solution showed that within the limits of detectability (<5%), no 7-chlorodibenzobicyclo[2.2.2]octadiene was contained in the reaction mixture. n-Propyl alcohol (0.046 g, 0.00076 mole) was allowed to react with 0.99 g (0.0083 mole) thionyl chloride, in the presence of 0.059 g (0.00076 mole) pyridine and 0.182 g (0.00076 mole) of the mixture of the [3.2.1] chlorides (14 and 33), in 15 ml purified toluene. After the reaction and work-up procedure, outlined previously, 0.180 g (99%) of a yellow oily residue remained. The infrared spectrum in carbon tetrachloride of the reaction product was identical to that of the starting material, and there was no absorption band at 620 cm^{-1}, characteristic of 7-chlorodibenzobicyclo[2.2.2]octadiene. An HR-100 nmr analysis of the same solution could not detect any [2.2.2] chloride, and it was found that the ratio of exo/endo [3.2.1] chloride had not changed under these reaction conditions: nmr (CCl_4) τ 4.68 (exo-H_4, 17%) and 5.00 (endo H_4, 83%).

Reaction of n-propyl alcohol with neat thionyl chloride and a molar amount of exo- and endo- [3.2.1] chorides, 14 and 33 - The mixture of [3.2.1] chlorides was analyzed by nmr and was shown to consist of 83% exo- [3.2.1] chloride, 14, and 17% endo- [3.2.1] chloride, 33, before the reaction. n-Propyl alcohol 0.043 g (0.00072 mole) was allowed to react in 3 ml (0.042 mole) of neat thionyl chloride an .160 g, (0.00072 mole) of the mixture of [3.2.1] chlorides. A yellow oily residue (0.160 g, 100%) was isolated. The infrared and nmr spectra in carbon tetrachloride were identical to those of the starting mixture of [3.2.1] chlorides.

Reaction of n-propyl alcohol with thionyl chloride in dioxane with a molar amount of 7-chlorodibenzobicyclo-[2.2.2]octadiene (15) added - This reaction was carried out in the same manner as the reactions of alcohols with thionyl chloride in dioxane. n-Propyl alcohol (0.125 g, 0.0021 mole) was allowed to react with 1.23 g (0.0104 mole) of purified thionyl chloride in 30 ml of purified dioxane with 0.500 g (0.0021 mole) of [2.2.2] chloride, 15, added. A white crystalline material (0.470 g, 94%), was reisolated. The infrared and nmr spectra in carbon tetrachloride were identical to those of authentic 7-chlorodibenzobicyclo[2.2.2]octadiene (15); mp 112.5 - 114°, mixture mp 112.5 - 114°.

Reaction of dibenzobicyclo[3.2.1]octadien-*exo*-2-ol (29) with 50 mole percent of thionyl chloride in toluene - A total of 0.246 g (0.00108 mole) of *exo*- [3.2.1] alcohol, 29, was allowed to react with 0.066 g (0.00055 mole) of purified thionyl chloride under the reaction conditions normally employed for the reaction of alcohol with thionyl chloride in toluene. A total of 0.245 g (96%) of reaction product was isolated. The nmr spectrum (CCl_4) of the crude mixture showed characteristic absorption bands for *exo*- [3.2.1] alcohol, 29, at τ 5.60, 6.22 and 6.69, and for the [2.2.2] chloride, 15, at τ 5.70 and 8.25. The amplified spectrum showed no absorption at τ 8.82, characteristic for the [2.2.2] alcohol, 13. The reaction mixture was chromatographed using Woelm neutral alumina/carbon tetrachloride. The fraction eluted with 50/50 carbon tetrachloride/chloroform (0.118 g, 96%) was isolated and analyzed. The infrared and nmr spectra ($CDCl_4$) were identical to those of authentic dibenzobicyclo[3.2.1]-octadien-*exo*-2-ol.

Reaction of dibenzobicyclo[2.2.2]octadien-2-ol (13) with 50 mole percent thionyl chloride in toluene - The [2.2.2] alcohol, 13, (0.190 g, 0.00086 mole) was allowed to react with thionyl chloride (0.05 g, 0.00045 mole) in 15 ml toluene, in the same manner as the reactions with excess thionyl chloride. The nmr spectrum of the reaction mixture (0.223 g) showed the following product distribution: exo- and endo-[3.2.1] chlorides, 14 and 33, (21%); dialkyl sulfite, 32, (25%); [2.2.2] alcohol, 13, (54%). A column chromatography of the reaction mixture, using Woelm neutral alumina/carbon tetrachloride, led to isolation of 0.139 g of dibenzobicyclo[2.2.2]octadien-2-ol (13), as shown by ir, nmr and mixture melting point.

Attempted Isolation of Intermediates from the Reaction of Dibenzobicyclo[2.2.2] and [3.2.1]octadienyl Alcohols with Thionyl Chloride under Various Reaction Conditions.

Bis-dibenzobicyclo[2.2.2]octadien-2-yl-sulfite (32) - Into a 50 ml three-necked round-bottomed flask fitted with a pressure equalizing dropping funnel, reflux condenser, magnetic stirring bar and a drying tube, was added 0.436 g (0.002 mole) of pure dibenzobicyclo-[2.2.2]octadien-2-ol (13) in 25 ml of purified toluene. The solution was cooled to 0° and from the dropping funnel was slowly added 1.5 ml (0.021 mole) of freshly purified thionyl chloride in 5 ml toluene. The mixture was allowed to stir for two hours, while the temperature gradually rose to 25°. Subsequently the solvent was removed by vacuum distillation, and 0.490 g (88%) of a white crystalline solid remained. The compound was recrystallized several times from pentane/carbon tetrachloride, to yield pure bis-dibenzobicyclo[2.2.2]octadien-2-yl-sulfite, 32: mp 159 - 161°; ir ($CDCl_3$) $\nu_{S=O}$ 1200 cm^{-1}, ν_{S-O} 710 - 805 cm^{-1} (broad band); nmr ($CDCl_3$) τ 2.50 - 3.18 (multiplet, 8H, aromatic), 5.1 - 5.54 (broad multiplet, 1H), 5.60 - 6.30 (broad multiplet, 2H), 7.60 - 8.20 (broad multiplet, 1H) and 8.36 - 9.33 (broad multiplet, 1H).

Anal. Calcd for $C_{32}H_{26}O_3S$; C, 78.34; H, 5.34. Found: C, 78.18; H, 5.44.

The sulfite, 32, was reduced with lithium aluminum hydride in an ether solution. The sole product isolated in 90% yield was dibenzobicyclo[2.2.2]octadien-2-ol (13). The structure of the alcohol was established by a comparison of its infrared and nmr spectrum with that of authentic [2.2.2] alcohol, 13, and by its mixture melting point, which was not depressed. An attempted purification of the sulfite, 32, by column chromatography (Woelm neutral alumina/carbon tetrachloride, and carbon tetrachloride/chloroform as the eluting solvent), resulted in the hydrolysis of the sulfite to yield the same alcohol as in the lithium aluminum hydride reduction reaction above (ir, nmr, mmp).

Various reaction conditions were employed in an attempt to synthesize the dialkyl sulfite or alkyl chlorosulfite from both alcohols 13 and 29. The results of these reactions are listed in Table 8.

TABLE 8

Attempted Preparations of Dibenzobicyclic Dialkyl Sulfites [a,b]

Alcohol Substrate	Reaction Conditions	Sulfite % Yield	Other Products Yield
13	$SOCl_2$/toluene pyridine [c], 0-25° [d] 2 hours	63	*exo*-[3.2.1]chloride, 14, (26%) *endo*-[3.2.1]chloride, 33, (11%)
13	$SOCl_2$/dioxane 0-25°, 2 hours	60	[2.2.2]alcohol, 13, (40%)
13	$SOCl_2$/dioxane 0-25°, 4 hours	100	—
13	$SOCl_2$ (2 ml) 0-25°, 4 hours	10	*exo*-[3.2.1]chloride, 14, (84%) *endo*-[3.2.1]chloride, 33, (6%)
13	$SOCl_2$/diethyl ether, 0-25° 2 hours	39	*exo*-[3.2.1]chloride, 14, (46%) *endo*-[3.2.1]chloride, 33, (15%)
29	$SOCl_2$/toluene 0-25°, 2 hours	—	*exo*-[3.2.1]chloride, 14, (81%) *endo*-[3.2.1]chloride, 33, (19%)

(continued.......)

TABLE 8 (continued)

29	$SOCl_2$/dioxane 0-25°, 2 hours	—	exo-[3.2.1]chloride, 14, (21%) endo-[3.2.1]chloride, 33, (6%) exo-[3.2.1]alcohol, 29, (73%)
29	$SOCl_2$/diethyl ether, 0-25° 2 hours	—	exo-[3.2.1]chloride, 14, (89%) endo-[3.2.1]chloride, 33, (1%)

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[a] A 10 molar excess of thionyl chloride was allowed to react with 0.07 M solutions of the bicyclic alcohols in various solvents, except where neat thionyl chloride was used.

[b] The product ratios were determined by nmr.

[c] A molar amount of pyridine was added.

[d] The reactants were added at 0° and then the reaction mixture gradually warmed to 25°.

Decomposition Reactions of Bis-dibenzobicyclo[2.2.2]-octadien-2-yl-sulfite (32).

Into a 50 ml three-necked round-bottomed flask, fitted with a reflux condenser, a magnetic stirring bar and a drying tube was added 35 mg (0.122 mmole) of the sulfite, 32, in 25 ml purified toluene. The solution was heated at reflux for 2 hours. The solvent was removed by vacuum distillation, and 33 mg (94%) of a solid crystalline material was isolated. The infrared and nmr spectra in $CDCl_3$, were identical to those of the starting material, 32; mixture melting point 158 - 161°.

The above reaction was repeated while dry hydrogen chloride was slowly bubbled through the solution. Again, spectral analysis showed that the dialkyl sulfite had not reacted under these reaction conditions.

Reaction of Bis-dibenzobicyclo[2.2.2]octadien-2-yl-sulfite with thionyl chloride - Two ml (0.03 mole) of purified thionyl chloride was cooled to 0° in a round-bottomed flask fitted with a magnetic stirring bar, a reflux condenser and a calcium chloride drying tube. To the thionyl chloride was then added 67 mg (0.235 mmole) of the sulfite, 32. The solution was stirred for two hours while the temperature gradually rose to 25°. After this reaction period the excess thionyl chloride was removed by vacuum distillation. An nmr spectrum ($CDCl_3$)

showed the reaction product to be a mixture of exo-4-chlorodibenzobicyclo[3.2.1]octadiene (14), (40%), endo-4-chlorodibenzobicyclo[3.2.1]octadiene (33), (10%), and unreacted bis-dibenzobicyclo[2.2.2]octadien-2-yl-sulfite (32), (50%). This reaction mixture was subsequently allowed to react with thionyl chloride at its refluxing temperature for 0.5 hours. Nmr analysis of the reaction mixture showed the following product distribution: exo- [3.2.1] chloride, 14, (54%), endo- [3.2.1] chloride, 33, (13%) and dialkyl sulfite, 32, (33%).

Chromatographic purification of a mixture of [3.2.1] chlorides, 14 and 33 employing Silica Gel - A mixture of [3.2.1] chlorides was shown by nmr to consist of 12% endo-[3.2.1] chloride, 33, and 88% exo-[3.2.1] chloride, 14. A total of 1.68 g (0.007 mole) of this mixture was chromatographed using 1000 g of Silica Gel (Woelm activity grade 1) packed in carbon tetrachloride. The fractions eluted with carbon tetrachloride (1.24 g, 83%) were shown by nmr and infrared to be 7-chlorodibenzobicyclo[2.2.2]octadiene (15). Elution with ethyl acetate gave rise to 0.195 g (13%) of a 50:50 mixture of [3.2.1] alcohols, 29 and 30.

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