PART I
STUDY OF SOME ISOMERS OF THE 1, 1-SPIROCYCLOHEXANE-Δ^4-TETRAHYDROINDAN-3-ONE SYSTEM

PART II
INVESTIGATION OF THE THERMAL AND FREE RADICAL REACTIONS OF PHENYL SUBSTITUTED OXIRANES

Thesis for the Degree of Ph. D.
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Ronald Weiss
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Part I: Study of Some Isomers of the 1, 1-Spirocyclohexane-Δ^4-tetrahydroindane-3-one System
Part II: Investigation of the Thermal and Free Radical Reactions of Phenyl Substituted Oxiranes

presented by

Ronald Weiss

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William H. Reusch
Major professor

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ABSTRACT

PART I

STUDY OF SOME ISOMERS OF THE 1,1-SPIROCYCLOHEXANE-Δ^4-TETRAHYDROINDANE-3-ONE SYSTEM

by Ronald Weiss

Marvel's cyclization products have been reinvestigated and shown unequivocally to have the same carbon skeletons, and previous structural assignments are incorrect and must be reversed.

PART II

INVESTIGATION OF THE THERMAL AND FREE RADICAL REACTIONS OF PHENYL SUBSTITUTED OXIRANES

by Ronald Weiss

Four phenyl substituted oxiranes (i.e., styrene oxide, trans-stilbene oxide, α-methyl-trans-stilbene oxide and tetraphenylethylene oxide) were studied at high temperatures ($T > 150^\circ$). They were investigated as neat samples and with the free radical initiators tertiary butyl hydroperoxide and 2,4,4-trimethyl-2-formylcyclopentanone.

Some of the earlier work reported on these oxiranes was reinvestigated and the results clarified.

None of the oxiranes studied showed a true unimolecular thermal reaction.

Substitution of phenyl groups on the oxirane ring retards radical abstraction of benzylic hydrogens.

The product of surface reactions were explained in terms of mild acid catalysis by Lewis acid sites on the Pyrex glass surface.

PART I

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PART II

INVESTIGATION OF THE THERMAL AND FREE RADICAL REACTIONS OF PHENYL SUBSTITUTED OXIRANES

By

Ronald Weiss

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To Tante

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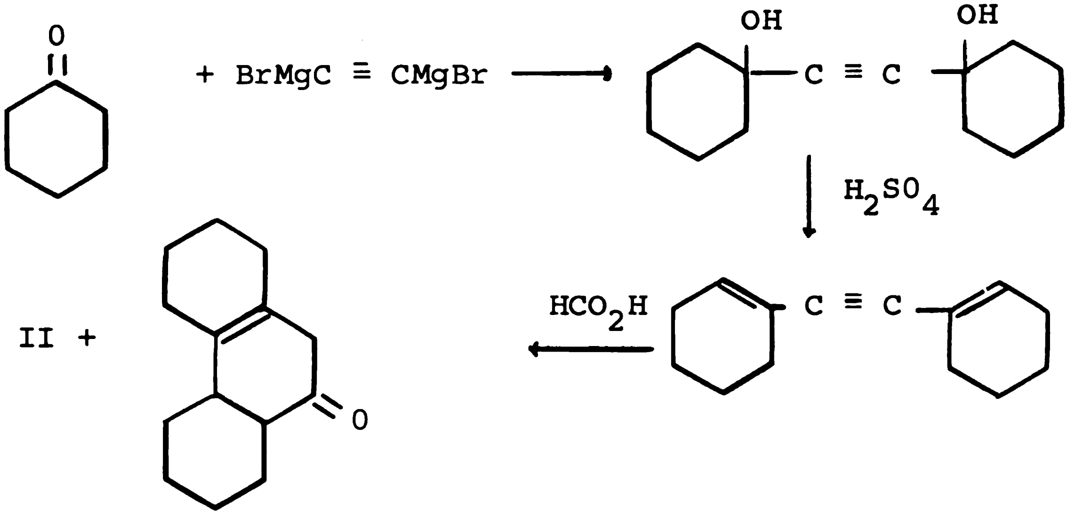
PART I

STUDY OF SOME ISOMERS OF THE 1,1-SPIROCYCLOHEXANE-Δ^4-TETRAHYDROINDAN-3-ONE SYSTEM

INTRODUCTION AND HISTORICAL

During the course of a general study of dieneyne cyclization,[1] Marvel _et al_. attempted to prepare Δ^{11}-dodecahydrophenanthrone-9 (I) from cyclohexanone and acetylene through the following sequence of reactions.



Two isomeric ketones, a solid I (melting point 94°) and a liquid II, were obtained. The structural elucidation of II was carried out by means of the Clemmensen reduction to give a compound, $C_{14}H_{22}$, whose properties agreed closely with those of a dodecahydrophenanthrene which had been prepared by the reduction of phenanthrene with phosphorous and iodine. Other reductions using Raney Nickel gave products with properties agreeing with those reported for perhydrophenanthrenes.

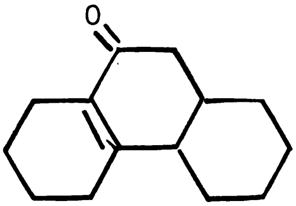
When the resulting dodecahydrophenanthrene was partially dehydrogenated by heating with selenium, the product was found to be identical with a known octahydrophenanthrene.[2]

The dodecahydrophenathrene was also dehydrogenated over platinum on a charcoal catalyst at 300° giving phenanthrene as the only product.[3]

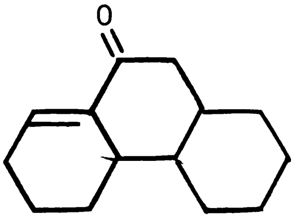
Reinvestigation of Marvel's cyclization product II by R. P. Linstead _et_ _al_.[4] showed this to be a low melting (melting point 39°) ketone, isomeric with II. Attempts to prove the skeletal configurations employed Clemmensen reduction and vapor phase dehydrogenation. Compounds obtained by these means were compared with those having the phenanthrene skeleton.

The position of the keto group was indicated by hydrogenation over palladised charcoal followed by dehydrogenation in the vapor phase.

The Linstead group found the lower melting isomer to be more stable than the higher melting isomer. Subsequent research by I. N. Narasov and I. I. Zaretskaya[5] showed that longer heating of the dieneyne produced a higher percentage of the lower melting isomer; also, when a crude mixture of the two isomers was heated, only the lower melting isomer was found. Furthermore, heating the higher melting isomer with acetic acid and hydrochloric acid for eight hours also produced the lower melting isomer. Correlating these findings with data already available on hydronaphthalenes led to the assignment of structure III to the more stable isomer (m.p. 39°) and structure IV to the higher melting isomer (m.p. 94°).



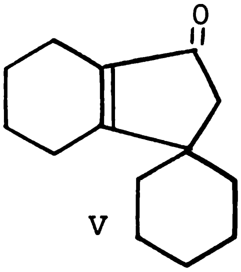
III



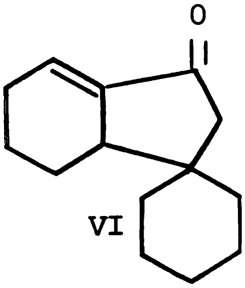
IV

A further study of the isomeric ketones III and IV by M T. Bogert et al.[6] introduced the possibility that these compounds are not hydrogenated phenanthrones but isomeric spiranones (this possibility was earlier rejected by Marvel[7]). Support for the required rearrangement of these spiranes was found in the reaction of cyclohexanespirocyclopentane with selenium at 280°-320° to give naphthalene.

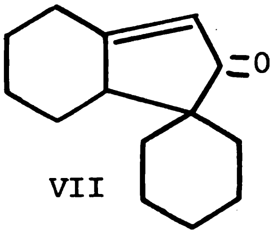
The spirane skeleton proposed by Bogert was later accepted by Linstead et al.[8], for this best supported their experimental results.



V



VI



VII

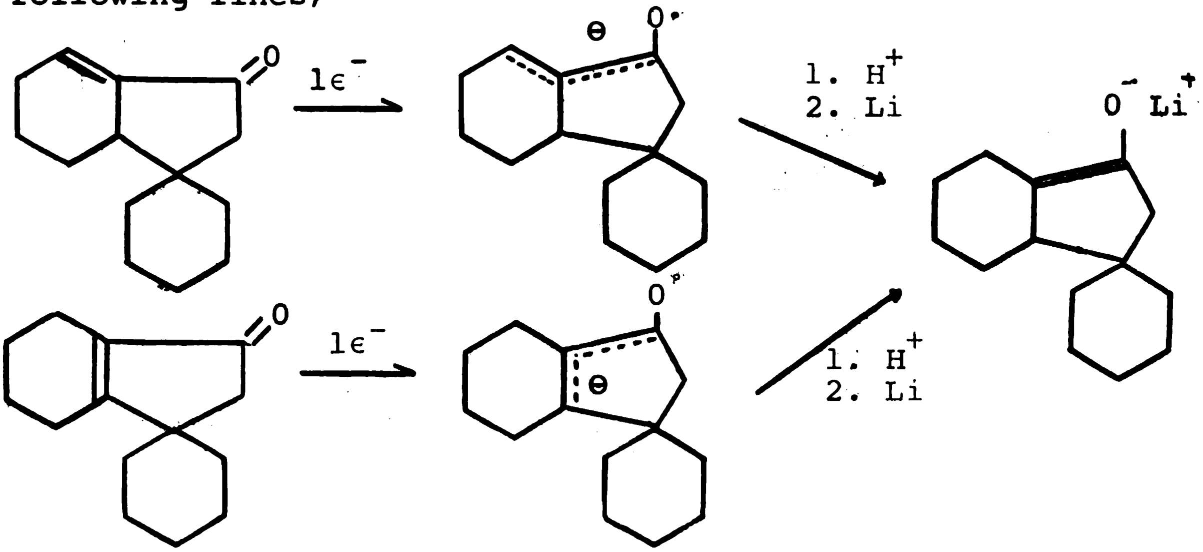
Structure VII was eliminated as a possibility because it could not give the same ketone on hydrogenation as either V or VI. In converting to the spiran system, III is V, and IV becomes VI.

Schwartzman[9] dehydrogenated the 39° isomer over a palladium charcoal catalyst and produced a ketone having a melting point similar to that of a $C_{14}H_{22}O$ ketone obtained by Bogert and co-workers by an alternate route. Derivatives of the dehydrogenated ketone were also similar to those reported by Bogert, although no mixed melting points were reported.

RESULTS AND DISCUSSION

Thus far, all of the experimental evidence used to show that the isomeric ketones were of the same skeletal configuration, has been obtained under conditions where rearrangement could have occurred (e.g., acidic media and metallic catalysts at high temperatures). Interpretation of such results has consequently been ambiguous. It was therefore necessary to find a reaction where rearrangement would not occur. The reduction of α,β-unsaturated ketones to the saturated ketone by lithium in liquid ammonia is known to be mild.[10] A generalization of the outcome of the reaction by Stork *et al*. states that "In reduction of an octalone system with lithium in ammonia the product will be the more stable of the two isomers (*cis* or *trans*) having the newly introduced hydrogen axial to the ketone ring."[11]

The action of lithium and liquid ammonia upon the two isomers in question should therefore proceed along the following lines,



terminating in a common product.

Reduction of the two isomeric ketones with lithium and liquid ammonia did in fact give products whose infrared spectra and vapor phase chromatography retention times were identical. Melting points and mixed melting points of the oximes of the reduced products were also identical. This proves identical skeletal configuration.

Assignments based upon ultraviolet absorption data[12,13] gave the 39° isomer structure VI and the 94° isomer structure V. However, when the correction factor for a cyclopentenone system[14] was applied to the calculations, the results were so close that a clear cut assignment could not be made.

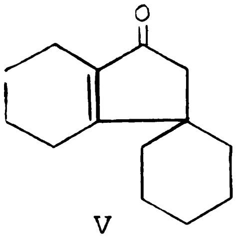
	I.R. (Found)	U.V. (Found)
lower melting isomer	5.93 μ	241 mμ ($\epsilon = 12 \times 10^3$)
higher melting isomer	5.85 μ	247 mμ ($\epsilon = 9 \times 10^3$)

V	
base	215 mμ
α-substituent	10
2β-substituent	24
(calculated uncorrected)	249 mμ
correction	-11
	238 mμ

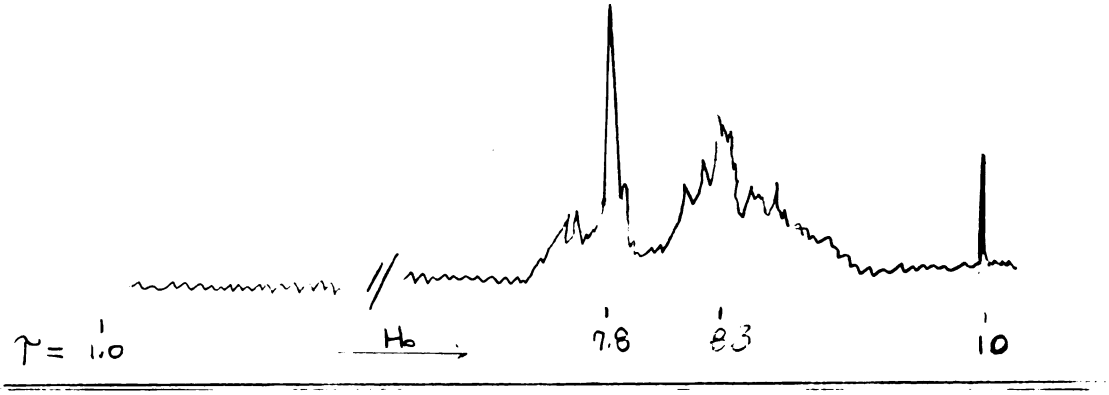
VI	
base	215 mμ
α-substituent	10
β-substituent	12
exo-double bond	5
	242 mμ

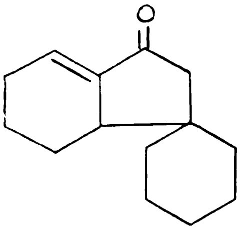
The key to the problem was nuclear magnetic resonance spectrometry. There was no olefinic proton absorption for the lower melting isomer while a broad doublet ($\tau = 3.45$) was found in the vinyl hydrogen region for the higher melting isomer. This data confirmed the presence of a tetrasubstituted double bond in the lower melting isomer.

Nuclear magnetic resonance spectrum of:

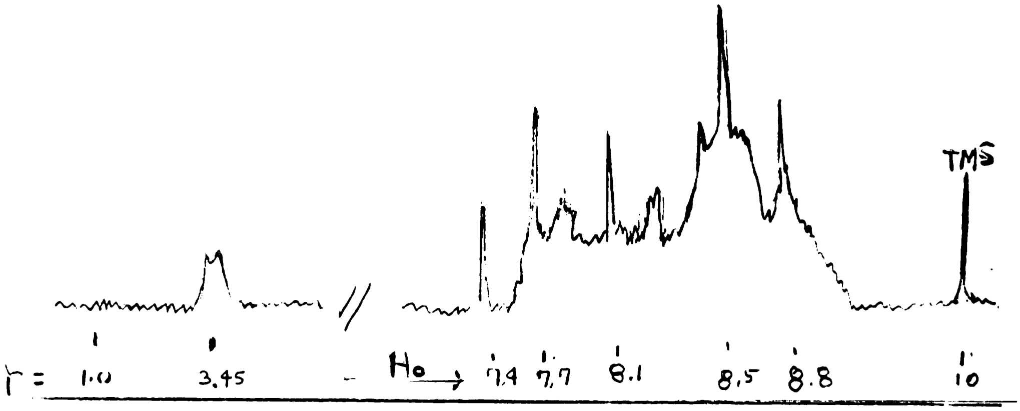


V





VI



Structure V is therefore the lower melting isomer and VI is the higher melting isomeric ketone.

EXPERIMENTAL

1,1-Spirocyclohexanehexahydroindan-3-oxime

290 mg. of 1,1-spirocyclohexane-$\Delta^{4(9)}$-tetrahydroindan-3-one[16] in 50 ml. of a dried 50:50 mixture of ethyl ether and dioxane was added to a flask containing 20 mg. of lithium metal in 25 ml. of liquid ammonia. The cooling bath used to liquefy the ammonia was removed, and the solution was stirred with the aid of a mechanical stirrer. After 5 minutes the reaction was quenched with dry tertiary-butyl alcohol. The solution was allowed to stir until all the ammonia had evaporated. The residue was extracted with ether several times; the ether extracts were washed with water and dried over anhydrous magnesium sulfate.

The ether was removed and the resultant residue taken up in benzene. The benzene solution was then run through a chromatography column containing Merck acid washed alumina in benzene. The eluted benzene solution was collected and stripped of solvent. An oxime was prepared from this material giving 1,1-spirocyclohexanehexahydroindan-3-oxime. The oxime, m.p. 138-140°, was recrystallized from water-ethanol.

Anal. Calcd. for $C_{14}H_{23}NO$: C, 75.96; H, 10.47; N, 6.33.
Found: C, 76.09; H, 10.49; N, 6.31.

The same procedure was used for converting 1,1-spirocyclohexane-$\Delta^{4(5)}$ tetrahydroindan-3-one to

1,1-spirocyclohexanehexahydroindan-3-oxime. A mixed melting point of the oximes of the reduced product of the two isomeric ketones showed no depression.

Infrared spectra were obtained on a Perkin-Elmer, Model 21, recording spectrophotometer, using sodium chloride optics. The ultraviolet spectra were determined in 1-cm. quartz cells using a Cary, Model 11, spectrophotometer.

Proton magnetic resonance spectra were determined in carbon tetrachloride solution using a Varian, A-60, high resolution spectrometer. All spectra were obtained at 60 MC using tetramethylsilane as an internal standard.

SUMMARY

Marvel's cyclization products have been reinvestigated and shown unequivocally to have the same carbon skeletons. The use of proton nuclear magnetic resonance spectroscopy was the key factor in showing that previous structural assignments are incorrect and must be reversed.

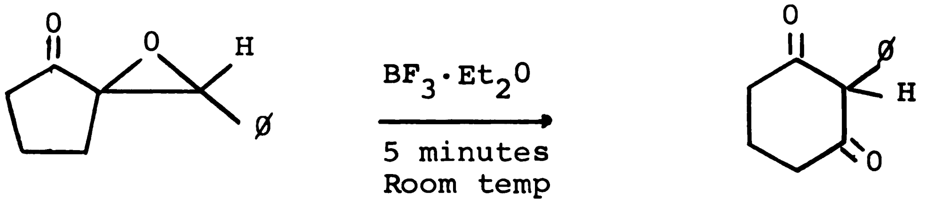
PART II

INVESTIGATION OF THE THERMAL AND FREE RADICAL REACTIONS OF PHENYL SUBSTITUTED OXIRANES

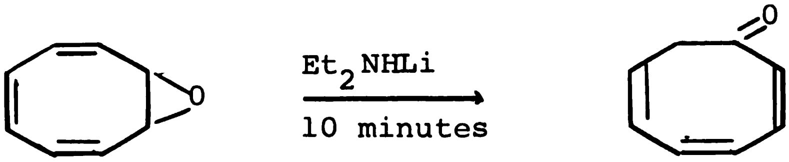
INTRODUCTION AND HISTORICAL

The oxirane system is well-known for its ability to react and undergo rearrangement.[17]

As a general rule, rather mild conditions suffice for acid or base reactions (e.g., i[18] and ii[19])

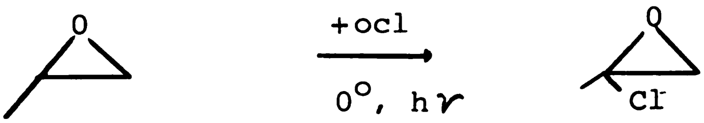


(i)



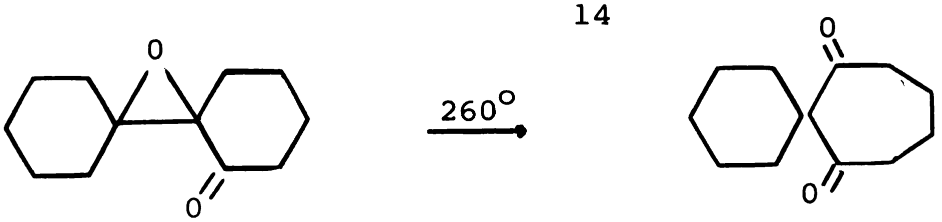
(ii)

and the abstraction of oxirane hydrogen by tertiary butyl hydroperoxide is reported[20] to be rapid at 0° (iii).

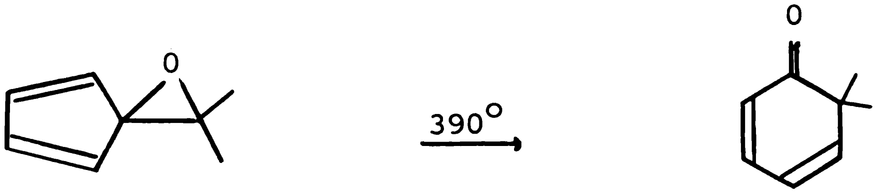


(iii)

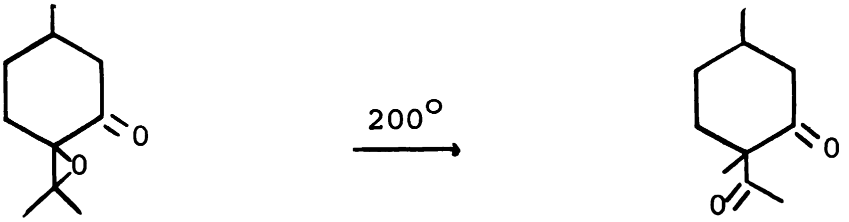
Reports of oxirane rearrangement at elevated temperatures (iv,[21] v[22] and vi[23]) are consequently of more than passing interest.



(iv)



(v)



(vi)

The question arises as to the role the higher temperature plays in the thermal rearrangement of the oxirane system. Since the intrinsic strain associated with the oxirane system makes it vulnerable to ring opening under a variety of conditions, and since early work on this system left ambiguities concerning experimental procedure, one may ask if the high temperature rearrangements are indeed caused by thermal rupture of the three-membered ring. It was toward this end that this investigation of the decomposition of the oxirane system was undertaken.

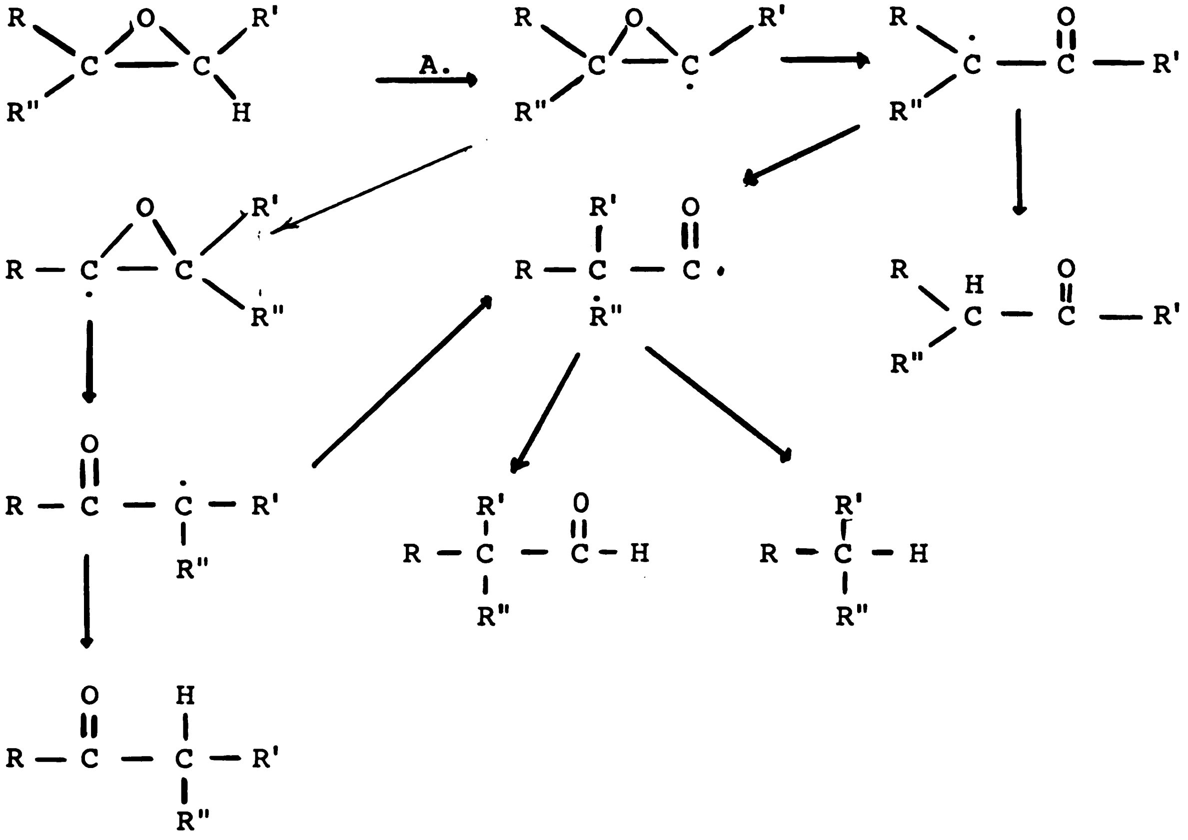
In much of the early work concerning decomposition of oxirane systems, experimental procedures were followed which gave equivocal results. The following points are of particular importance: (1) Yields were often poor and only the major product was isolated. (2) The carbonyl compounds produced in the decomposition of the oxirane systems were characterized as hydrazones, oximes or semicarbazone. Preparation of those derivatives usually involves an acid medium which could cause rearrangement of any unreacted material. (3) The presence of oxygen may give rise to radical species which could then promote further reaction.[24] (4) Reactions may occur at the surface of the reaction vessel. Rondestvedt[25] has demonstrated that acidic sites on silica gel catalyze the decomposition of 1,3-dioxanes. A similar catalysis could presumably occur at acidic sites on the surface of the Pyrex reaction ampule. No previous attempt has been made to differentiate between this possibility and true thermal reactions; consequently one must proceed with caution when interpreting data obtained by early investigators.

Previous studies of oxirane systems at high temperatures suggest that at least three types of reactions can be observed: (1) a free radical chain reaction initiated by hydrogen abstraction, (2) a unimolecular decomposition involving rupture of an oxirane bond and (3) a heterogeneous reaction catalyzed by acidic sites on the surface of pyrex glass.

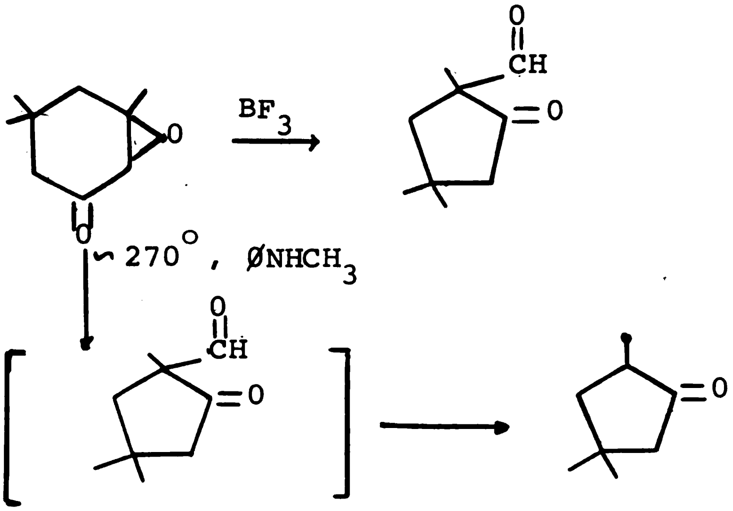
Several decomposition modes (Diagram I) are formally available to the oxirane radical generated by α-hydrogen abstraction. Examples of some of these possibilities have been reported,[26,27] while others are unknown and improbable. Hydrogen abstraction at the β-position of cyclohexene oxide has also been observed.[28]

A true thermal unimolecular decomposition involving rupture of an oxirane bond is a rare phenomena, a likely example being Pulegone oxide.

Diagram I

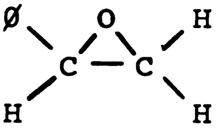


Catalysis by acidic sites on the surface of pyrex glass may be suspected when the products parallel acid catalyzed products, e.g., equation 1.[29]

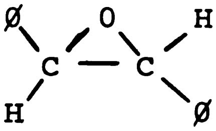


Extreme care must therefore be taken in assuring cleanliness of the apparatus used.

In our work four epoxides (I-IV) were investigated at high temperatures ($T > 150^{\circ}$), and the decomposition products identified.



I



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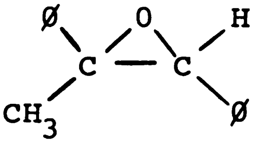
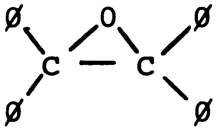


III



IV

Each epoxide was investigated as a neat sample and with the free radical initiators tertiary butyl hydroperoxide and 2,4,4-trimethyl-2-formylcyclopentanone. Surface reactions were identified by observing the effect of added Pryex glass.

RESULTS

I. Sytrene Oxide

Tiffeneau and co-workers[30] studied reactions of styrene oxide (I) with a variety of acid catalysts. They found that distillation in the presence of a catalyst (e.g., Al_2O_3) produced phenylacetaldehyde.

In beginning our work, styrene oxide was distilled (b.p. $>200^o$) from a Pyrex vessel in the presence of air; a thin layer chromatograph (T.L.C.) of the distillate demonstrated that no reaction had occurred.

Considering the possible radical and thermal reactions of styrene oxide (e.g., diagram I, see page 16), one arrives at phenylacetaldehyde, acetophenone and toluene as the most likely products from thermal decomposition. With the exception of toluene these were distinguished from each other and from styrene oxide by the T.L.C. technique employed here. Toluene is easily recognized by vapor phase chromagraphic analysis.

The infrared spectra and T.L.C. of the high temperature reaction products from I showed that acetophenone was not present among the products; acetophenone was found to be stable under the reaction conditions. Consequently a reliable quantitative method for following the decomposition of I need only encompass the starting material and phenylacetaldehyde. For this purpose several experimental procedures were eliminated.

(a) Gas chromatographic procedures while valuable for detecting toluene could not be used as a general purpose tool, since the epoxide decomposed on the column (toluene is not a product of this decomposition).

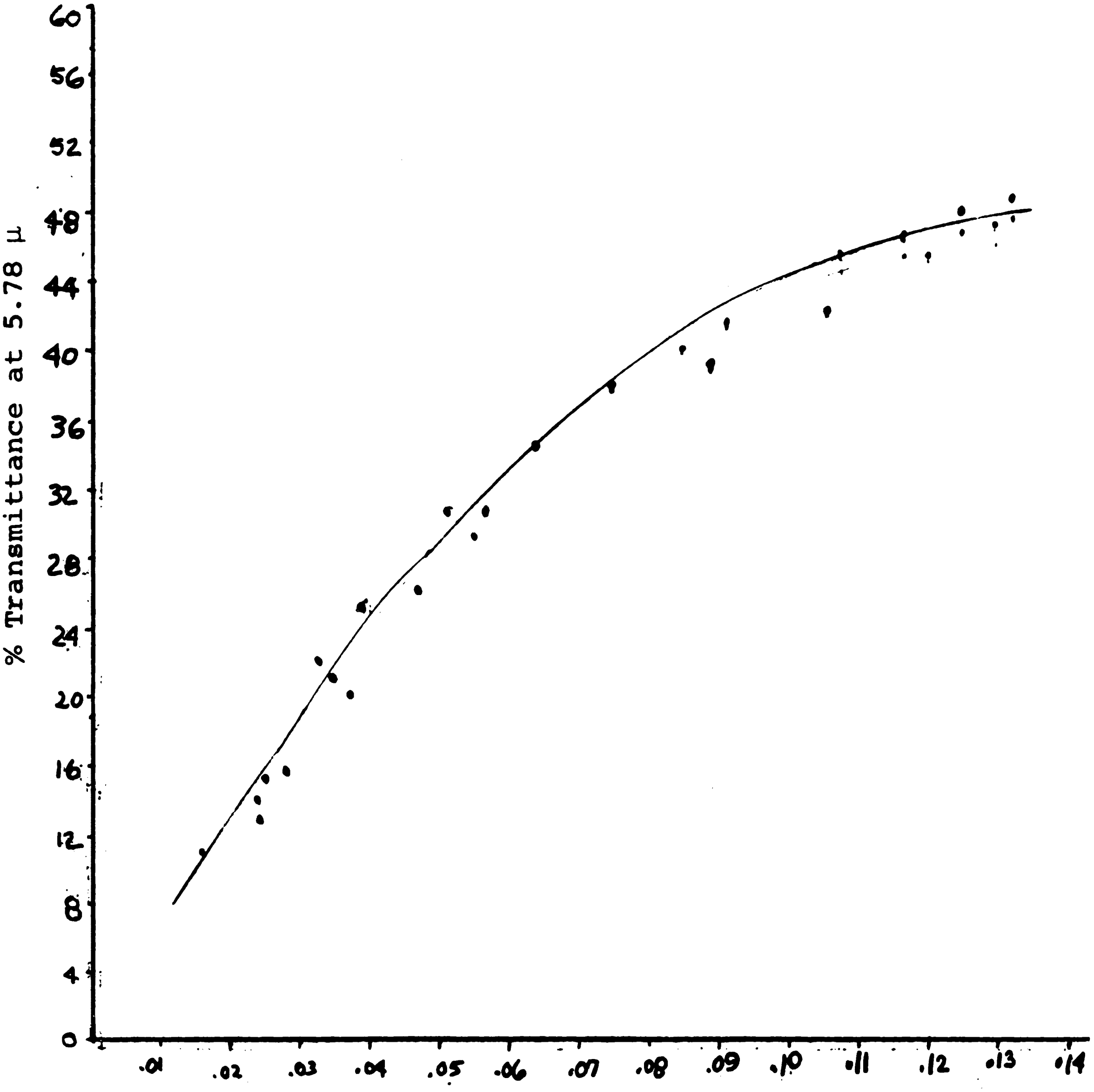
(b) Ultraviolet spectrophotometry was likewise undesirable since peak overlapping occurred.

Fortunately, infrared spectra showed a characteristic absorption for phenylacetaldehyde at 5.78 μ and styrene oxide at 11.43 μ; thus permitting determination of the percentage of I which had gone to recognizable product (i.e., phenylacetaldehyde) and the percentage to other product (i.e., tars).

The plot of percent transmittance, at the respective absorbancies, vs. molar concentration of the pure materials in question gave smooth curves (see Figures I and II).

An infrared spectrum of a weighed amount of decomposition sample was taken. The peak heights of reactant and product were measured, and their corresponding concentrations determined.

Table I shows the results of the thermal and free radical reactions of styrene oxide as followed by infrared spectrophotometry.



moles/liter of phenylacetaldehyde

Figure I. % Transmittance at 5.78 μ vs. moles/liter of phenylacetaldehyde (Perkin Elmer Model 21).

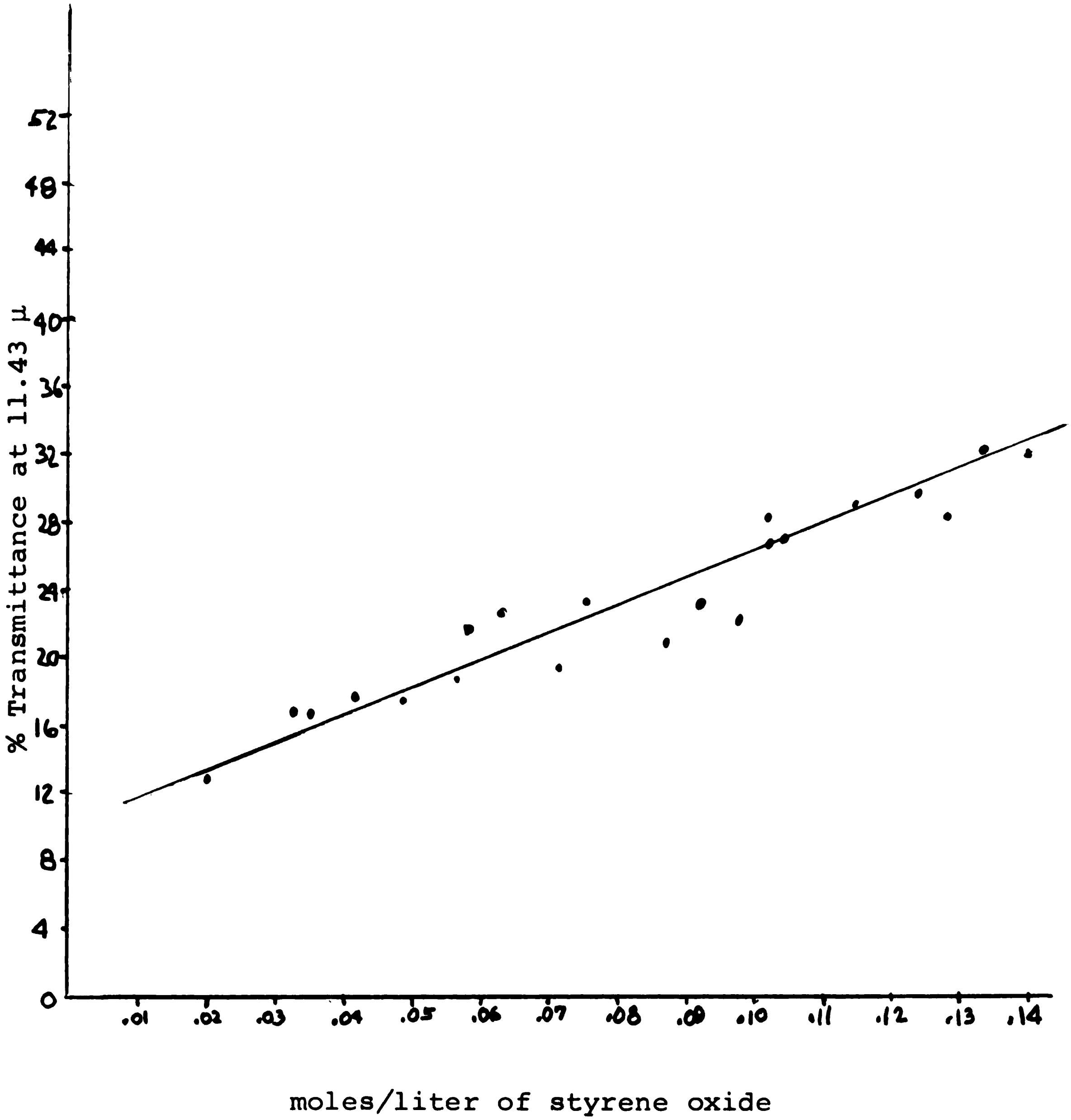


Figure II. % Transmittance at 11.43 μ <u>vs</u>. moles/liter of styrene oxide (Perkin Elmer Model 21).

Table I. Thermal and free radical reactions of styrene oxide.

Furnace Temperature (°C)	Time (hrs.)	Sample Condition	Additives[a]	% $\emptyset CH_2CHO$
170°	24	neat	none	6.1
200°	6	neat	air	*
200°	6	10% decalin	none	b
200°	24	neat	none	7.7
200°	24	neat	100% increase of surface area	21.7
230°	4	neat	none	14.4
230°	5	neat	none	17.7
230°	78	neat	none	*
170°	16	neat	c	9.1
170°	18	neat	c	19.1
200°	6	neat	c	6.8
200°	6	neat	5x increase of c	16.3
200°	12	neat	c	15.9
200°	16	neat	c	22.5
200°	18	neat	c	*
230°	1	neat	c	10.8
230°	2	neat	c	28.1
230°	4	neat	c	*
170°	16	neat	d	13.2
170°	18	neat	d	23.4
200°	6	neat	d	9.5
200°	12	neat	d	17.5
200°	16	neat	d	34.7
200°	18	neat	d	*
230°	1	neat	d	31.4
230°	2	neat	d	35.2
230°	4	neat	d	*

[a] Unless otherwise stated ~2%.

[b] A qualitative analysis was made, starting material and phenylacetaldehyde were the only substances present.

[c] Tertiary butyl hydroperoxide.

[d] 2,4,4-trimethyl-2-formylcyclopentanone.

*The percentage of product varied and the concentrations of tar were considerable.

II. Trans-Stilbene Oxide

House *et. al.*[31] have studied the acid catalyzed rearrangement of *trans*-stilbene oxide (II) with various Lewis acids. When treated with BF_3-etherate, II formed diphenylacetaldehyde. Small amounts of deoxybenzoin were found accompanying the aldehyde when magnesium bromide and zinc bromide were the Lewis acid catalysts. Tiffeneau *et. al.*[32] reported that the distillation of *trans*-stilbene oxide gave benzaldehyde and *trans*-stilbene; under acid conditions deoxybenzoin and diphenylacetaldehyde were observed.

II was distilled (b.p. $> 250^{\circ}$) in this investigation and only starting material was recovered.

The use of infrared spectroscopy for following the decomposition of II had to be abandoned, because the percent yield of recognizable product (i.e., deoxybenzoin and diphenylacetaldehyde) was low compared to the amount of tarry uncharacterizable material, thus producing a large error.

Nuclear magnetic resonance was a useful tool, the methine hydrogens of II appearing at 8.17τ, the methylene hydrogens of deoxybenzoin at 7.9τ and the methine hydrogen of diphenylacetaldehyde at 7.65τ. Therefore one may determine which substances were present and their relative amounts.

Table II shows the results of the thermal and free radical reactions of *trans*-stilbene oxide, as followed by nuclear magnetic resonance spectroscopy.

Table II. Thermal and free radical reactions of <u>trans</u>-stilbene oxide.

Furnace Temperature (°C)	Time (hrs.)	Sample Condition	Additives[a]	% deoxybenzoin	% diphenyl-acetaldehyde[b]
23° [c]					
200°	24	neat	none	0	0
230°	12	neat	none	< 3	0
230°	6	neat	benzoic acid	< 3	< 10
230°	12	neat	air	11	0
250°	12*	neat	none	< 3	< 3
200°	24	neat	d	0	0
230°	12	neat	d	< 3	< 3
250°	12*	neat	d	< 3	< 3
200°	24	neat	e	0	0
230°	12	neat	e	< 3	< 3
250°	12*	neat	e	< 10	< 10

[a] Unless otherwise stated ~2%.

[b] When diphenylacetaldehyde was heated at 200° for six hours a gummy unrecognizable material was obtained.

[c] When p-toluenesulfonic acid was used as a catalyst, a very viscous material was obtained after degassing; which showed no epoxide band in the infrared.

[d] Tertiary butyl hydroperoxide.

[e] 2,4,4-trimethyl-2-formylcyclopentanone.

III. α-Methyl-Trans-Stilbene Oxide

Tiffeneau[33] reported that distillation of α-methyl-trans-stilbene oxide (III) in air gave α,α-diphenylpropionaldehyde, and that reaction of III with hydrochloric acid produced methyldeoxybenzoin.

When III was distilled in air (b.p. $>$ 300°) in our laboratory and the product examined by T.L.C., three spots (1,2-diphenylallyl alcohol, methyldeoxybenzoin and α,α-diphenylpropionaldehyde) appeared in addition to the starting material. This is a good illustration of the tendency in early investigations of identifying and reporting only the major product.

When III is treated with BF_3-etherate for one minute at room temperature, T.L.C. established that quantitative conversion to α,α-diphenylacetone and α,α-diphenylpropronaldehyde had occurred.

Considering reaction by α-hydrogen abstraction from III (see diagram I, page 16) three possible products are methyldeoxybenzoin, α,α-diphenylpropronaldehyde and α,α-diphenylacetone.

In view of Gritter's findings regarding β-hydrogen abstraction[28] the possibility of encountering 1,2-diphenylallyl alcohol should also be considered.

α-Methyl-trans-stilbene oxide and the four likely products (i.e., methyldeoxybenzoin, α,α-diphenylacetone, α,α-diphenylpropionaldehyde and 1,2-diphenylallyl alcohol) are easily resolvable on thin layer chromatography, making this a useful tool for the qualitative identification of the products from the thermal and free radical reactions of III.

Quantitative analysis of the reaction mixture was by nuclear magnetic resonance spectroscopy. The chemical shifts (τ) for the characteristic protons used for analysis are given in Table III.

Table III. The chemical shifts (τ) for the characteristic protons used for analysis of α-methyl-*trans*-stilbene oxide and its likely decomposition products.

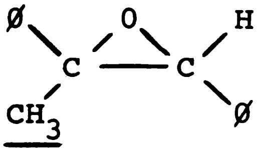
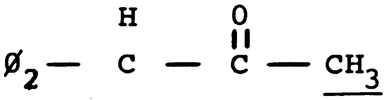
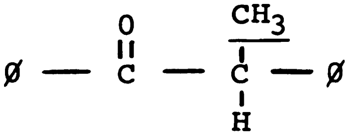
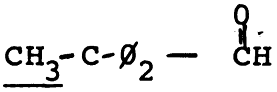
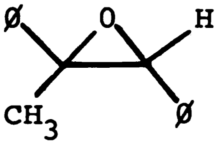
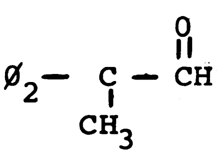
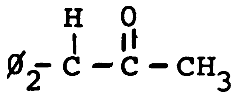
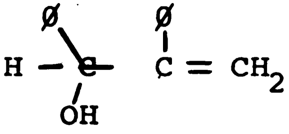
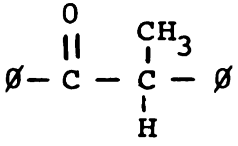
	Compound	Chemical Shift values (τ)
(a)		8.60
(b)	 $\emptyset_2-\overset{H}{C}-\overset{O}{\overset{\Vert}{C}}-\underline{CH_3}$	7.90
(c)	 $\emptyset-\overset{O}{\overset{\Vert}{C}}-\underset{H}{\overset{\underline{CH_3}}{C}}-\emptyset$	8.50(d)
(d)	 $\underline{CH_3}-C-\emptyset_2-\overset{O}{\overset{\Vert}{C}}H$	8.05
(e)	$\emptyset C\underline{H}(OH)C\emptyset=C\underline{H_2}$	4.62 and 4.72

Table IV shows the findings of the thermal and free radical reactions of α-methyl-*trans*-stilbene oxide.

Table IV. The thermal and free radical reactions of α-methyl-*trans*-stilbene oxide.

Conditions[a] Temperature (°C) Time Additives*	% Yield of Products 	 $Ø_2-\underset{CH_3}{C}-\overset{O}{\overset{\|}{C}}H$ [d]	 $Ø_2-\overset{H}{C}-\overset{O}{\overset{\|}{C}}-CH_3$ [d]	 [e]	 $Ø-\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{CH_3}{C}}-Ø$
200° 24 hrs. None	59, 43	0, 0	Small	23, 27	18, 30
200° 24 hrs. powdered glass	0, 0	14	15, 8	43, 81	28, 11
230° 6 hrs. None	62, 69	13		12, 9	13, 9
200° 24 hrs. b	27, 28	34, 20		19, 29	20, 23
230° 6 hrs. b	41, 22	9, 27		20, 37	30, 14
200° 24 hrs. c	0, 0	10, 7	20, 11	54, 62	16, 20

[a] All reactions were run neat.

[b] 2,2,4-trimethyl-2-formyl-cyclopentanone

[c] tertiary butyl hydroperoxide.

[d] Methyldeoxybenzoin and α,α-diphenylacetone were found to be stable at 200° for 24 hrs.

[e] When 1,2-diphenylallyl alcohol was heated at 200° for 24 hrs. a tarry mess was formed.

IV. Tetraphenylethylene Oxide

Benzpinacalone was the only product obtained when tetraphenylethylene oxide (IV) was treated with acid.[34]

Since the aromatic hydrogen atoms in tetraphenylethylene oxide are relatively unreactive to radical attack, this substrate affords an opportunity to study thermal rearrangement in the absence of interfering radical reactions.

Benzpinacalone was the only product found in the thermal decomposition of IV, using infrared spectrophotometry, nuclear magnetic resonance spectrometry and thin layer chromatography for analysis.

In one case benzpinacalone was actually isolated and identified by classical methods.

The decomposition of IV was followed by nuclear magnetic resonance spectrometry. A multiplet at 2.82τ represents resonance by the twenty aromatic protons of tetraphenylethylene oxide. The nuclear magnetic resonance spectrum of benzpinacalone shows a characteristic resonance at 2.67τ. This peak is due to the fifteen aromatic protons β to the carbonyl. The five α-aromatic protons appear at lower field.

Table V shows the results of the thermal reactions of tetraphenylethylene oxide as followed by nuclear magnetic resonance spectroscopy.

Table V. The thermal reactions of tetraphenylethylene oxide.

Furnace Temperature (°C)	Reaction Time (hrs.)	% benzpinacalone produced in neat samples of tetraphenylethylene oxide.		
			Initiators	
		None	a	b
200°		c, d		
	6	74.8		
	12	84.5		
	24	> 90	> 90	> 90

[a] Tertiary butyl hydroperoxide

[b] 2,2,4-trimethyl-2-formylcyclopentanone

[c] Increasing the surface area by the addition of powdered Pyrex glass gave complete conversion to benzpinacalone after one hr. at 200°.

[d] When methylaniline was added with the powdered glass, complete conversion to benzpinacalone was noted in two hrs.

DISCUSSION

Recently Russell et. al.[35] have shown that electron-withdrawing substituents deactivate and electron-supplying substituents activate substituted styrenes in addition reactions involving peroxy radicals. In contrast, the Iowa State group also found that the autoxidation of benzyl phenyl ethers and benzyl alkyl ethers which involves peroxy radicals is insensitive to polar effects of substituents in either the phenyl or benzyl group. It was suggested that the oxygen atom acts as a powerful electron supplying group and overshadows any effects of polar substituents.

The oxirane system is an ether and its oxygen atom should also be capable of acting as an electron supplying group. In fact, the findings of Walling[20] pertaining to the chlorination of propylene oxide (see page 13, iii) show that oxirane hydrogen abstraction is favored over methyl hydrogen abstraction.

That the activation due to the oxirane-oxygen may not be as great as that observed in unstrained ethers may be seen in the reluctance of radical initiators to abstract a hydrogen atom from trans-stilbene oxide (Table II) and the absence of acetophenone in the radical reactions of styrene oxide (Table I). Apparently, the electron withdrawing phenyl group overcomes the activating effect of the oxygen in these instances. Since the polar effects studied by Russell _et al_.[35] were due to substituents in the para position of the benzyl and phenyl groups, his data may not apply here where a phenyl group is being substituted for a hydrogen atom in the different oxiranes.

Gritter _et al_.[28] have reported that cyclohexene oxide undergoes β-hydrogen abstraction in a free radical chain reaction. This mode of reaction becomes possible in the case of α-methyl-_trans_-stilbene oxide (III); and in fact, thermal decomposition of III in the presence of radical initiators gave large amounts of 1,2-diphenylallyl alcohol.

In addition to the radical chain reactions described above, surface reactions seem to be occurring in some of the more highly substituted oxiranes (i.e., III and IV). If we accept Rondestvedt's[25] hypothesis suggesting the presence of Lewis acid sites on the surface of silica--said sites being responsible for the surface reactions--the formation of intermediates B and C (Diagram II) follows logically. These intermediates may aid in rationalizing the course of the surface reaction.

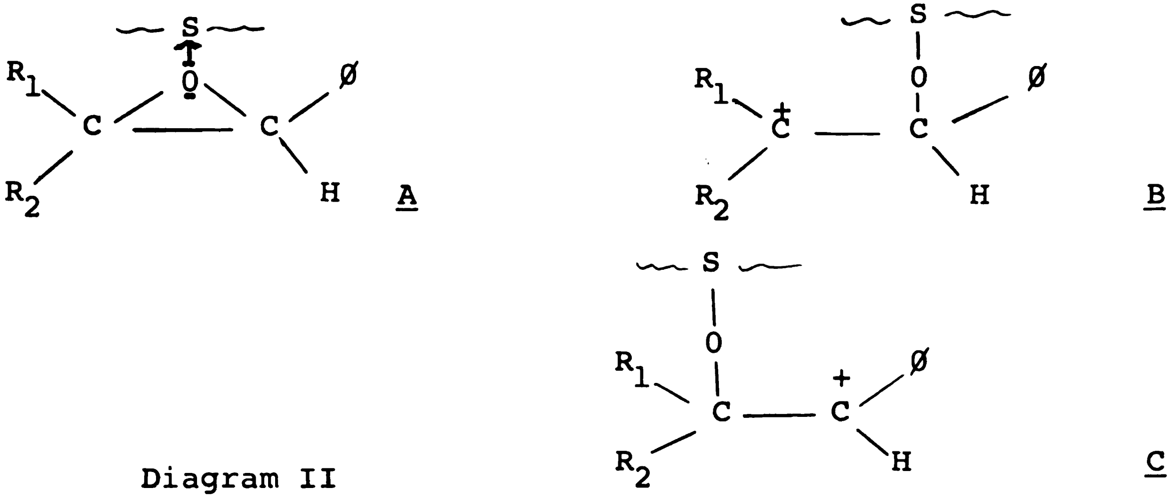
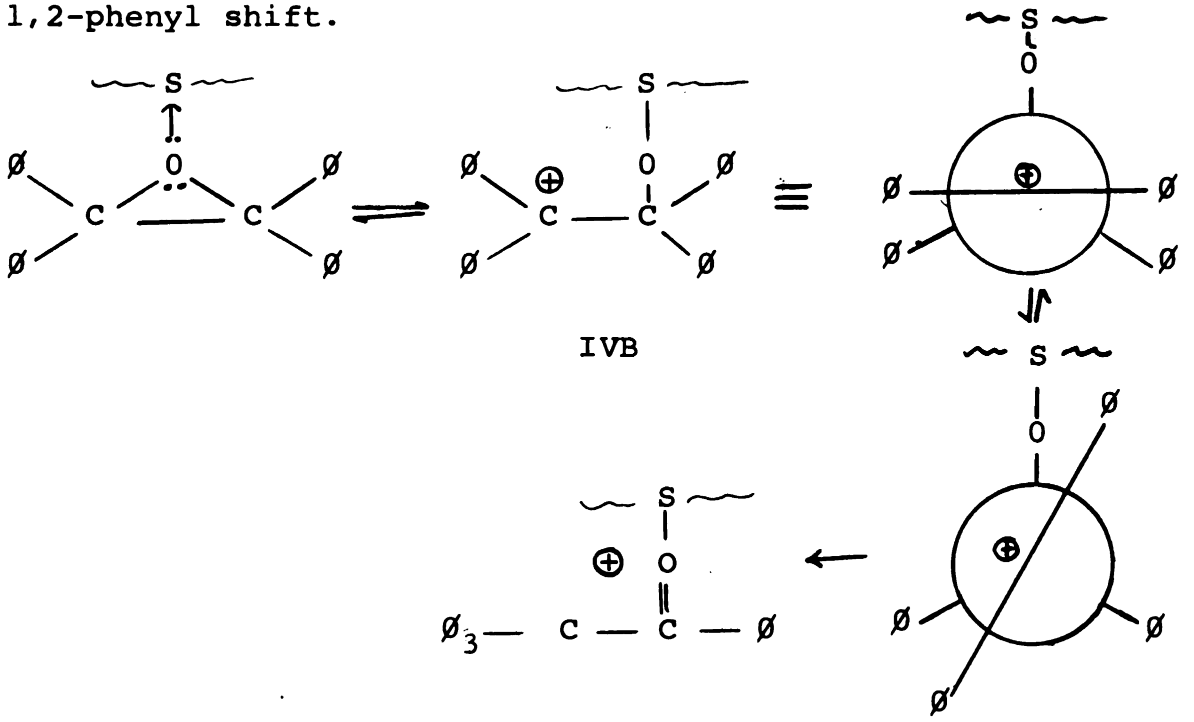


Diagram II

An important fact is that III and IV show significant surface reaction (at 200°) while I and II do not. I and II give rise to intermediate ions of lower stability than those derived from III and IV; therefore this aspect of the hypothesis agrees with the observed reactivities.

IV yields only one possible carbonium ion intermediate, which upon formation may collapse and return to reactant, or undergo phenyl migration to benzpinacalone. Since the reaction goes rapidly and in high yield, one must conclude that the intermediate ion persists long enough to twist into a higher energy conformation (i.e., IV C) favorable to a 1,2-phenyl shift.

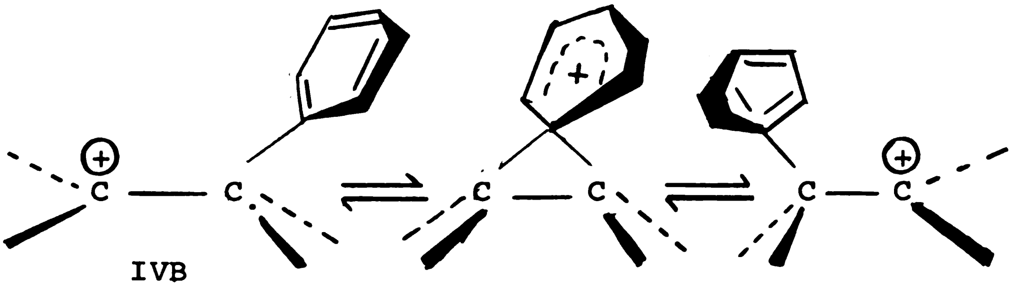


IVB

IVC

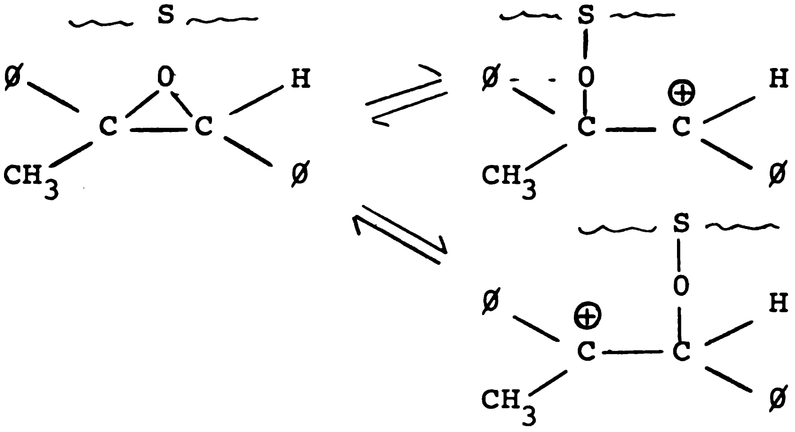
It is assumed here that optimum geometry (i.e., an orientation of the migrating phenyl group as in equation vii) is a critical factor in the occurrence of rearrangement, and that conformation IVC is subject to severe steric interaction of a non-migrating phenyl group with the surface.

(vii)



IVB

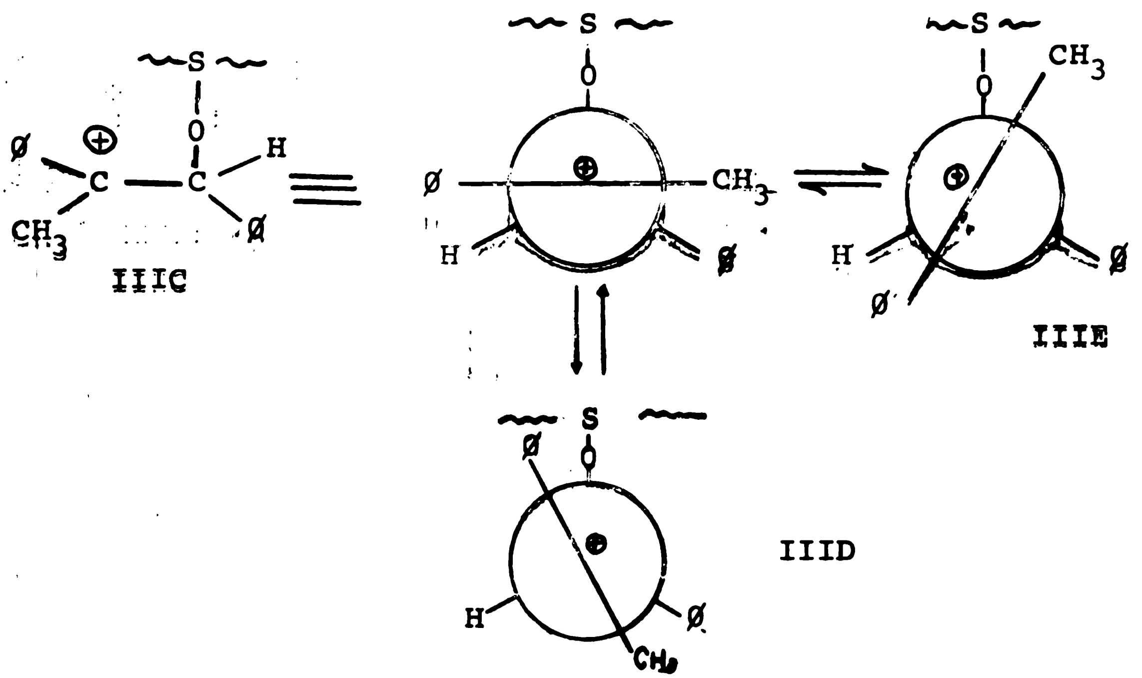
The surface reaction of III is slower than that observed for IV. Consideration of the possible intermediates from III (i.e., IIIB and IIIC), permits one to eliminate IIIB as an important contributor (note the low reactivity of II).



IIIB

IIIC

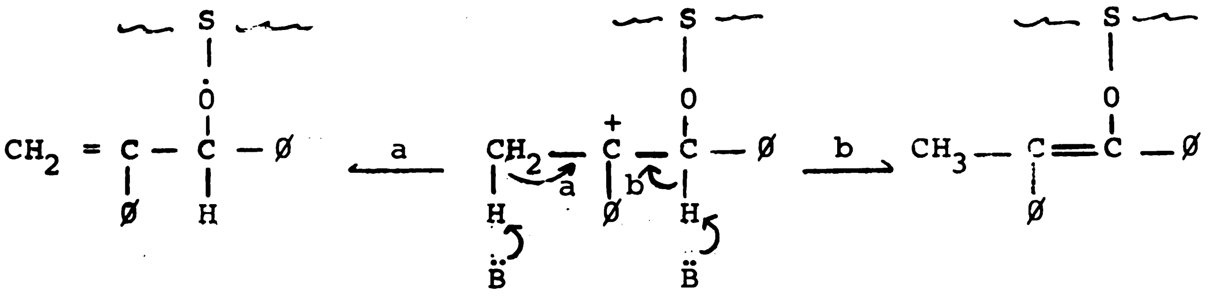
In order for IIIC to be an effective intermediate in rearrangement, it must persist long enough to convert to the high energy conformations (IIID and IIIE) necessary for 1,2-shifts.


IIIC

IIIE

IIID

Since IIIE should be more stable than IIID (fewer and less severe non-bonded interactions) one would expect to find α,α-diphenylpropionaldehyde among the major products from the reaction if rearrangements are occurring. One way to account for the fact that this aldehyde is not a product in the high temperature surface reaction of III is to assume that the mean life span of intermediate ion IIIC is so short that conversion to the high energy confirmations IIID and IIIE is improbable. If ion IIIC is not undergoing rearrangement one of the few alternate reaction paths is the elimination of a proton to produce an olefin. Indeed the neat reactions of III produce 1,2-diphenylallyl alcohol in relatively good yield, by a surface reaction (equation viii, path a). The other major product, methyldeoxybenzoin may also be accounted for by a proton loss (equation viii, path b).



(viii)

We make here the reasonable assumption that the transition state geometry of E_1 elimination is less demanding than that for migration.

Another explanation for the products found in the decomposition of III would parallel current views of the aldehyde-ketone rearrangement.[36] That is to say, the aldehyde is the primary product of the thermal reaction as is predicted from consideration of ions IIID and IIIE, but the aldehyde is not stable under the conditions of thermalysis and is converted to methyldeoxybenzoin. Unfortunately, we have not been able to obtain this aldehyde in sufficient quantity to test this fact. However, experience with other aldehydes suggests that a rapid clean thermal rearrangement of this aldehyde to methyldeoxybenzoin is unlikely.

No evidence of a true unimolecular thermal reaction was found in any of the oxiranes investigated.

EXPERIMENTAL

I. General Procedures

The experimental procedure employed to prepare samples was similar to that used by C. K. Johnson in his study of some α, β-epoxy ketones.[37]

A. Apparatus

The infrared spectra were obtained on a Perkin-Elmer Model 21 or a Beckman I.R. 7 recording spectophotometer using sodium chloride cells. The band positions were recorded in microns. The ultraviolet spectra were determined in 1-cm. quartz cells using a Cary Model 11 spectrophotometer. Proton nuclear magnetic resonance spectra of samples in carbon tetrachloride solution were determined using a Varian A-60 high resolution spectrometer. All nmr spectra were obtained at 60 Mc using tetramethylsilane as an internal standard.

Vapor phase chromatography analyses were made using a 1/4-inch, 6-foot column of 20% silicon on chromasorb. Thin layer chromatographic analyses were carried out on glass plates with silica gel G, with a 30:70 pentane-benzene mixture as the eluting solvent.

B. Furnace

The sample vials were heated in an aluminum block furnace. A temperature constant to within ± 2° was maintained.

C. Preparation of Pryex Sample Vials

For all sealed tube reactions, the tubes were prepared in the following way. Pyrex tubing was cut and the sections placed in a large beaker. The glass was covered with concentrated nitric acid and heated on a steam bath for 24 hours. The acid was removed and the tubes rinsed thoroughly with distilled water. Concentrated ammonium hydroxide was added and the tubes allowed to stand for 30 minutes. The ammonium hydroxide was removed, the tubes thoroughly rinsed with distilled water, and finally baked in an oven at 200° for 24 hours. The tubes were converted to vials which were heated for several hours at 200° and then stored in a desiccator over Drierite.

Powdered pyrex tubing, used to increase surface area in the vials, was treated in the same manner as the tubing used to make the vials.

D. Degassing

Degassing is a procedure whereby all oxygen is removed from a system and the vial is sealed under a nitrogen atmosphere. The degassing procedure used was:

1. The system containing the vial is evacuated by means of a vacuum pump.

2. A three-way stopcock is adjusted to cut the vacuum off and to allow dry nitrogen to flow into the vial.
3. The contents of the vial are frozen, the nitrogen is cut off and the system is once again opened to the vacuum pump.
4. The contents of the vial are allowed to warm to room temperature.* Steps one through four are repeated five times.
5. Under a nitrogen atmosphere, the tube is sealed as close to the material in the vial as is feasible, to insure a liquid phase reaction at high temperature.

*At this point, it is best if the material in the vial is a liquid so all the oxygen can be eliminated. If the sample is a solid, the temperature required for liquification under these conditions may cause (a) decomposition of free radical initiators and/or (b) partial reaction of the sample.

Compound I.

Styrene oxide is a liquid and degassing proceeded smoothly.

Compound II.

trans-Stilbene oxide is a solid melting at 68-69°.

a. _trans_-Stilbene oxide was dissolved in decalin and degassed in solution. This method was discarded because of the difficulties in the degassing procedure.

b. _trans_-Stilbene oxide was melted with the aid of a hot water bath and the complete degassing sequence was performed. The system was then opened to the atmosphere, the initiators added, and the degassing sequence repeated without heating.

Compound III.

α-Methyl-trans-stilbene oxide is a solid melting at 38.5-40°. At 40° no decomposition occurred and the initiators were not eliminated.

Compound IV.

Tetraphenylethylene oxide is a solid melting at 209-210°. The system was degassed without heating since melting would require high temperatures.

E. Nitrogen

Oil pumped nitrogen was purified by passing the gas through Fieser's solution[38] before use.

F. Handling of Samples

In all cases, except where otherwise noted, 0.1 grams of sample was used with one drop of initiator and the sample was degassed. After the prescribed time, the sample was removed from the furnace and quenched in dry ice. The vials were not opened until the spectra were to be run. In each case two identical samples were run in order to check reproducibility.

II. Synthesis of Oxiranes

Compounds I,[39] II,[40] III,[41] and IV[42] have been previously reported in the literature, and their synthesis was carried out according to these procedures.

III. 1,2-Diphenylallyl Alcohol

Brown and Brown[43] report the preparation of 1,2-diphenylallyl alcohol by lithium aluminum hydride reduction of 2-phenylcinnamic acid.

A nuclear magnetic resonance spectrum of the allyl alcohol (τ = 3.0 (m), 3.5 (t), 5.75 (d) and 7.68 (S) which is concentration dependent) indicates it to be 2,3-diphenylallyl alcohol rather than 1,2-diphenylallyl alcohol.

Lithium aluminum hydride reduction of methylene-deoxy benzoin yielded a compound which has a nuclear magnetic resonance spectrum [τ = 2.93 (m), 5.67 (d) and 6.95 (S) which is concentration dependent], ultraviolet absorption spectrum ($\lambda_{max}^{EtOH} \simeq 240$ mμ), thin layer chromatography retention time and an infrared spectrum which are different from the compound reported by Brown and Brown.[43]

The physical evidence indicates this compound (i.e., the reduced product of methylenedeoxybenzoin) to be 1,2-diphenylallyl alcohol.

Ingold's method of allyl alcohol isomerization[44] was attempted by Brown and Brown[43] on their apparent 2,3-diphenylallyl alcohol and in this work on 1,2-diphenylallyl alcohol, no evidence of isomerization was noted.

Five grams of methylenedeoxybenzoin[45] in 25 ml. of dry ether was added slowly to a cooled stirred solution of 0.95 gms. of lithium aluminum hydride in ether. The mixture was allowed to warm to room temperature, then with continued stirring, refluxed for three hours. A saturated solution of soidum sulfate was added to the cooled flask, the mixture was then filtered. The filtrate was taken up in ether and dried over anhydrous magnesium sulfate. The residue was extracted with methanol. The methanol extracts were evaporated and the remaining material taken up in ether to remove any inorganic material. The combined ether extracts were stripped of solvent and an oily compound was obtained. This substance had a retention time on thin layer chromatography, using silica gel G and 30:70 of $HCCl_3$: benzene as the eluting solvent, different from the substance reported by Brown and Brown,[43] $\lambda_{max}^{EtOH} \cong 240$ mμ compared to $\lambda_{max}^{EtOH} = 257$ mμ reported by Brown and Brown.[43] Nuclear magnetic resonance showed a doublet ($\tau = 4.62$ and 4.72) which had an area ratio of 3:1 compared to the hydroxyl hydrogen ($\tau = 6.95$ which is concentration dependent).

SUMMARY

None of the oxiranes (i.e., I-IV) studied showed a true unimolecular thermal reaction.

Some of the earlier work reported on these oxiranes were reinvestigated and their results were shown to be ambiguous.

Substitution of phenyl groups on the oxirane ring retards radical abstraction of benzylic hydrogens.

The products of surface reactions were explained in terms of mild acid catalysis by Lewis acid sites on the Pyrex glass-surface.

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