71-5360

VERZINO, Jr., William John, 1940-
DIPHENYLMETHYLBISHYDROPEROXIDE:
AN ANOMALOUS PRODUCT FROM THE OZONOLYSIS
OF TETRAPHENYLETHYLENE.

Colorado State University, Ph.D., 1970
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

THESIS

DIPHENYLMETHYLBISHYDROPEROXIDE: AN ANOMALOUS PRODUCT FROM THE OZONOLYSIS OF TETRAPHENYLETHYLENE

Submitted by

William J. Verzino, Jr.

In partial fulfillment of the requirements

for the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

August, 1970

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

COLORADO STATE UNIVERSITY

August, 1970

WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR SUPERVISION BY WILLIAM J. VERZINO, JR. ENTITLED DIPHENYLMETHYLBISHYDROPEROXIDE: AN ANOMALOUS PRODUCT FROM THE OZONOLYSIS OF TETRAPHENYLETHYLENE BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

Committee on Graduate Work

F. P. Stein

C. G. Warren

W. L. Lindsay

Arnold Robertson

Adviser

Head of Department

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ABSTRACT OF THESIS

DIPHENYLMETHYLBISHYDROPEROXIDE: AN ANOMALOUS PRODUCT FROM THE OZONOLYSIS OF TETRAPHENYLETHYLENE

The ozonolysis of tetraphenylethylene in methyl alcohol produced the anomalous product, diphenylmethylbishydroperoxide. The observation of a bishydroperoxide during the ozonoylsis of an olefin under hydroxylic conditions has not been previously reported. Aliphatic bishydroperoxides are usually prepared by the action of hydrogen peroxide on the ketone. This technique, however, was unsuccessful on the aromatic ketone, benzophenone.

Diphenylmethylbishydroperoxide appears to engage in intramolecular hydrogen bonding. Its thermal decomposition to benzophenone follows very nearly first order kinetics.

Acetyl chloride readily converts the bishydroperoxide to the diperester. When thermally decomposed, the diperester produced phenyl benzoate by means of a phenyl migration to oxygen. The decomposition follows first order kinetics and has activation parameters similar to that of benzoyl peroxide. Electron spin resonance studies showed the migration to involve free radicals. Reported observations of an aryl migation to oxygen by a radical pathway are limited.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Phenyl benzoate was also observed when the diperester was decomposed with trifluoroacetic acid. The decomposition with trifluoroacetic acid produced a greater quantity of phenyl benzoate than the thermal decomposition.

William J. Verzino, Jr.
Department of Chemistry
Colorado State University
Fort Collins, Colorado, 80521
August, 1970

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to his major professor, Dr. Jerold C. Robertson, for his guidance and encouragement throughout the course of this problem.

The author is also indebted to Drs. Frank R. Stermitz, C. Gerald Warren, and Willard L. Lindsay for serving as members of the graduate committee and also for their suggestions during the preparation of this manuscript.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Dedication

To my families

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

TABLE OF CONTENTS

	Page
INTRODUCTION	1
RESULTS AND DISCUSSION	7
I. Diphenylmethylbishydroperoxide (XXIII)	9
A. Structural Evidence	9
B. Mechanism of Formation	11
C. Hydrogen Bonding Study	13
D. Attempted Alternate Preparations of XXIII	14
E. Decomposition Studies on XXIII	15
F. Singlet Oxygen Experiment	27
G. Other Possible Syntheses of XV	28
II. Diphenylmethylbisacetylperoxide (XXXIII)	30
A. Decomposition	30
B. Substituted Diphenylmethylbisacetylperoxide	45
C. Decomposition Kinetics of Diphenylmethylbisacetylperoxide	48
D. Preliminary Investigation of the Trifluoracetic Acid Decomposition of XXXIII	57
EXPERIMENTAL	59
A. Ozonolysis Procedure	61
B. Diphenylmethylbishydroperoxide (XXIII)	61
C. Analysis for Active Oxygen	62
D. Attempted Alternate Preparations of XXIII	63
E. Kinetic Study of the Thermal Decomposition of XXIII	63
F. Singlet Oxygen Experiment	64
G. Other Attempted Syntheses of XV	65
1. Benzhydry methyl ether (XXXI)	65
2. p-Nitrobenzhydryl methyl ether (XXXII)	65

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

TABLE OF CONTENTS (Continued)

Page

H. Acylation of XXIII 66

1. Diphenylmethylbisacetylperoxide (XXXIII) 66
2. Diphenylmethylbisbenzoylperoxide 67

I. Phenyl-N-t-butylnitrone, PBN, (XXXV) 68

1. Peracetic Acid 68
2. N-Benzylidiene-t-butylamine 68
3. 2-t-Butyl-3-phenyloxazirane 69
4. Phenyl-N-t-butylnitrone, PBN, (XXXV) . . . 69

J. ESR Technique 69
K. 1,2-Bis-p-nitro-phenyl-1,2-diphenyl-ethylene (XL) 70

1. p-Nitrobenzyhdrol 70
2. p-Nitrobenzhydrylidenedibromide 70
3. 1,2-Bis-p-nitro-phenyl-1,2-diphenyl-ethylene (XL) 70
4. Ozonation of 1,2-Bis-p-nitro-phenyl-1,2-diphenylethylene 71

L. Decomposition of Diphenylmethylacetyl-peroxide (XXXIII) 72

1. Gas Chromatographic Yield Analysis 72
2. Decomposition Kinetics of XXXIII 72

M. Preliminary Investigation of Trifluoroacetic Acid Decomposition of XXXIII 73

SUMMARY 75

LITERATURE CITED 77

APPENDIX (Spectra) 83

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

LIST OF TABLES

Table		Page
I	Kinetic Data for Thermal Decomposition of XXIII, Run 1 at 90°. (Ultraviolet Analysis)	21
II	Kinetic Data for Thermal Decomposition of XXIII, Run 2 at 90°. (Ultraviolet Analysis)	22
III	Kinetic Data for Thermal Decomposition of XXIII, Run 1 at 95°. (Ultraviolet Analysis)	23
IV	Kinetic Data for Thermal Decomposition of XXIII, Run 2 at 95°. (Ultraviolet Analysis)	24
V	Kinetic Data for Thermal Decomposition of XXIII, Run 1 at 98°. (Ultraviolet Analysis)	25
VI	Kinetic Data for Thermal Decomposition of XXIII, Run 2 at 98°. (Ultraviolet Analysis)	26
VII	Kinetics of Thermal Decomposition of XXIII in 2, 2, 4-Trimethlypentane	27
VIII	Hyperfine Splitting Constants of Phenyl, Acetoxy, and Methyl Spin Adducts (50)	34
IX	Hyperfine Splitting Constants of Acetoxy Spin Adducts	36
X	Kinetics of Decomposition of XXXIII in Diphenyl Ether	49
XI	Kinetic Data for Thermal Decomposition of XXXIII, Run 1 at 69°. (NMR Analysis)	52
XII	Kinetic Data for Thermal Decomposition of XXXIII, Run 2 at 69°. (NMR Analysis)	53
XIII	Kinetic Data for Thermal Decomposition of XXXIII, at 75°. (NMR Analysis)	54

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

LIST OF TABLES (Continued)

Table		Page
XIV	Kinetic Data for Thermal Decomposition of XXXIII, at 90°. (NMR Analysis)	55
XV	Product Ratios for the Decomposition of XXXIII	58

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

LIST OF FIGURES

Figure		Page
1	Cumulative Ultraviolet Spectrum for the Decomposition of XXIII to Benzophenone at 98°	16
2	First Order Kinetic Plot for the Thermal Decomposition of XXIII at 90°, Run 1	18
3	First Order Kinetic Plot for the Thermal Decomposition of XXIII at 90°, Run 2	18
4	First Order Kinetic Plot for the Thermal Decomposition of XXIII at 95°, Run 1	19
5	First Order Kinetic Plot for the Thermal Decomposition of XXIII at 95°, Run 2	19
6	First Order Kinetic Plot for the Thermal Decomposition of XXIII at 98°, Run 1	20
7	First Order Kinetic Plot for the Thermal Decomposition of XXIII at 98°, Run 2	20
8	Theoretical esr Spectrum for a PBN Spin Adduct	33
9	The esr Spectrum Obtained from the Decomposition of XXXIII in the Presence of PBN in SkellySolve-H	35
10	The esr Spectrum Obtained from the Decomposition of XXXIII in PBN in the Absence of Solvent. The Theoretical Composition of the Spectrum is Attributed to Phenyl, Methyl, and Acetoxy Spin Adducts	40
11	The esr Spectrum Obtained from the Photolysis of Iodobenzene in PBN Melt	42
12	First Order Kinetic Plot for the Thermal Decomposition of XXXIII at 69°, Run 1	50

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

LIST OF FIGURES (Continued)

Figure		Page
13	First Order Kinetic Plot for the Thermal Decomposition of XXXIII at 69°, Run 2	50
14	First Order Kinetic Plot for the Thermal Decomposition of XXXIII at 75°.	51
15	First Order Kinetic Plot for the Thermal Decomposition of XXXIII at 90°.	51
16	Activation Plot for the Thermal Decomposition of XXXIII	56

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

LIST OF SCHEMES

Scheme		Page
I	Criegee Mechanism of Ozonolysis	3
II	Mechanism of Thermal Decomposition of XXXIII	44

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

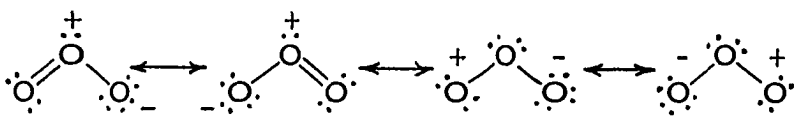
LIST OF APPENDIX FIGURES

Figure		Page
17	The ir Spectrum of Diphenylmethylbishydroperoxide (XXIII) in Nujol	84
18	The ir Spectrum of Diphenylmethylbishydroperoxide (XXIII) in KBr	85
19	The ir Spectrum of Diphenylmethylbisacetylperoxide (XXXIII) in Nujol	86
20	The ir Spectrum of Diphenylmethylbisacetylperoxide (XXXIII) in KBr	87
21	The ir Spectrum of Diphenylmethylbisbenzolyperoxide in Nujol	88
22	The ir Spectrum of cis, 1,2-Bis-p-nitrophenyl-1,2-diphenylethylene (XLI) in KBr	89
23	The ir Spectrum of trans, 1,2-Bis-p-nitrophenyl-1,2-diphenylethylene (XLII) in KBr	90
24	The Mass Spectrum of Diphenylmethylbishydroperoxide (XXIII) with Source at 130°.	91
25	The Mass Spectrum of Diphenylmethylbishydroperoxide (XXIII) with Source at 50°	92
26	The Mass Spectrum of Diphenylmethylbisacetylperoxide (XXXIII).	93
27	The Ultraviolet Spectrum of Diphenylmethylbisbenzolyperoxide in Methyl Alcohol	94
28	The NMR Spectrum of Diphenylmethylbishydroperoxide (XXIII) in CH_3CN	95
29	The NMR Spectrum of Diphenylmethylbisacetylperoxide (XXXIII).	96

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

INTRODUCTION

The combination of an oxygen atom with an O_2 molecule yields the triatomic modification -- ozone. The microwave spectrum of ozone reveals two bonds of equal length (1.28 Å) enclosing an angle of 117° (1). This bond length is intermediate between those associated with single and double O-O bonds (2). This, in conjunction with an electric moment of 0.53 D indicates a mesomeric ground state in which ozone may be considered a 1,3-dipole.



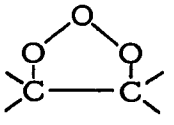
The reactions of ozone with organic compounds display considerable specificity. In some cases there is a transfer of only one oxygen atom, while the other two are evolved as molecular oxygen. Amines and sulfides react in this manner. Olefins and acetylenes are able to accept all three oxygen atoms of the ozone molecule.

The first observation of an ozone reaction with an olefin was in 1855 by Schönbein (3), who reported that ozone and ethylene react to give carbonic acid, formaldehyde, and formic acid. The first ozonide was isolated in 1873 by Houzeau (4). From these early beginnings ozone reactions have grown into one of the most versatile methods for oxidative cleavage of a double bond.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

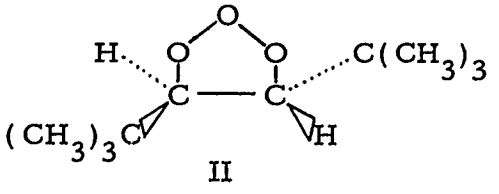
Extensive reviews on organic ozone chemistry have been written by Long (5), Bailey (6), and Criegee (7).

Currently there is a considerable controversy over the mechanism of ozonolysis (8). The term ozonolysis will be used to describe that reaction of ozone with a double bond which leads to cleavage of that bond. Huisgen (9) considers the initial interaction of ozone with alkenes to be a 1, 3-dipolar cycloaddition reaction. This type of addition would lead to a five-membered 1, 2, 3-trioxolane ring structure (I) for the initial adduct.



I

In 1960, Criegee and Schröder (10) isolated a crystalline primary ozonide (II) with an intact C-C bond. This adduct was obtained from trans-1, 2-di-t-butylethylene and ozone at -75°.



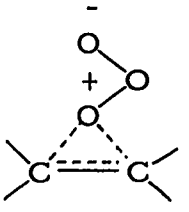
II

The nmr spectrum of this adduct showed a single methine proton absorption (11).

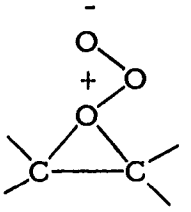
There are several instances where it appears that the initial adduct does not have the structure I (12-15). In these cases

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

one of the ozonolysis products is the epoxide derived from the olefin. Occasionally the epoxide is the major ozonolysis product, particularly from 1-olefins in which one side of the double bond is heavily substituted (12, 13, 15). It is possible that the epoxide product may derive from the five membered structure I, but it seems more plausible that the precursors in these cases must have a different structure. One possible structure is a π (III) or δ (IV) complex (14-16) which eliminates molecular oxygen to give the epoxide.

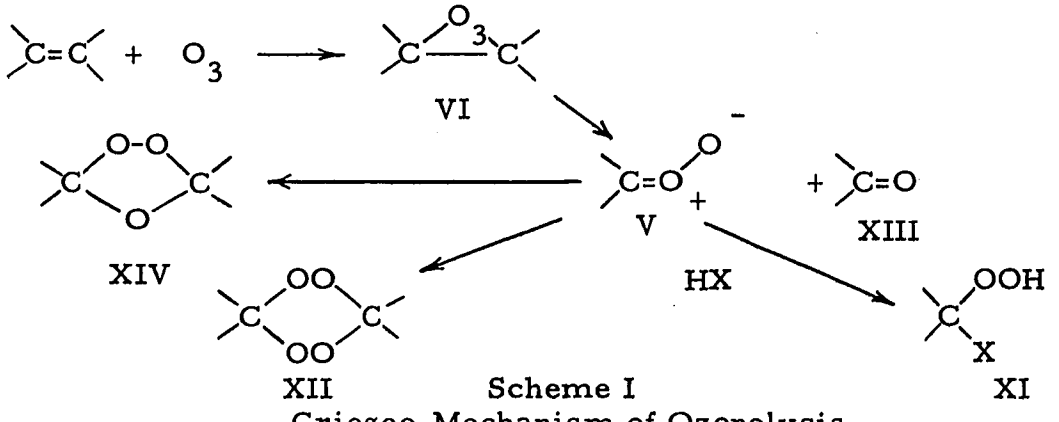


III



IV

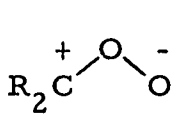
Perhaps the mechanism most successful in explaining a large percentage of the accumulated experimental data was proposed by Criegee (17, 18) after several years of work by himself and his co-workers. The Criegee mechanism is represented in Scheme I.



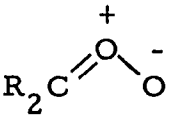
Scheme I
Criegee Mechanism of Ozonolysis

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

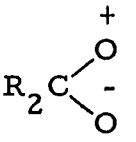
The key intermediate in the Criegee mechanism is the zwitterion (V) formed from the collapse of the initial ozonide (VI). The zwitterion is thought to be a hybrid of structures VII, VIII and IX (6). The hybrid may be conveniently represented by structure X.



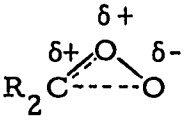
VII



VIII



XI

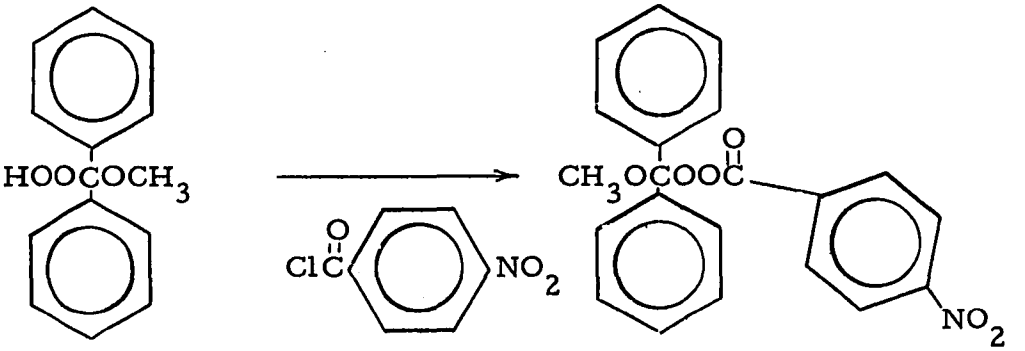


X

The nature of the ultimate products then depends on the partitioning of the zwitterion among a number of possible routes. In the presence of a protic reagent, HX, (e.g. HOH, $HOCH_3$, $HO\overset{O}{\overset{\|}{C}}CH_3$, HNH_2, or HCN), the hydroperoxide (XI) may be isolated in high yield. If the solvent is inert and the carbonyl compound does not readily undergo carbonyl addition, the zwitterion may self-react to give the diperoxide (XII) together with higher polymers or oligomers (19). If the carbonyl compound (XIII) readily undergoes addition the ozonide (XIV) and its polymers may be formed.

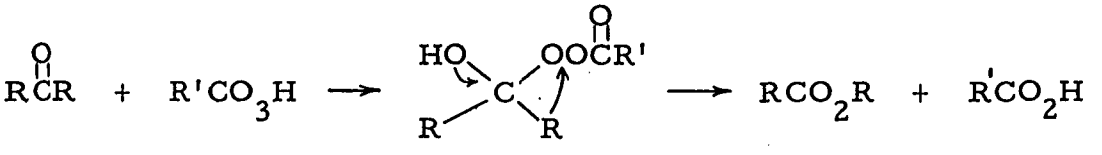
Predicated on the Criegee ozonolysis mechanism, the synthesis of diphenylmethoxy methyl hydroperoxide (XV) was undertaken. Tetraphenylethylene was ozonized in the presence of methyl alcohol.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.



XV XVI

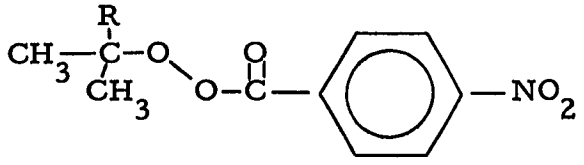
The peroxy ester(XVI), obtained through acylation of XV, is of interest as a model for the intermediate adduct XVII, proposed by Criegee(20), in the Baeyer-Villiger reaction of ketones with per-acids.



XVII

The ionic decomposition of peresters, involving a 1,2 rearrangement of carbon to electron-deficient oxygen, has received a number of mechanistic investigations. Hedaya and Winstein (21, 22) have studied the migration to electron-deficient oxygen and anchimeric acceleration of peroxide-bond heterolysis during ionic decomposition of 2-substituted 2-propyl-p-nitro perbenzoates (XVIII).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.



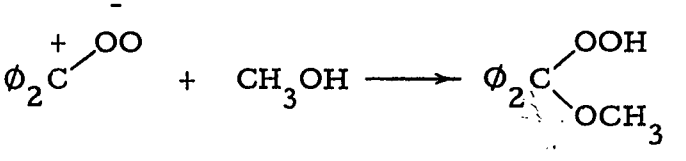
XVIII

We felt that kinetic decomposition studies on XVI designed to explore the structure-reactivity relationships in the phenyl system would be of value in understanding the Baeyer-Villiger reaction. However, ozonolysis of tetraphenylethylene in methyl alcohol did not yield the expected methoxy hydroperoxide, but a new, anomalous compound (23). This compound was unique enough to warrant exclusive investigation of its chemistry and to become the subject of this dissertation.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

RESULTS AND DISCUSSION

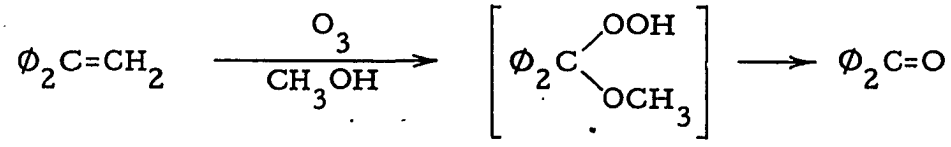
The ozonolysis of tetra-alkyl and unsymmetrical dialkyl-substituted olefins in an alcoholic medium follows the Criegee pathway yielding an alkoxy hydroperoxide (24). Similarly, the ozonolysis of monosubstituted aromatic olefins, like styrene, trans-propenylbenzene, and 2-methyl-propenylbenzene in methyl alcohol leads to the expected α-methoxybenzyl hydroperoxide (25). Tetraphenylethylene has been ozonized in the presence of methyl alcohol (26, 27), but the resultant hydroperoxide (XV) from the interception of the Criegee zwitterion XIX has never been reported in the literature.



XIX XV

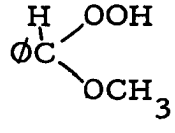
Ozonolysis of tetraphenylethylene in the inert solvent, carbon tetrachloride, yields the expected product, dimeric benzophenone peroxide, resulting from the dimerization of XIX (28). Recently, Fliszar (29) unsuccessfully attempted to prepare XV through ozonolysis of 1, 1-diphenylethylene (XX) in methyl alcohol at 0^{o}.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.



XX XV XXI

He reported that XV readily goes to benzophenone (XXI). However, Criegee (30) reports that Gunther (31) synthesized XV by ozonizing tetraphenylethylene in methyl alcohol at -78°. Further, that XV is a stable compound melting at 91° but is readily hydrolyzed by water to benzophenone and hydrogen peroxide. It is interesting that α-methoxy hydroperoxide (XXII) is resistant toward hydrolysis and is extracted into water during the work-up procedure used by Keaveney, et al. (25). There is conflicting evidence for the



XXII

existence of XV. The characterization of "XV" by Gunther (31) was equivocal. The structural evidence consisted of an infrared spectrum, an active oxygen analysis, and a combustion analysis. The combustion analysis was off 0.8% in carbon, 0.5% in hydrogen, and 0.4% in oxygen. The molecular weight of XV is 230 and the molecular weight of XXIII is 232. The decisive piece of evidence, an nmr, was not taken. We have made numerous attempts to

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

prepare XV through ozonolysis of tetraphenylethylene at temperatures ranging from -78° to 0° and have isolated only the expected benzophenone and the completely unexpected diphenylmethylbishydroperoxide (XXIII). A bishydroperoxide during ozonolysis in a

$$\phi_2C=C\phi_2 \xrightarrow[CH_3OH/CHCl_3]{O_3/O_2} \phi_2C(OOH)_2 + \phi_2C=O$$

XXIII

hydroxylic solvent has not been previously observed. The aliphatic bishydroperoxides are usually prepared by the action of hydrogen peroxide on the ketone (acetone, (32) ethyl methyl ketone (33), diethyl ketone (34), and cyclohexanone (35-37).

I. Diphenylmethylbishydroperoxide

A. Structural Evidence

The ozonolysis of tetraphenylethylene in a chloroform-alcohol solution produced a clear, colorless oil after removal of the solvent. Tlc analysis of this oil, on silica gel at -5°, indicated the presence of only two components in the mixture. One would expect these to be, based on previously reported work (6, 7, 17), benzophenone and diphenylmethoxy hydroperoxide (XV) (or the ethoxy derivative, depending on the alcohol used in the solvent system). We were able to isolate both components of the mixture and readily identified one as benzophenone. The other component, a white crystalline solid, gave

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ir and nmr spectra which were not compatible with XV. The ir spectrum showed no aliphatic C-H absorptions in the 2900 cm^{-1} region while the nmr gave no indication of any aliphatic protons. A multiplet was observed at δ 7.25-7.73 and a broad singlet at δ 9.70 (integration ratio 5:1) which disappeared on addition of deuterium oxide. The white solid reacted readily with starch-iodide paper, and a quantitiative titration for active oxygen gave an equivalent weight of 60.8 (equivalent weight of XV is 115). Owing to the overwhelming evidence against XV, it was rejected as the structure for the other component in the ozonolysis mixture.

Structure XXIII fits the experimental evidence much better than does XV. The equivalent weight of XXIII is 58, and for the nmr spectrum one would expect a multiplet due to the aromatic protons and a broad singlet downfield, integrating in the ratio 5:1, as was observed. In addition, the ir spectrum is compatible with what would be expected for structure XXIII. Confirmation for structure XXIII was obtained from a low temperature (source at 50°) mass spectrum which gave a parent ion of mass 232, the molecular weight of XXIII, intensity 1%.

Chemical evidence for XXIII was obtained from the thermal behavior and pyrolysis products of the white solid. Compound XXIII readily converts to benzophenone and oxygen on heating. For example, a KBr pellet of XXIII was prepared and the ir spectrum

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

obtained, but after heating the pellet for 20 min. at 130° a new spectrum was obtained. These two ir spectra were completely different, and the latter was superimposable on the ir spectrum of benzophenone, with the exception of a few very weak peaks due to residual XXIII. In addition, when XXIII was decomposed in the gas chromagraph, only two peaks resulted, which by comparison with authentic samples were identified as benzophenone and oxygen. Again, these results were confirmed by mass spectrometry. A moderate temperature (source at 130°) mass spectrum of XXIII gave only the spectrum of benzophenone and a large oxygen 32 peak.

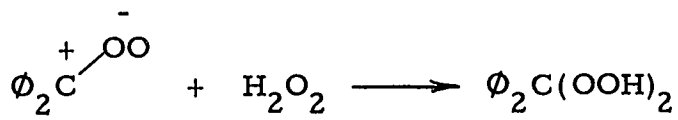
Elemental analysis of XXIII was difficult due to partial decomposition to benzophenone during recrystallization. This accounts for the somewhat high equivalent weight obtained. However, an acceptable analysis was obtained for the diacetyl derivative.

B. Mechanism of Formation

It is possible that XXIII could be formed through an excess of ozone in the reaction mixture. This possibility was eliminated by terminating the ozonolysis before completion and isolating the components in the solvent. The compounds so isolated were tetraphenylethylene, benzophenone, and XXIII.

The bishydroperoxide (XXIII) was thought to be formed by the reaction of XIX with hydrogen peroxide. To test this hypothesis

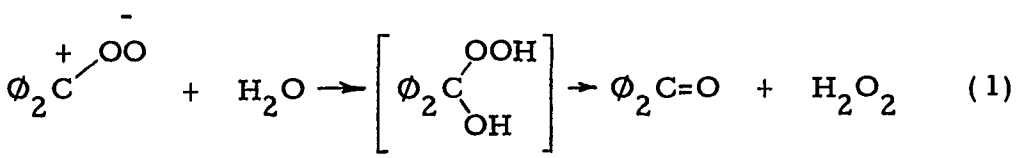
Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.



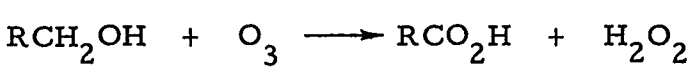
XIX XXIII

two drops of 90% hydrogen peroxide was added to the reaction mixture before ozonolysis. The yield of isolatable XXIII increased from 50% to 71%. However, when the hydrogen peroxide was added to the ozonolysis product mixture after removing the solvents, no increase in the yield of XXIII was observed. Apparently XXIII was formed during the ozonolysis reaction and not from the decomposition of some intermediate such as XV.

There are at least two possible sources of hydrogen peroxide in this system, as shown by reactions 1 and 2. Reaction 1



(1)



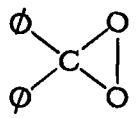
(2)

requires residual water within the system and may be the source of only a small amount of hydrogen peroxide, while reaction 2 is very likely the main source of hydrogen peroxide. Whiting and coworkers (38) indicate that this reaction occurs readily at -78°.

These results indicate that the diphenyl-substituted Criegee zwitterion (XIX) is quite stable and selective as to its requirements for reaction with a nucleophile. This stability may be due either to a

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

large delocalization energy via resonance with the π system of the phenyl rings or to the formation of the dioxirane intermediate (XXIV). In any case, neither the ozonide, the alkoxy hydroperoxide, nor the

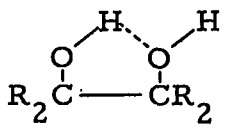


XXIV

Criegee zwitterion dimer forms when better nucleophiles are present.

C. Hydrogen Bonding Study

The presence of two OH bands (3400, 3400 cm^{-1}) in the ir of XXIII prompted investigation of possible hydrogen bonding. Usually compounds having two OH bands exist in the form (39):

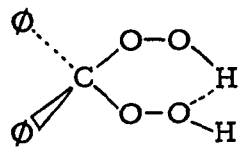


The high frequency band is caused by the free OH and the low frequency band is caused by the bonded OH. One of the criterion for intramolecular hydrogen bonding is that the ratio of the two bands is independent of concentration (40).

The Perkin-Elmer Model 457 infrared grating spectrophotometer has a five-fold area magnification capability which allowed easy observation of the effect of dilution on the two OH bands in

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

XXIII. The initial concentration used was less than 0.005 M to avoid intermolecular bonding (40). The ratio of the two bands remained essentially constant through six dilutions to approximately half the initial concentration. This indicates that XXIII has intramolecular hydrogen bonding and perhaps exists in the form XXV. It has been shown by Badger (41) that the stronger the hydrogen bond, the greater



XXV

is the separation of the two bands (Δ v). Also in the range of value of H···O distances available, namely, 1.6 to 3.3 Å, a linear relationship was found between Δv and the reciprocal of the H···O distance. This relationship can be expressed in the form

$$\Delta v = \frac{250 \times 10^{-8}}{L} - 74$$

where L is the H···O distance in cm. In the case of XXIII, Δ v is 38 cm^{-1} and L is computed to be 2.2 Å. These figures are comparable to those for cis-cyclohexane-1, 2-diol (Δ v = 38 cm^{-1} and L = 2.2 Å) (42).

D. Attempted Alternate Preparations of XXIII

The synthesis of XXIII by an alternate pathway would provide additional structural evidence and perhaps be a simpler way to

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

synthesize larger quantities. Cadogan, et al. (43), may have observed XXIII from the reaction of 85% hydrogen peroxide with benzophenone. They isolated a peroxide, mp 90-92°, but did not establish the structure of the compound. Our attempts to reproduce this synthesis under a variety of conditions were unsuccessful.

E. Decomposition Studies on XXIII

The kinetics of thermal decomposition of XXIII were of interest in further characterizing the new compound. The decomposition of XXIII to benzophenone could easily be followed by ultraviolet spectrophotometry since benzophenone has an absorptivity of 18,900 in cyclohexane at 252 mμ (44).

The decomposition of XXIII was accomplished in a constant temperature oil bath. Fractions were taken out periodically and quenched in an ice bath. The uv spectrum was then taken of the fraction. Taking uv spectra at room temperature was a satisfactory procedure, since there was no decomposition of XXIII after three hours at 45°--the initial uv spectrum was superimposable on the spectrum taken after three hours at 45°. Figure 1 is a typical, cumulative uv spectrum for the thermal decomposition of XXIII. This decomposition at 98° was observed over a two hour period.

The kinetic data obtained from uv analysis, consisting of absorptivity and elapsed time were analyzed by a CDC 6400 computer, using a first order kinetic program developed by Dr. J. C.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

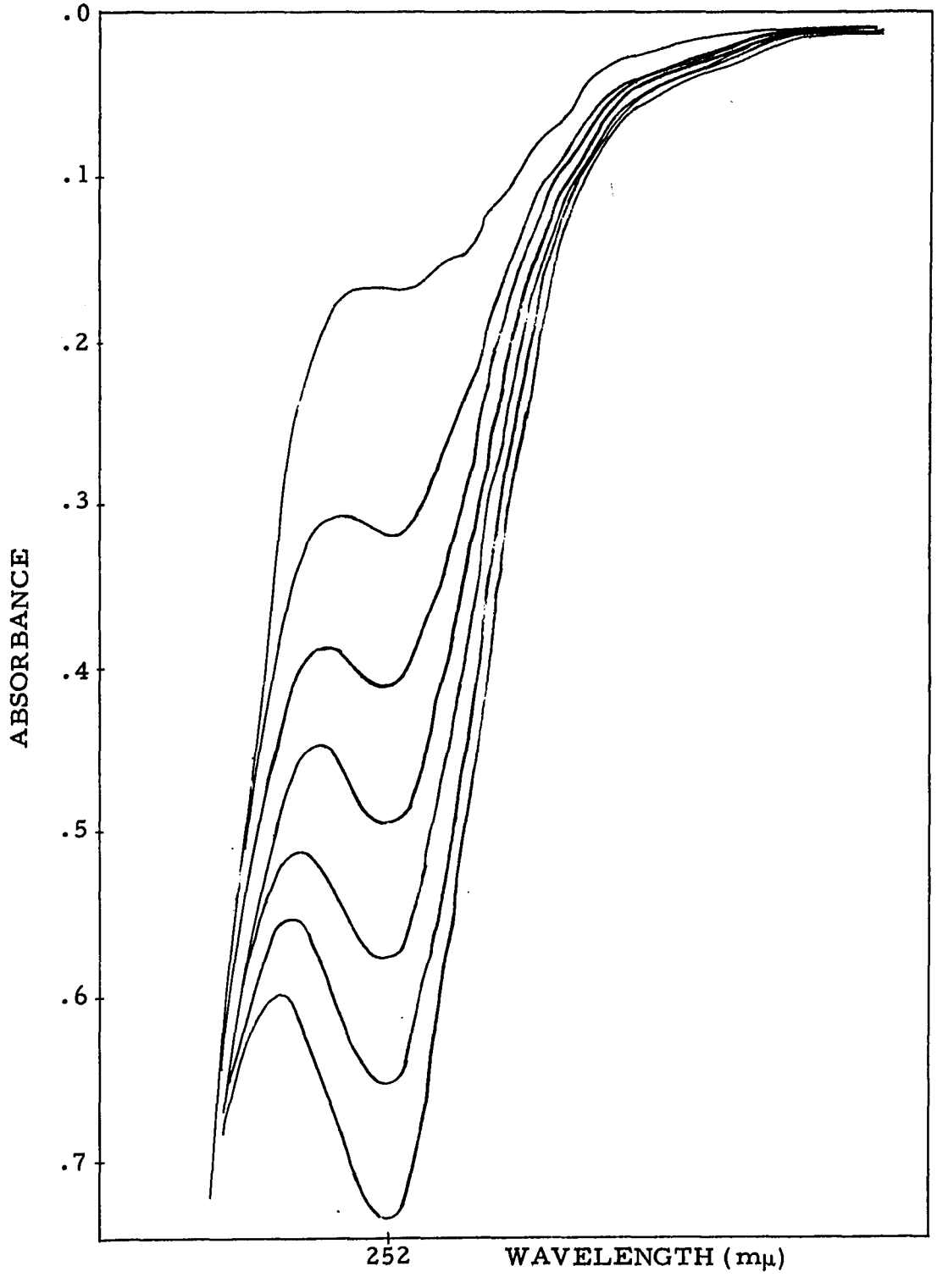


Figure 1. Cumulative Ultraviolet Spectrum for the Decomposition of XXIII to Benzophenone at 98°.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Robertson. The program is based on the first order law, $\ln(a/a-x)= kt$, where "x" refers to the extent of reaction and "a" refers to the initial concentration of the reactant or any other quantity that is proportional to concentration. The program is flexible accepting either disappearance of reactant or appearance of product as input. For the decomposition of XXIII, the appearance of product, benzophenone, was used as input. Regardless of the input, the program determines the value of $\ln(a-x)$ for each point and plots these values against time in seconds to obtain a line whose slope is equal to the rate constant k. The computer determines the best fitting straight line by a least squares analysis.

The decomposition reaction was followed at three temperatures. Figures 2 through 7 represent the results of six kinetic determinations. The data is shown in Tables I-VI. The data appears to fit the least squares line for most cases fairly well. However, in others there appears to be a systematic downward curvature indicating that the reaction speeds up with time. The deviation in rate constants at the same temperature, reflected in Table VII, may be a consequence of some type of uncontrolled catalysis. It is generally known that the thermal decomposition of secondary and tertiary alkyl hydroperoxides is relatively complex. A unimolecular homolysis is complicated by association of the hydroperoxide molecules and by their sensitivity to induced decomposition (45, 46).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

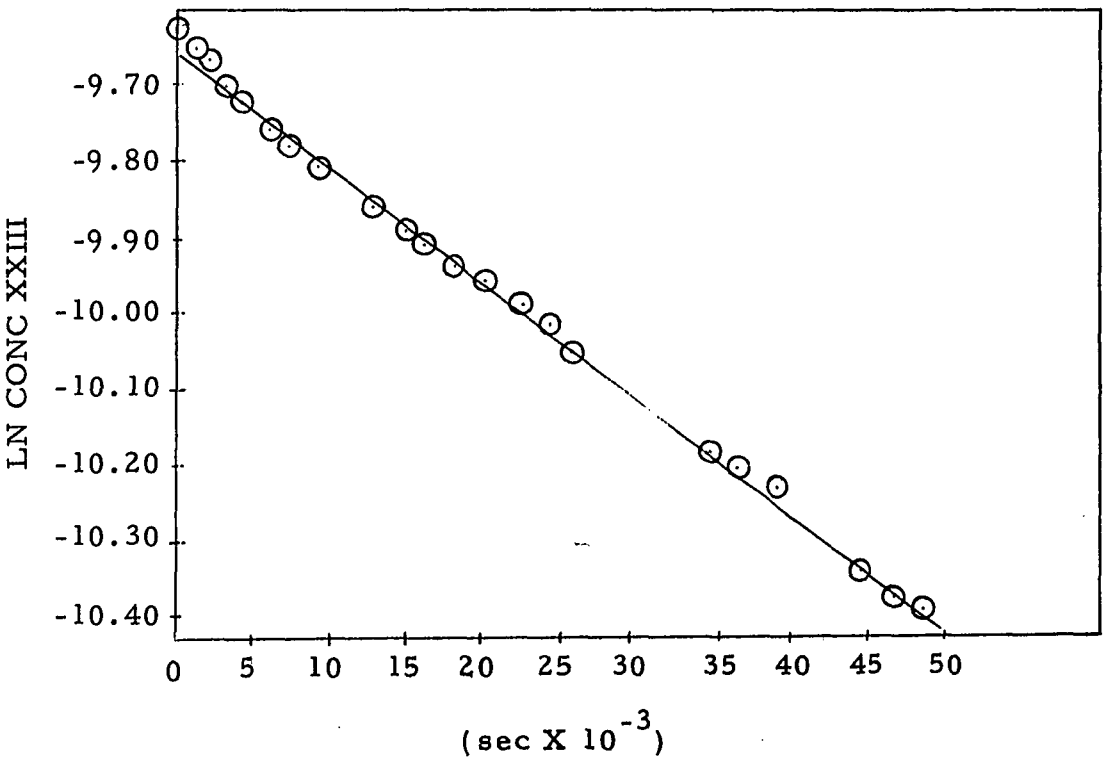


Figure 2. First Order Kinetic Plot for the Thermal Decomposition of XXIII at 90°, Run 1.

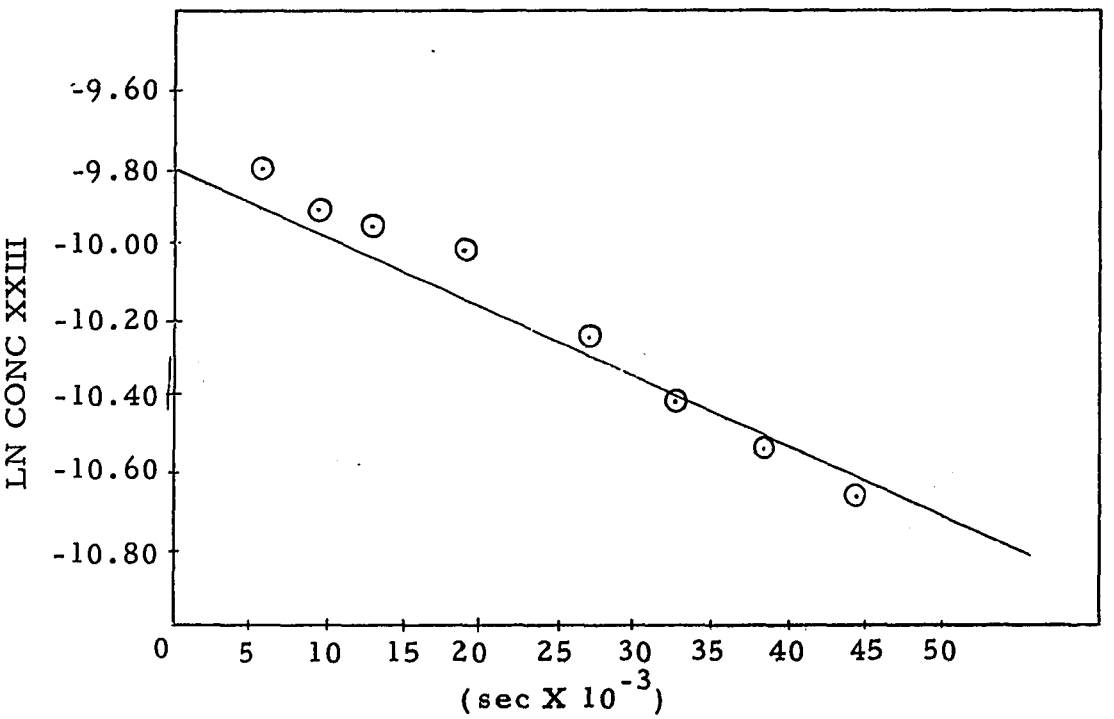


Figure 3. First Order Kinetic Plot for the Thermal Decomposition of XXIII at 90°, Run 2.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

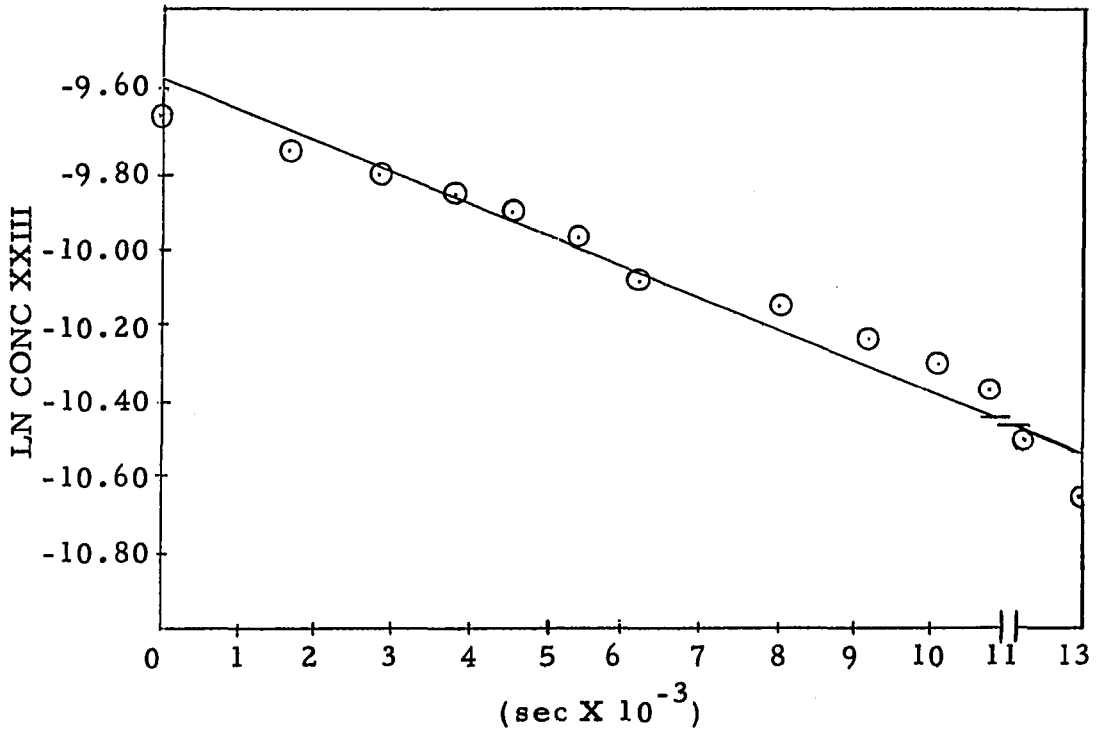


Figure 4. First Order Kinetic Plot for the Thermal Decomposition of XXIII at 95°, Run 1.

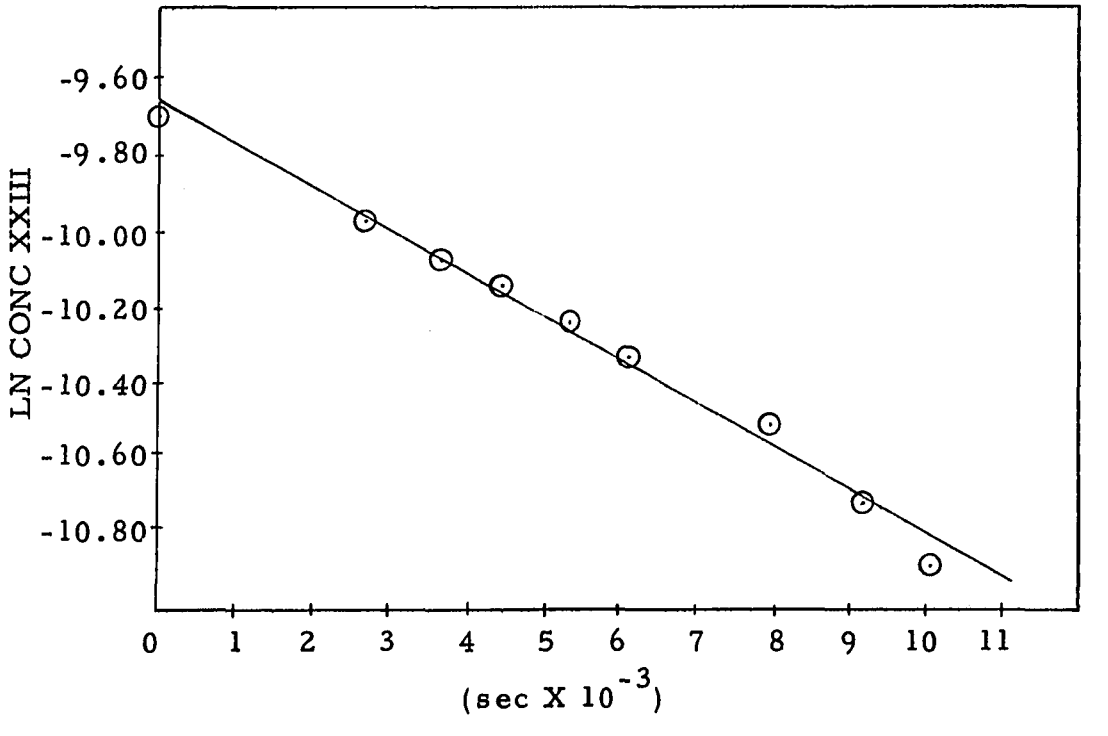


Figure 5. First Order Kinetic Plot for the Thermal Decomposition of XXIII at 98°, Run 2.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

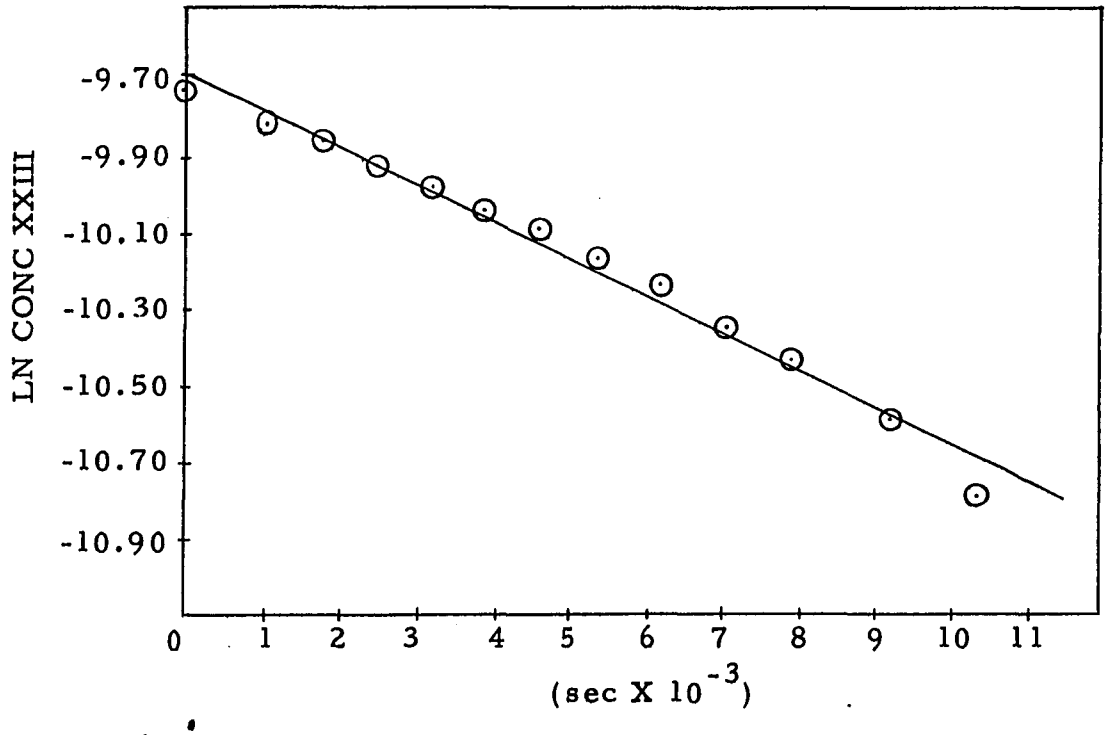


Figure 6. First Order Kinetic Plot for the Thermal Decomposition of XXIII at 98°, Run 1.

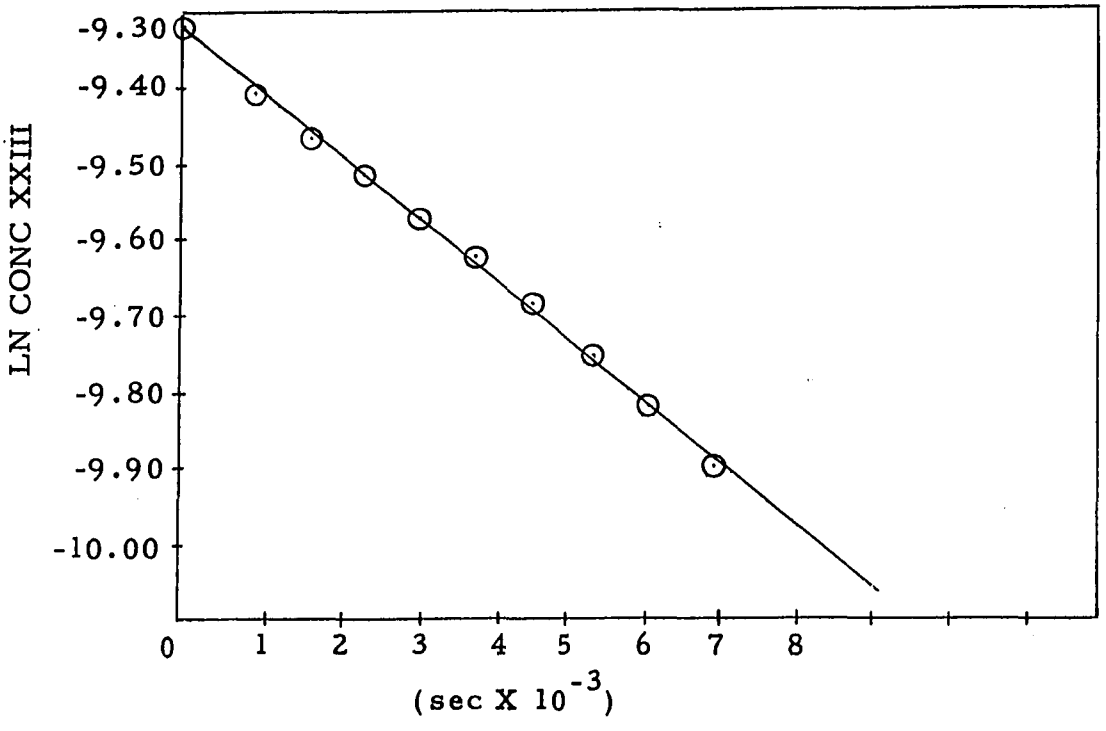


Figure 7. First Order Kinetic Plot for the Thermal Decomposition of XXIII at 98°, Run 2.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table I. Kinetic Data for Thermal Decomposition of XXIII, Run 1 at 90°. (Ultraviolet Analysis)

Reaction Time (sec)	Absorptivity of Product (benzophenone)	Residual from Least Squares Line
0	0.119	2.40×10^{-2}
1020	0.144	2.03×10^{-2}
1800	0.175	7.83×10^{-3}
3240	0.213	-9.60×10^{-4}
4260	0.237	-5.33×10^{-3}
6120	0.282	-1.54×10^{-2}
7260	0.297	-1.12×10^{-2}
9360	0.335	-1.33×10^{-2}
12840	0.388	-9.88×10^{-3}
15000	0.418	-6.18×10^{-3}
16020	0.442	-1.46×10^{-2}
18000	0.464	-6.96×10^{-3}
19980	0.485	1.22×10^{-3}
22440	0.518	3.18×10^{-3}
24300	0.538	9.35×10^{-3}
25860	0.565	2.42×10^{-3}
34800	0.676	1.43×10^{-3}
36660	0.690	1.10×10^{-2}
38940	0.713	1.42×10^{-2}
44460	0.783	-4.22×10^{-3}
46800	0.805	-3.11×10^{-3}
48420	0.820	-2.67×10^{-3}
50700	0.840	-1.21×10^{-3}

$k = 1.52 \times 10^{-5}\ sec^{-1}$

Conc. XXIII = 7.16×10^{-5} M

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table II. Kinetic Data for Thermal Decomposition of XXIII, Run 2 at 90°. (Ultraviolet Analysis)

Reaction Time (sec)	Absorptivity of Product (benzophenone)	Residual from Least Squares Line
0	0.113	1.69×10^{-1}
5520	0.318	9.80×10^{-2}
9360	0.420	7.03×10^{-2}
12600	0.460	8.80×10^{-2}
18840	0.589	5.65×10^{-2}
26580	0.713	3.49×10^{-2}
29220	0.750	-4.45×10^{-1}
32700	0.810	-1.88×10^{-3}
38340	0.880	-2.16×10^{-2}
44340	0.948	-4.75×10^{-2}

$k = 1.80 \times 10^{-5}$ sec^{-1}

Conc. of XXIII = 7.11×10^{-5} M

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table III. Kinetic Data for Thermal Decomposition of XXIII, Run 1 at 95°. (Ultraviolet Analysis)

Reaction Time (sec)	Absorptivity of Product (benzophenone)	Residual from Least Squares Line
0	0.076	-8.20×10^{-2}
1685	0.176	-3.10×10^{-2}
2824	0.249	-5.45×10^{-3}
3790	0.310	1.37×10^{-2}
4566	0.355	3.07×10^{-2}
5464	0.418	3.61×10^{-2}
6244	0.518	-1.55×10^{-2}
8060	0.573	5.92×10^{-2}
9247	0.639	6.42×10^{-2}
10152	0.690	6.14×10^{-2}
10808	0.730	-5.08×10^{-2}
12480	0.855	-4.13×10^{-2}
13869	0.949	-1.41×10^{-1}

$k = 7.86 \times 10^{-5}$ sec^{-1}

Conc. of XXIII = 6.77×10^{-5} M

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table IV. Kinetic Data for Thermal Decomposition of XXIII, Run 2 at 95°. (Ultraviolet Analysis)

Reaction Time (sec)	Absorptivity of Product (benzophenone)	Residual from Least Squares Line
0	0.130	-3.86×10^{-2}
2709	0.440	-1.03×10^{-2}
3668	0.528	2.16×10^{-3}
4442	0.585	2.24×10^{-2}
5342	0.655	3.39×10^{-2}
6112	0.720	2.85×10^{-2}
7927	0.846	2.47×10^{-2}
9131	0.925	1.73×10^{-3}
10031	0.995	-6.44×10^{-2}

$k = 1.17 \times 10^{-4}$ sec^{-1}

Conc. of XXIII = 6.85×10^{-5} M

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table V. Kinetic Data for Thermal Decomposition of XXIII, Run 1 at 98°. (Ultraviolet Analysis)

Reaction Time (sec)	Absorptivity of Product (benzophenone)	Residual from Least Squares Line
0	0.155	5.85×10^{-4}
960	0.308	-7.85×10^{-3}
1676	0.400	-5.45×10^{-3}
2400	0.482	9.02×10^{-4}
3116	0.564	3.63×10^{-3}
3839	0.637	1.03×10^{-2}
4560	0.720	5.99×10^{-3}
5350	0.796	7.27×10^{-3}
6124	0.885	-5.22×10^{-3}
6959	0.963	-1.01×10^{-2}

$k = 8.21 \times 10^{-5}$ sec^{-1}

Conc. of XXIII = 9.74×10^{-5} M

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table VI. Kinetic Data for Thermal Decomposition of XIII, Run 2 at 98°. (Ultraviolet Analysis)

Reaction Time (sec)	Absorptivity of Product (benzophenone)	Residual from Least Squares Line
0	0.116	-4.80×10^{-2}
1090	0.227	-3.66×10^{-2}
1797	0.281	-1.70×10^{-2}
2515	0.340	-4.18×10^{-3}
3238	0.390	1.52×10^{-2}
3960	0.448	2.25×10^{-2}
4680	0.490	4.46×10^{-2}
5397	0.552	3.80×10^{-2}
6239	0.605	4.99×10^{-2}
7077	0.677	2.66×10^{-2}
7979	0.736	1.96×10^{-2}
9179	0.820	-1.74×10^{-2}
10378	0.908	-9.33×10^{-2}

$k = 9.96 \times 10^{-5}$ sec^{-1}

Conc. of XXIII = 6.58×10^{-5} M

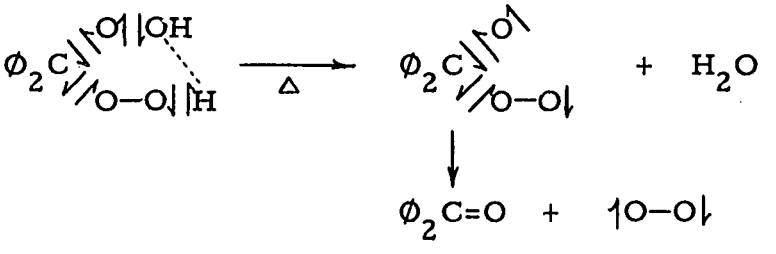
Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table VII. Kinetics of Thermal Decomposition of XXIII in 2, 2, 4-Trimethylpentane

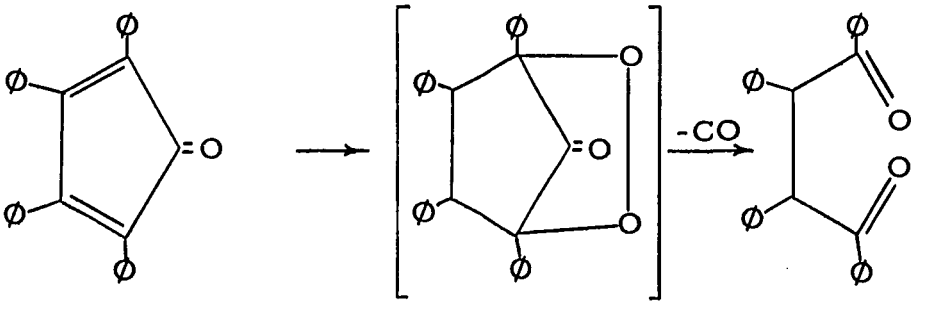
Run No.	$T^{o}(C)$	$10^{5}k(sec^{-1})$
1.	90	1.8
2.	90	1.5
3.	94	11.7
4.	94	7.9
5.	98	9.7
6.	98	8.6

F. Singlet Oxygen Experiment

It was thought that perhaps XXIII produced singlet oxygen when it was decomposed.



The decomposition of XXIII in the presence of a singlet oxgen trap was attempted. Tetraphenylcyclopentadienone is reported to yield cis-dibenzoylstilbene when reacted with singlet oxygen (47).

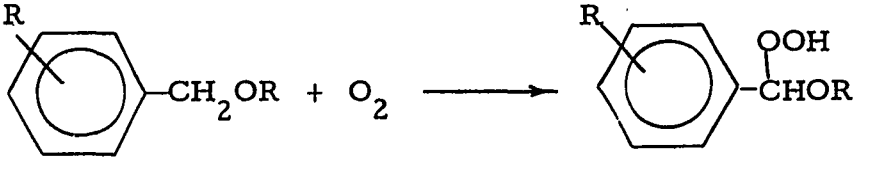


Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

An ethanol solution of XXIII and tetraphenylcyclopentadienone was gently heated and then refluxed. The ir spectra showed only tetraphenylcyclopentadienone and benzophenone to be present. The diphenylmethylbishydroperoxide had apparently decomposed. The intense rose color of tetraphenylcyclopentadienone never faded. Theoretically, the reaction with singlet oxygen can be followed by loss of the intense color.

G. Other Possible Syntheses of XV

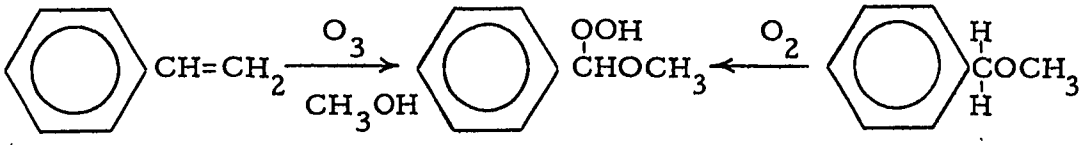
Sharp and Patrick (48) have autoxidized some alkyl benzyl ethers (XXVI) at 100° in liquid phase to α-alkoxybenzyl hydroperoxides (XXVII).



XXVI XXVII

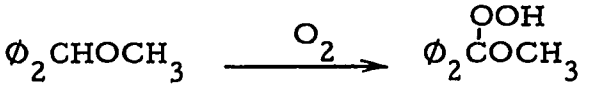
The α-alkoxybenzyl hydroperoxides ought to have the structure of one cleavage product of an ozonide formed in alcohol. The ozonolysis of styrene (XXVIII) in methyl alcohol, for example, should yield the same α-methoxybenzyl hydroperoxide (XXIX) as the autoxidation of benzyl methyl ether (XXX).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.



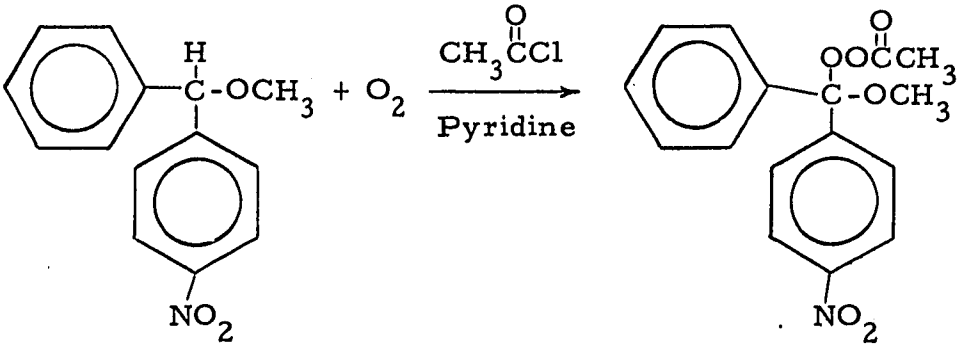
XXVIII XXIX XXX

On this basis the synthesis of XV by autoxidation of benzhydryl methyl ether (XXXI) was undertaken. Oxygen was passed through the heated ether for varying lengths of time. Examination of the reaction mixture by ir and gas chromatography did not disclose any desired product (XV).



XXXI XV

In a similar fashion the autoxidation of p-nitrobenzhydrol methyl ether (XXXII) in the presence of acetyl chloride and



XXXII

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

pyridine was attempted. It was thought that the presence of acetyl chloride would acylate any transitory hydroperoxide. However, after the reaction mixture was chromatographed on silica gel, no perester or hydroperoxide was observed.

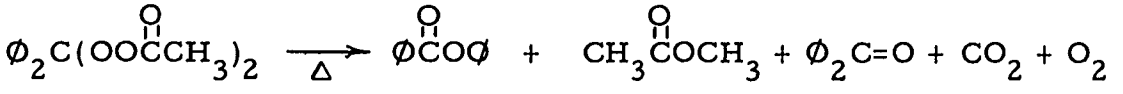
II. Diphenylmethylbisacetylperoxide

A. Decomposition

Acylation of XXIII, with acetyl chloride in pyridine at 0° produced diphenylmethylbisacetylperoxide (XXXIII). Acylation was also accomplished with benzoyl chloride.

XXIII XXXIII

It was found that thermal decomposition of XXXIII produced phenyl benzoate (XXXIV) along with other products.



XXXIII XXXIV + other products

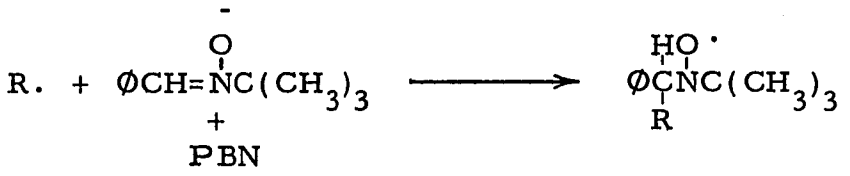
The decomposition yielded 26% phenyl benzoate, 20% methyl acetate, and 15% benzophenone. A quantitative gas analysis was not done. The deficit in the yield might be accounted for by higher molecular weight aromatic compounds, since the nmr of the decomposition

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

residue had several peaks not accounted for by the above products. However, numerous attempts on various gas chromatographic columns did not reveal any aromatic system larger than phenyl benzoate.

The observation of phenyl benzoate in the decomposition mixture requires a phenyl migration to oxygen, or a 1, 2 shift. This phenyl migration could be accomplished through either a radical or ionic mechanism, either stepwise or concertedly. Since homolytic cleavage of a peroxide bond occurs quite frequently, it was decided to look for a radical mechanism. Cleavage of a peroxide bond would produce an acetoxy radical. This radical is very short lived and the concentration in most reactions would be below the detection limit of commonly used electron spin resonance (esr) spectrometers. However, Janzen and Blackburn (49, 50) have developed a technique for detection and identification of short-lived free radicals. The method involves the use of an efficient radical trap such that the radical-trap adduct is reasonably stable and detectable by esr. In addition, the hyperfine spectrum of the radical adduct has a characteristic feature which is sensitive to the detailed structure of the attached groups. This information can be used to identify the radical which is trapped. The trapping agent or spin trap is phenyl-N-t-butyl-nitrone (XXXV), PBN. The free radical adduct (XXXVI) is called a spin adduct. The information required to define the structure of the

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.



XXXV XXXVI

radical trapped lies in the magnitude of the β-hydrogen and nitrogen hyperfine coupling (hfc) constants (A). The β-hydrogen hfc constant is dependent on the dihedral angle which in turn is dependent on the bulk of R. The magnitude of the hydrogen hfc decreases with increase in the bulk size of attached groups (51, 52). The nitrogen hfc is sensitive to the electronegativity of R, inductive withdrawal producing a smaller nitrogen hfc (53). The magnitude of the β-hydrogen and nitrogen hfc constants under given temperature and solvent conditions are a unique set of parameters which define the nature of the particular radical trapped once these values have been established from experiments with known radicals.

Since the nuclear spin quantum number for nitrogen is 1 (54), there are 2I + 1 orientations of the angular momentum, I. Consequently, an odd electron interacting with nitrogen produces a 3 line esr spectrum. However, in the case of a phenyl-t-butylnitrone adduct the β-hydrogen splits each of the nitrogen peaks producing a 6 line spectrum as illustrated in Figure 8. Table VIII illustrates the magnitude (in gauss) of some hyperfine coupling constants.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

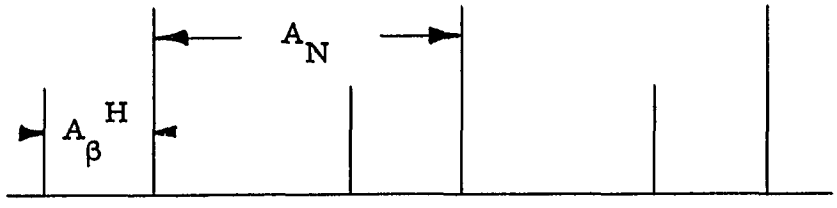


Figure 8. Theoretical esr Spectrum for a PBN Spin Adduct.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table VIII. Hyperfine Splitting Constants of Phenyl, Acetoxy, and Methyl Spin Adducts (50).

Source	R·	A_N	A_β^H
$(C_6H_5)_2Pb(OAc)_2$	C_6H_5	13.85	2.11
Me_3PbOAc + hv	CH_3CO_2	13.03	1.93
Me_3PbOAc	CH_3	14.22	3.45

Diphenylmethylbisacetylperoxide and PBN were dissolved in distilled Skellysolve-H and placed in a quartz tube fitted with a vacuum stopcock. The solution was frozen in liquid nitrogen and placed under vacuum (<1 mm). It was then allowed to thaw, was refrozen and placed back on the vacuum line. This freeze-thaw technique was necessary in order to remove any dissolved oxygen (paramagnetic) from the solvent. Decomposition of XXXIII was initiated by the thermal control unit on the esr spectrometer. A spectrum thought to be due to the acetoxy-PBN adduct was recorded (Figure 9). To confirm that the signal was due to the acetoxy-PBN adduct, lead tetraacetate (a known source of acetoxy radicals when subjected to thermal decomposition) was run under the same conditions. The resulting spectrum was superimposable on that obtained from decomposition of XXXIII, and yielded the hyperfine coupling data shown in Table IX.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

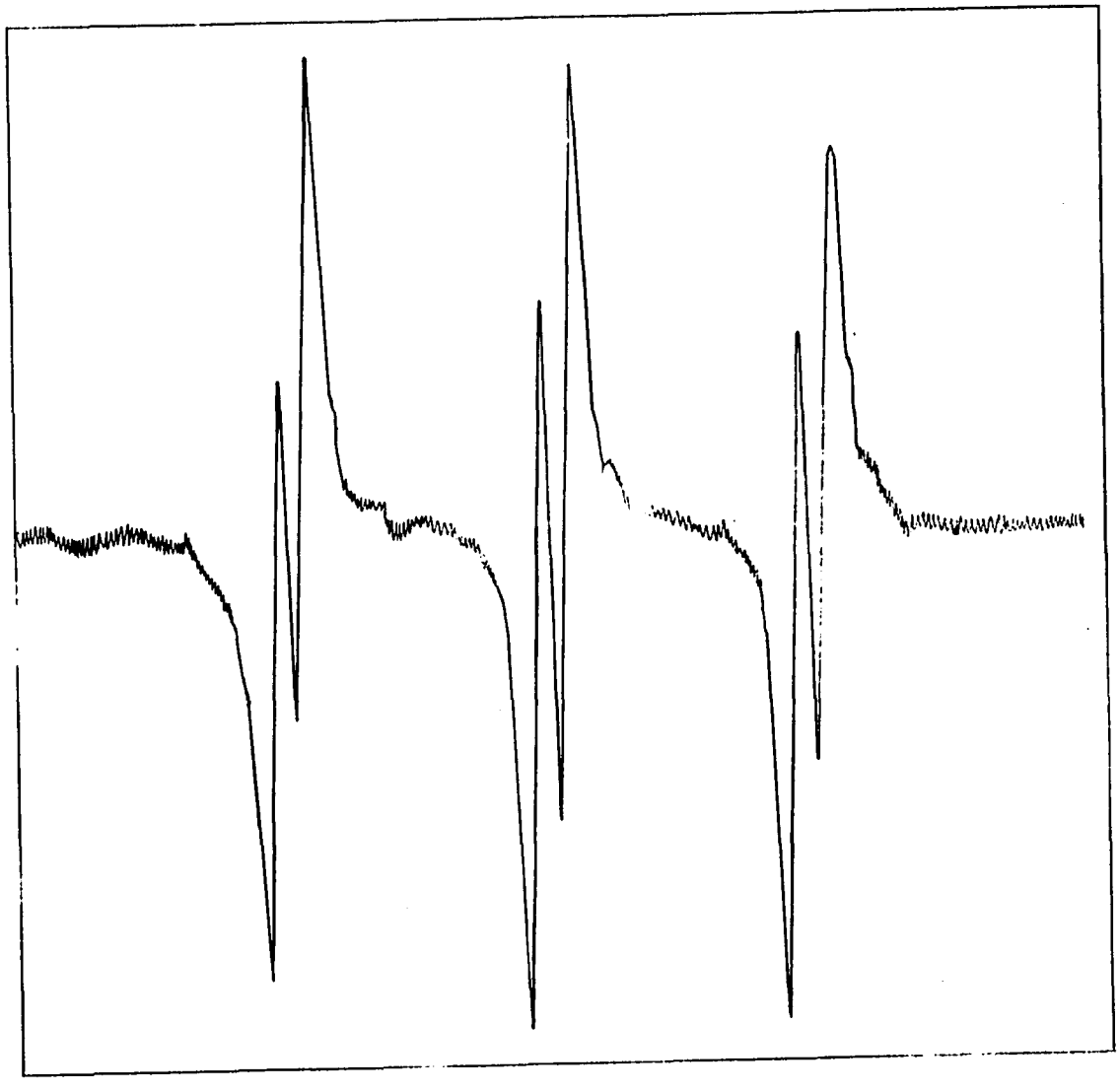


Figure 9. The esr Spectrum Obtained from the Decomposition of XXXIII in the Presence of PBN in SkellySolve-H.

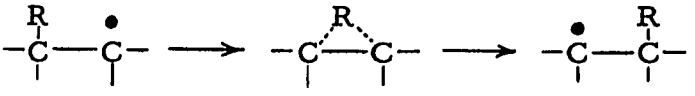
Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table IX. Hyperfine Splitting Constants of Acetoxy Spin Adducts

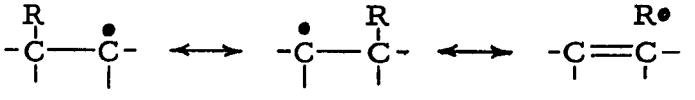
Source	R•	A_N	A_β^H
$Pb(OAc)_4$	CH_3CO_2	13.24	1.73
XXXIII	CH_3CO_2	13.22	1.72

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

The trapping of acetoxy radical indicates that homolytic cleavage of the peroxide bond is taking place and that the phenyl ring may migrate by a radical mechanism to oxygen. Aryl groups have been observed to migrate to oxygen in certain alkoxy radicals (55). However, it is not known whether the peroxide bonds cleave simultaneously or step-wise. The occurrence of a 1, 2 shift in a radical system necessarily requires some knowledge of the structure and energy of the transition state involved. If the 1, 2 shift is truly intramolecular, it must pass through some triangular arrangement of groups which represents either the transition state or a metastable intermediate of relatively high energy and short life (56).



In addition, if such a triangular arrangement actually represents a lower energy path than simple dissociation and recombination, it must be stablized by delocalization of the odd electron. In terms of resonance structures, it might be illustrated as;



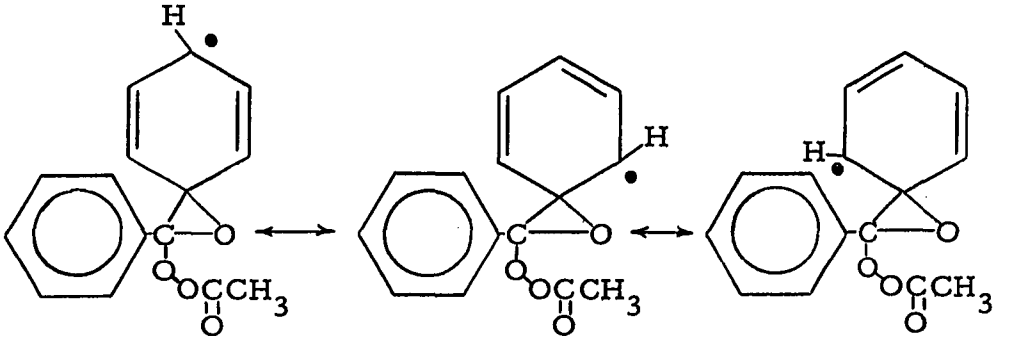
In terms of molecular orbital theory, the equilvalent statement is that the odd electron and the electron pair of the bond which is shifting must occupy delocalized three-center orbitals constructed

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

from p orbitals of the two carbons and, depending on its structure, a p or s orbital of the migrating group. The simple Hückel (57) treatment gives a qualitative picture of the energetics of such orbitals, stating that it will consist of a single low-lying bonding orbital and two higher energy nonbonding orbitals which are degenerate if the triangular arrangement is symmetric. In carbonium ion rearrangements only two electrons are involved and both can be accommodated in the bonding orbital, the result is that such bridged intermediates are easily formed. For the radical case, however, the third electron must occupy a higher energy nonbonding orbital. Consequently, it should be less stable in respect to either the initial or the rearranged radical. For example, a phenyl carbonium ion migration has an energy of activation of 6.22 (ev) compared to 7.84 (ev) for phenyl radical migration (58).

In this case, where the migrating group is a phenyl ring, additional structures are available to the bridged intermediate. Structures which contain a covalent cyclopropane ring and a radical stablized by allylic resonance.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.



This decomposition was also investigated in the absence of solvent. Solid PBN and XXXIII were placed in an esr tube under vacuum. The mixture was then melted in the cavity of the esr spectrometer by means of the thermal control unit. The melted PBN acted as the solvent system. The resulting spectrum, Figure 10 is more complicated than that obtained using Skellysolve-H as the solvent system. There appears to be two additional spin adducts present. Janzen and Blackburn (49) have reported that during the observation of acetoxy spin adducts, the methyl adduct was observed. This may be due to a very minute amount of acetoxy radical not being trapped but decomposing to methyl radical and carbon dioxide. This escaped methyl radical, then forms a spin adduct. More likely, in the case of this decomposition there is an independent source of methyl radicals. This will become apparent in the mechanism proposed later. In addition, only the methyl-PBN adduct has a large

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

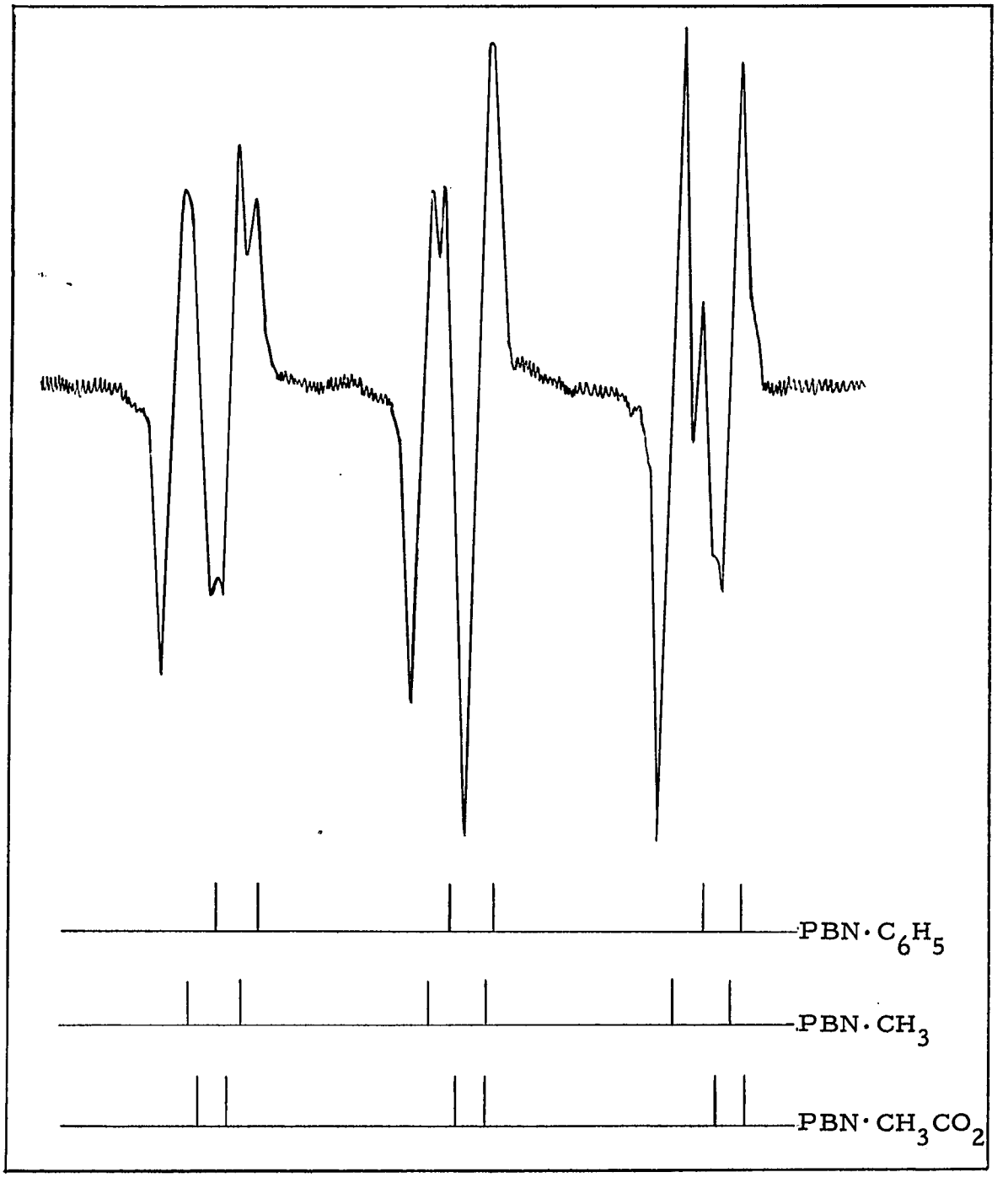


Figure 10. The esr Spectrum Obtained from the Decomposition of XXXIII in PBN in the Absence of Solvent. The Theoretical Composition of the Spectrum is Attributed to Phenyl, Methyl, and Acetoxy Spin Adducts (shown below).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

enough β-hydrogen hfc constant to accomodate those observed in Figure 10. The other radical adduct has hfc constants comparable to that of the phenyl adduct. This was verified by photolysis of iodobenzene in the presence of PBN, a known source of phenyl radicals. The spectrum for the spin adduct is shown in Figure 11. The complex esr spectrum, Figure 10, can now be accounted for in terms of three spin adducts as shown at the bottom of Figure 10. Numerous gas chromatographic attempts failed to show any simple radical-radical adducts, such as toluene, produced from a methyl radical and a phenyl radical.

The trapping of a phenyl radical during the thermal decomposition of XXXIII means it must be a discrete entity. This phenyl radical may be participating in the 1, 2 phenyl shift. Seubold (59) has shown that radical 1, 2 aryl shifts do not have to go through a bridged species but may go by way of a free phenyl radical.

A wavemeter placed on the esr spectrometer permitted measurement of the frequency. Using the frequency and the magnetic field resonance value the g value for the nitrone system can be calculated. The calculation is based on the equation

$$g = \frac{h\nu}{\beta H}$$

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

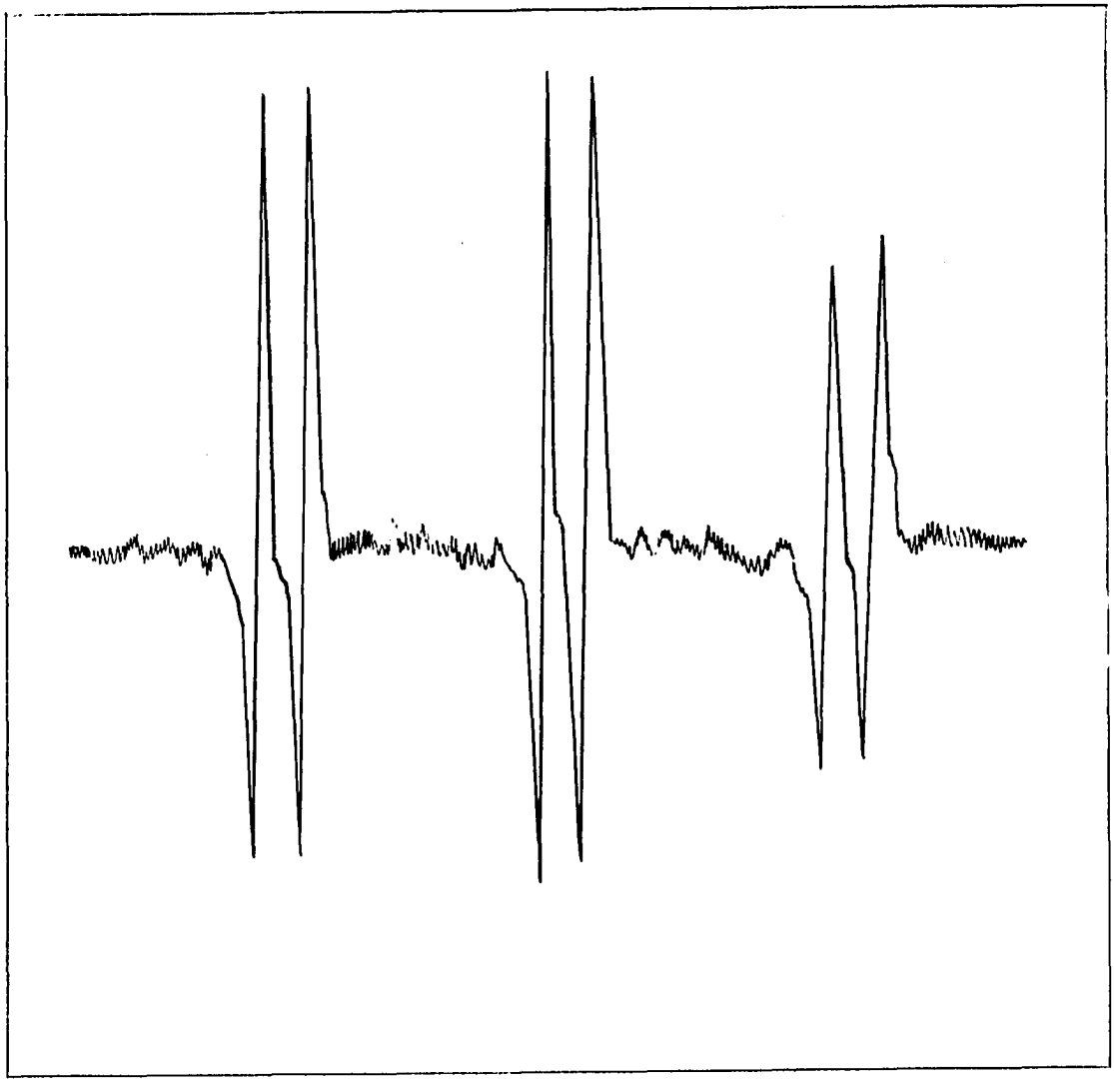


Figure 11. The esr Spectrum Obtained from the Photolysis of Iodobenzene in PBN Melt.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

where

h = Planck's constant = 6.624×10^{-27} erg sec

v = frequency = 9.033×10^{9} cycles/sec

β = Bohr magneton = 9.273×10^{-21} erg/gauss

H = magnetic field = 3.219×10^{3} gauss

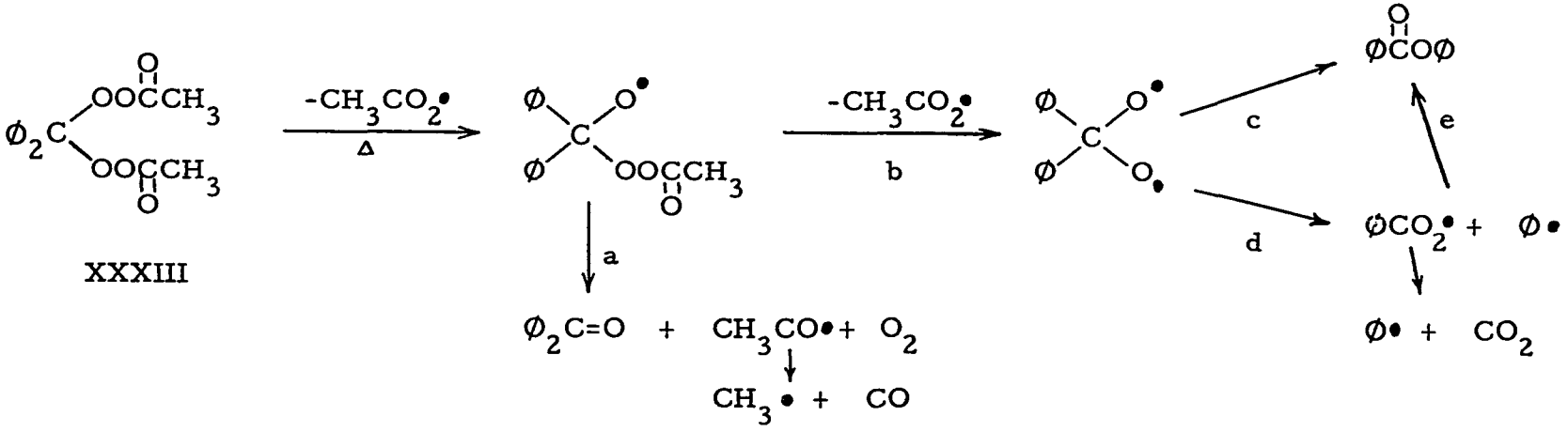
Evaluation of the equation results in g = 2.004. This g value is nearly the same as that which has been observed for the disec-butylnitrone system (g = 2.006) (60).

A possible mechanism accounting for the observed products of thermal decomposition of XXXIII is shown in Scheme I.

The initial step of the perester decomposition is most likely a simple scission of the O-O bond analogous to that occurring in peroxides. The loss of acetoxy radical produces another radical which can partition itself between two pathways ("a" and "b"). Pathway "a" involves an intramolecular elimination of oxygen producing benzophenone and an acetyl radical. The acetyl radical could further decompose to carbon monoxide and a methyl radical. This may be the independent source of methyl radical referred to in the discussion of Figure 10. Methyl acetate would be formed by the combination of methyl radicals and acetoxy radicals. Pathway "b" involves the loss of the second acetoxy radical producing the di-phenylmethylenedioxy-diradical. This intermediate was proposed by Cadogan et al. (43) to explain the formation of phenyl benzoate during

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.



XXXIII

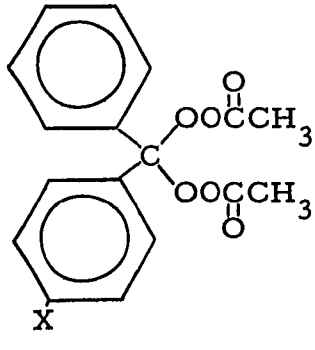
SCHEME II

Mechanism of Thermal Decomposition of XXXIII

the thermal decomposition of dimeric benzophenone peroxide. The diradical could partition itself between two pathways ("c" and "d"). Pathway "c" involves a concerted intramolecular rearrangement to phenyl benzoate. Pathway "d" is a further breakdown of the diradical producing the benzoyloxy radical and phenyl radical. This pathway would account for the trapping of phenyl radicals. The recombination of these two radicals would produce phenyl benzoate via pathway "e". The benzoyloxy radical could also breakdown to phenyl radical and carbon dioxide.

B. Substituted Diphenylmethylbisacetylperoxide

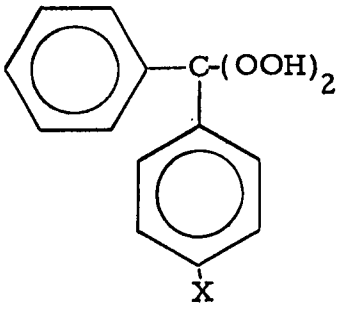
The observed phenyl migration presented the interesting possibility of a migratory aptitude study on the decomposition of substituted diperesters (XXXVII).



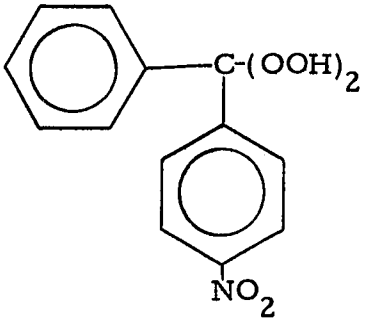
XXXVII

These diperesters (XXXVII) would be synthesized by acylation of the precursor (XXXVIII). The study would begin with the nitro substituted compound (XXXIX).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

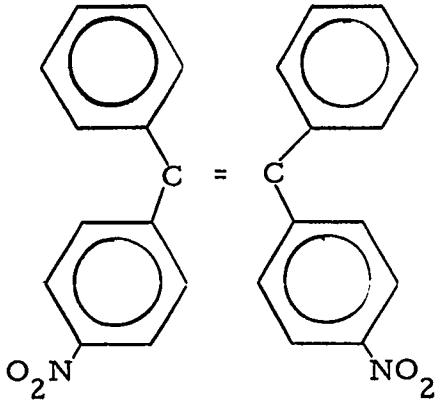


XXXVIII



XXXIX

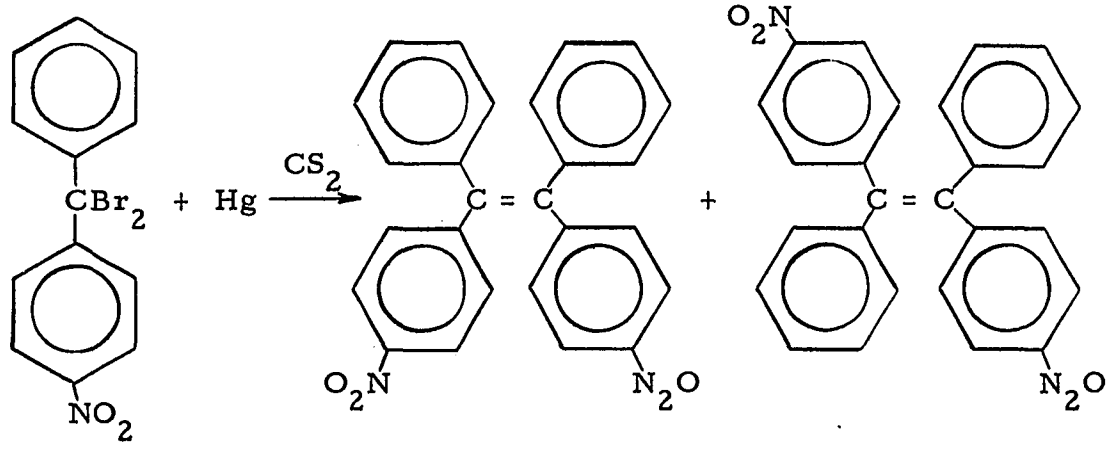
The synthesis of XXXIX would be accomplished in a manner similar to that for XXIII, i.e., ozonation of 1,2-bis- p-nitro-phenyl -1,2-diphenylethylene (XL).



XL

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

The preparation of XL was accomplished in a manner similar to that used by Kuhn and Blum (60) e.g.,



XLI XLII

The separation of cis (XLI) and trans (XLII) was accomplished on neutral alumina using a Skellysolve H-chloroform mixture as the eluant. The trans isomer was eluted first. This was found to be simpler than the fractional crystallization technique used by Kuhn and Blum. The separation was verified by comparison of the ir spectra in the 900-700 cm^{-1} region (Appendix). The initial ozonation of the cis (XLI) and trans (XLII) isomers for the calculated contact time resulted in a large quantity of unreacted starting material being isolated. It appears that XLI and XLII were more reluctant to react with ozone than tetraphenylethylene. Periodic examination of another ozonolysis reaction mixture showed only p-nitrobenzophenone

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

and unreacted starting material to be in the ozonolysis vessel. Finally, all the reactant was converted to p-nitrobenzophenone without the observance of the desired product XXXIX.

C. Decomposition Kinetics of Diphenylmethylbisacetylperoxide

The kinetics of thermal decomposition of XXXIII were studied to understand further the mechanism of decomposition. The disappearance of the methyl protons of the perester carbonyl could easily be followed by nmr analysis. Since nitromethane was found to be inert to hot 30% hydrogen peroxide, it was used as an internal standard in the nmr study. Decomposition of XXXIII in diphenyl ether was accomplished in an nmr tube by means of an constant temperature water bath. The nmr tube was taken out periodically and quenched in an ice bath. Since there was no thermal decomposition of the perester at 48° (4 hours), nmr examination at 40° was a satisfactory procedure.

The proton signal intensity for XXXIII (δ 1.88) and nitromethane (δ 4.33) at any given time were read into the first order computer program previously described. In addition, the computer also plotted ln k versus 1/T and determined the best fitting least squares straight line.

The results of the data analysis by the computer fitted the first order kinetic law. The rate constants are shown in Table X and the kinetic plots in Figures 12-15. The data is shown in Tables

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

XI-XIV. In these tables "A_r" refers to the integration of the singlet at δ 1.88 representing the six protons of the reactant (XXXIII). "A_s" refers to the integration of the singlet at δ 4.33 representing the three protons of the standard (nitromethane).

Table X. Kinetics of Decomposition of XXXIII in Diphenyl Ether

Run No.	T^{o}(C)	$10^{5}k(sec^{-1})$
1.	70	2.40
2.	70	2.75
3.	75	5.98
4.	90	41.2

The activation plot for the thermal decomposition is shown in Figure 16 and yielded the following activation parameters:

$$Ea = 32.7 \text{ Kcal/mole}$$

$$\Delta H^{\neq} = 32.0 \text{ Kcal/mole}$$

$$\Delta S^{\neq} = 13.8 \text{ e.u.}$$

$$\Delta F^{\neq} = 27.2 \text{ Kcal/mole}$$

The enthalpy of activation, $\Delta H^{\neq}$, and entropy of activation, $\Delta S^{\neq}$, for thermal decomposition of XXXIII are comparable to those obtained for the thermal decomposition of di-t-butyl peroxide (62) ($\Delta H^{\neq}$ = 37.8 Kcal/mole, $\Delta S^{\neq}$ = 13.8 e.u.) and benzoyl peroxide (63) ($\Delta H^{\neq}$ = 32.7 Kcal/mole, $\Delta S^{\neq}$ = 13.3 e.u.).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

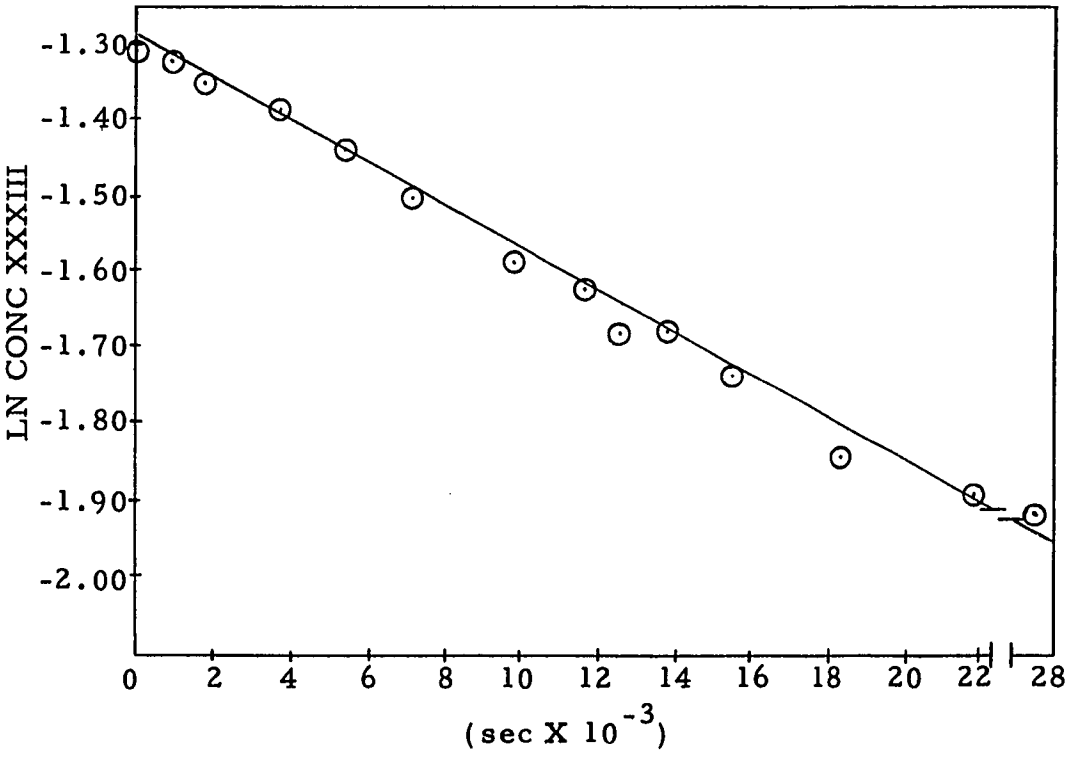


Figure 12. First Order Kinetic Plot for the Thermal Decomposition of XXXIII at 69°, Run 1.

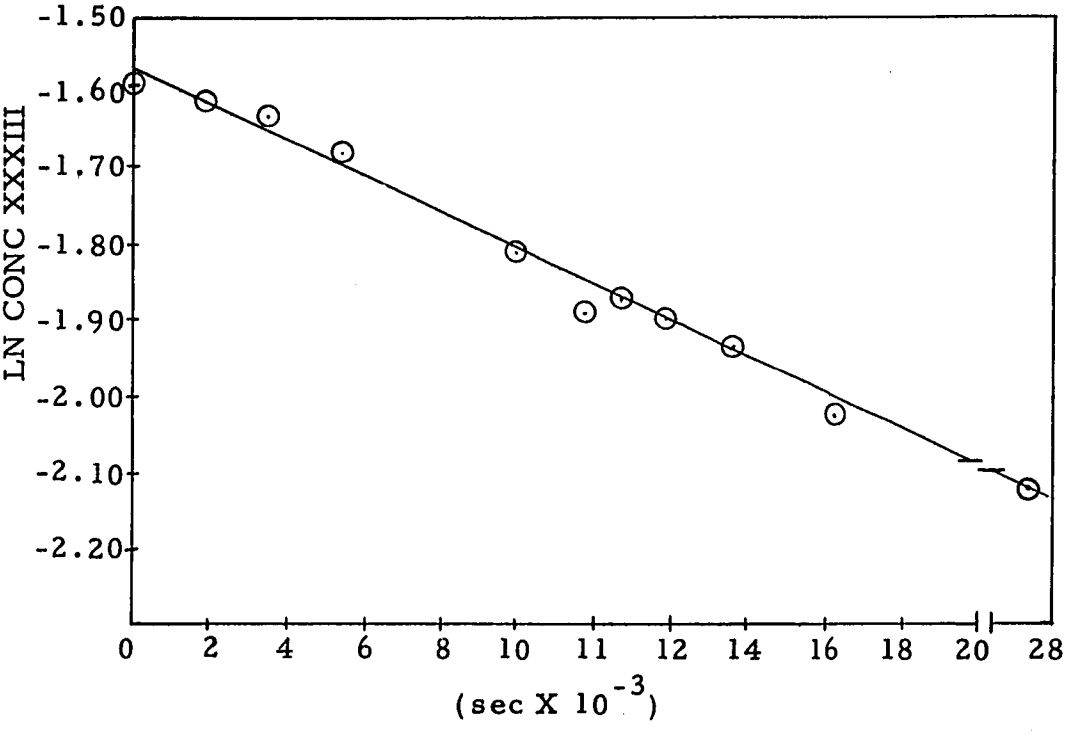


Figure 13. First Order Kinetic Plot for the Thermal Decomposition of XXXIII at 69°, Run 2.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

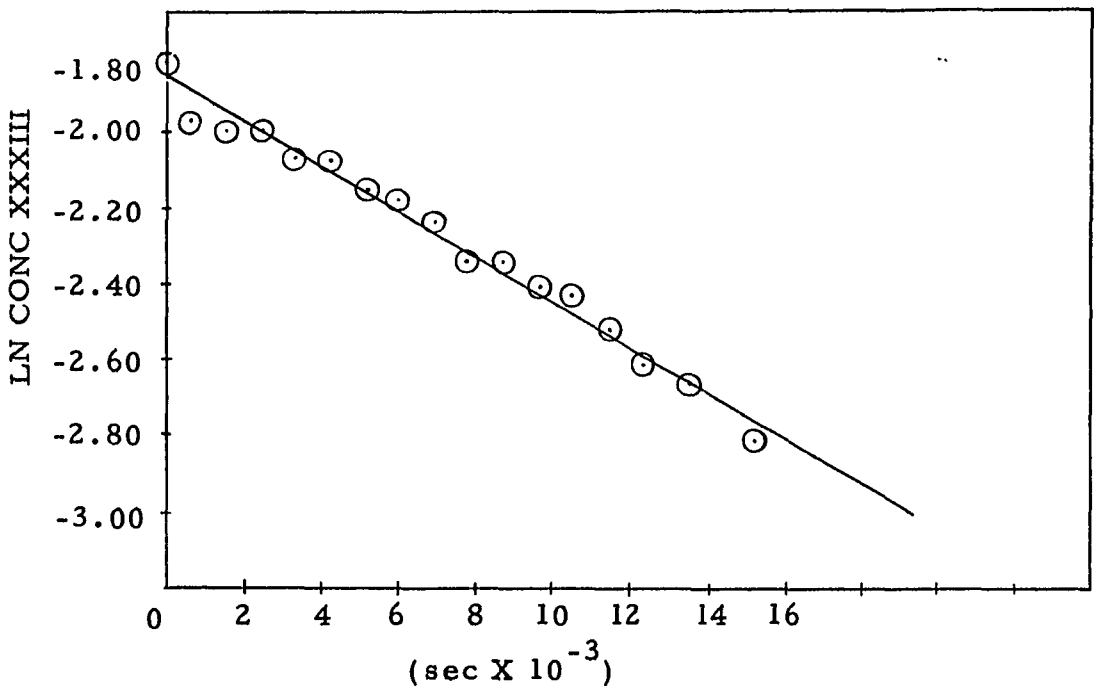


Figure 14. First Order Kinetic Plot for the Thermal Decomposition of XXXIII at 75°.

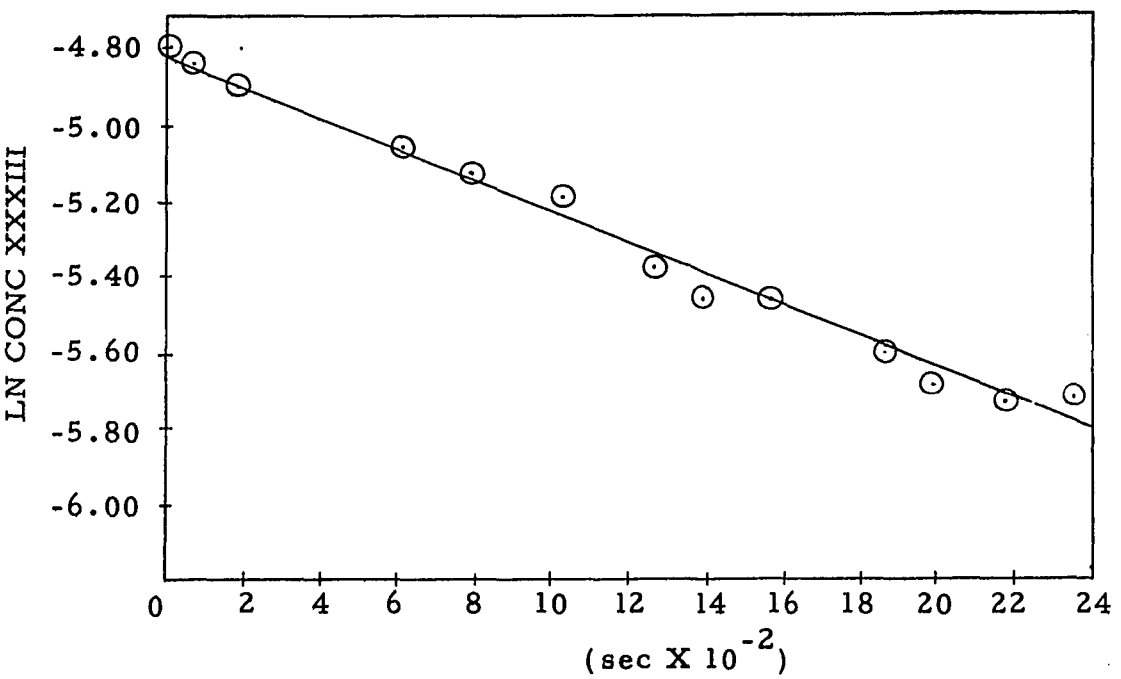


Figure 15. First Order Kinetic Plot for the Thermal Decomposition of XXXIII at 90°.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table XI. Kinetic Data for Thermal Decomposition of XXXIII, Run 1 at 69°. (NMR Analysis)

Reaction Time (sec)	A_r	A_s	Residual from Least Squares Line
0	87.92	147.6	7.81×10^{-4}
900	89.75	153.5	6.63×10^{-3}
1800	85.49	150.4	3.18×10^{-3}
3600	82.20	149.8	1.76×10^{-2}
5400	77.75	148.4	2.08×10^{-2}
7200	73.47	151.0	-3.61×10^{-3}
9900	67.77	150.6	-7.93×10^{-3}
11700	63.71	150.8	-2.14×10^{-2}
12600	60.96	149.4	-3.18×10^{-2}
13800	62.52	150.8	1.73×10^{-2}
15600	57.77	150.0	-6.83×10^{-3}
18300	50.74	146.7	-4.04×10^{-2}
21900	46.90	141.8	1.36×10^{-2}
27300	41.88	144.2	3.21×10^{-2}

$k = 2.75 \times 10^{-5}$ sec^{-1}

Conc. of perester = 0.274 M

Conc. of standard = 0.909 M

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table XII. Kinetic Data for Thermal Decomposition of XXXIII, Run 2 at 69°. (NMR Analysis)

Reaction Time (sec)	A_r	A_s	Residual from Least Squares Line
0	87.28	136.5	-2.10×10^{-2}
900	88.92	140.3	-7.80×10^{-3}
1800	86.77	138.8	-7.46×10^{-5}
3600	83.80	136.4	2.56×10^{-2}
5400	79.06	135.0	2.07×10^{-2}
7200	75.85	135.5	1.88×10^{-2}
9900	68.17	133.1	-5.30×10^{-3}
11700	65.67	138.1	-3.58×10^{-2}
12600	66.42	137.2	3.59×10^{-3}
13800	63.81	135.7	2.86×10^{-3}
15600	61.58	136.4	5.78×10^{-3}
18300	54.61	133.5	-1.88×10^{-2}
26100	45.23	129.1	4.13×10^{-3}
27300	45.06	131.9	7.40×10^{-3}

$k = 2.40 \times 10^{-5}\ sec^{-1}$

Conc. of perester = 0.216 M

Conc. of standard = 0.637 M

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table XIII. Kinetic Data for Thermal Decomposition of XXXIII at 75°. (NMR Analysis)

Reaction Time (sec)	A_r	A_s	Residual from Least Squares Line
0	69.72	161.2	4.12×10^{-2}
600	67.40	182.6	-8.12×10^{-2}
11500	67.46	185.8	-4.36×10^{-2}
2400	64.16	178.0	3.00×10^{-3}
3300	57.86	174.4	-2.64×10^{-2}
4200	58.62	175.4	3.51×10^{-2}
5100	53.10	171.1	1.50×10^{-2}
6000	51.80	173.1	3.23×10^{-2}
6900	48.16	171.0	2.54×10^{-2}
7800	43.62	170.5	1.69×10^{-2}
8700	43.66	171.9	2.99×10^{-2}
9600	40.42	169.0	2.33×10^{-2}
10500	39.60	169.4	5.45×10^{-2}
11400	33.70	159.6	6.77×10^{-3}
12300	35.06	181.6	-2.94×10^{-2}
13500	33.18	181.2	-1.02×10^{-2}
15300	27.86	177.9	-5.90×10^{-2}

$k = 5.98 \times 10^{-5}$ sec^{-1}

Conc. of perester = 0.155 M

Conc. of standard = 0.754 M

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Table XIV. Kinetic Data for Thermal Decomposition of XXXIII at 90°. (NMR Analysis)

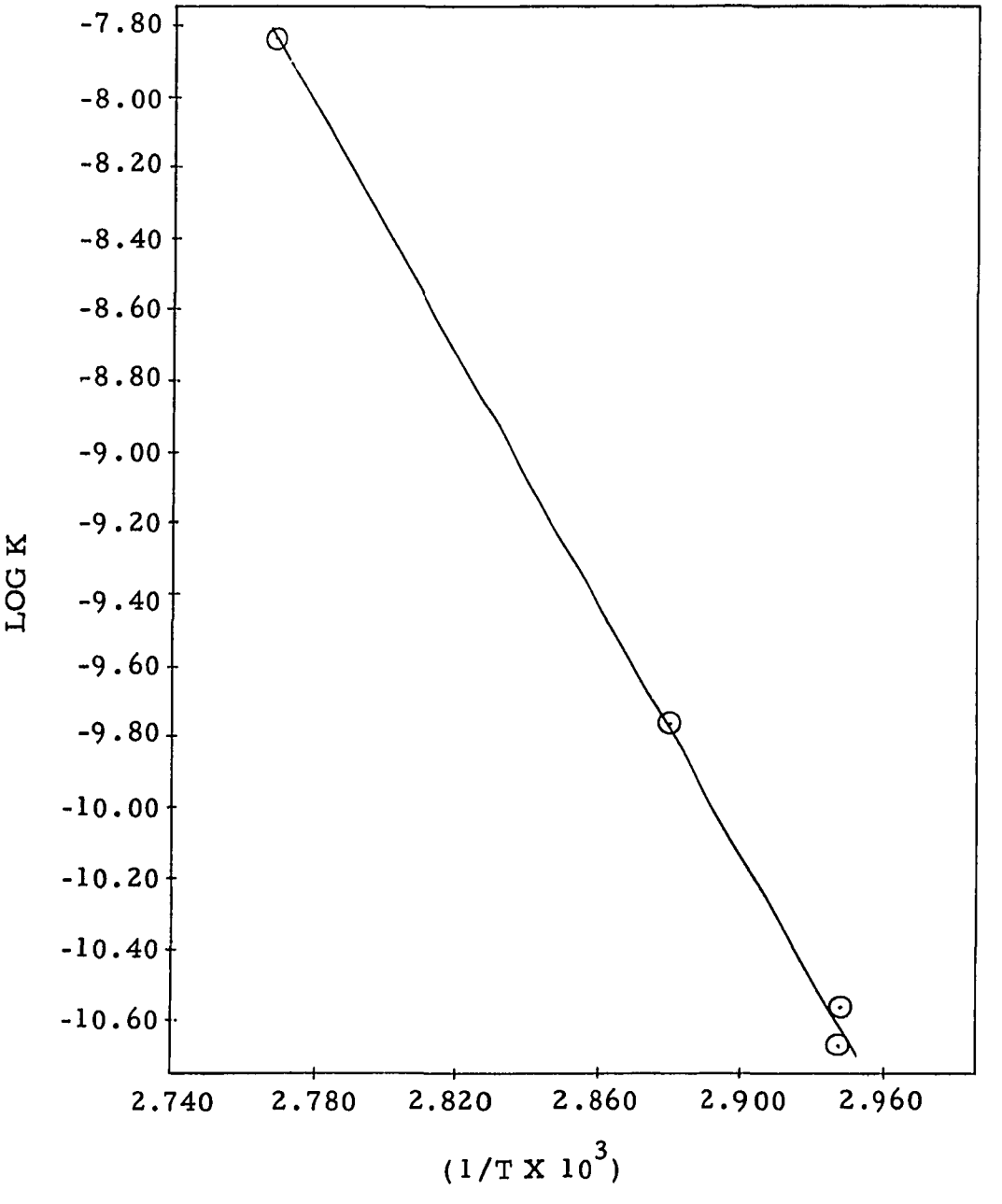
Reaction Time (sec)	A_r	A_s	Residual from Least Squares Line
0	17.80	90.75	1.66×10^{-2}
60	17.70	93.70	3.74×10^{-3}
180	15.90	89.50	-8.17×10^{-3}
600	12.85	84.90	4.79×10^{-3}
780	12.50	88.50	9.86×10^{-3}
1020	11.46	87.00	3.90×10^{-2}
1260	9.75	87.75	-3.22×10^{-2}
1380	9.00	88.00	-6.56×10^{-2}
1560	9.00	89.25	-5.48×10^{-3}
1860	7.70	87.75	-2.09×10^{-2}
1980	8.15	91.95	3.87×10^{-2}
2160	6.85	89.90	-3.83×10^{-2}
2340	7.30	93.72	5.79×10^{-2}

$k = 4.12 \times 10^{-4}\ sec^{-1}$

Conc. of perester = 0.008 M

Conc. of standard = 0.840 M

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.



Residual for Point 1 = -2.83×10^{-2}
Residual for Point 2 = 8.93×10^{-3}
Residual for Point 3 = -5.76×10^{-2}
Residual for Point 4 = 7.69×10^{-2}

Figure 16. Activation Plot for the Thermal Decomposition of XXXIII.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

D. Preliminary Investigation of Trifluoracetic Acid Decomposition of XXXIII

An experiment revealed that trifluoracetic acid decomposition of XXXIII, like thermal decomposition, produced phenyl benzoate and benzophenone. A comparative study of the two decompositions, based on the production of phenyl benzoate, was conducted.

Two samples of XXXIII were decomposed separately by thermal and trifluoracetic acid means. Each sample was then injected into a gas chromatograph linked to the mass spectrometer. On this particular column separation of benzophenone and phenyl benzoate was not possible. However, this problem was surmounted by taking "cuts" of the gas chromatograph peak (composed of benzophenone and phenyl benzoate) and sending it to the mass spectrometer. The intensity of both parent peaks (benzophenone = 182, phenyl benzoate = 198) could be plotted independently as a function of time for the various "cuts". If sufficient "cuts" were made two smooth curves, one for each component, could be drawn. This would essentially apportion the one gas chromatograph peak into its two component peaks. In addition, a standard mixture consisting of a 50-50 (weight) benzophenone and phenyl benzoate was analyzed. This enabled the sensitivity of the compounds to ionization in the mass spectrometer to be taken into account. Comparison of the three systems was made at approximately the same position on the gas chromatograph peak.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

The peak width represented a retention time of approximately 180 seconds. The "cuts" on the three systems were taken within 10 seconds of each other. The ratio of the intensity of parent peaks (phenyl benzoate/benzophenone) for the three systems is shown in Table XV.

Table XV. Product Ratios for the Decomposition of XXXIII

	Intensity of Parent Ion of Phenyl Benzoate / Intensity of Parent Ion of Benzophenone		
	1	2	3
1.	0.042	0.058	0.068
2.	0.072	0.082	0.096
3.	0.14	0.17	0.31

1. Standard mixture (50-50).
2. Thermal decomposition.
3. Trifluoracetic acid decomposition.

It appears that trifluoracetic acid decomposition produces a significantly greater amount of phenyl benzoate than thermal decomposition. It is not know whether the trifluoracetic acid decomposition goes by way of a radical or ionic mechanism. An esr experiment indicates that it is an ionic mechanism, since a spectrum was not obtainable under decomposition conditions in the presence of PBN. A carbonium ion could be involved in the mechanism of decomposition.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

EXPERIMENTAL

Instrumentation

Ozone Generators. Initial ozonations were performed with a home-made silent arc discharge generator (64). It was with this ozonator that XXIII was first synthesized. Later ozonations were performed on an Orec O_3V_2 ozone generator.

Infrared Spectra. The infrared absorption spectra were determined on one of three instruments: Perkin-Elmer Grating Spectrophotometers, Models 337 or 457, Beckman IR5. Solid samples were run as KBr pellets or nujol mulls. Liquids were run as thin films.

Nuclear Magnetic Resonance Spectra. A Varian A-60 was used to obtain nmr spectra. Tetramethylsilane was used as a reference.

Mass Spectra. Mass spectra were obtained on A.E.I. Model MS-12 Spectrometer.

Gas Chromatograms. Gas chromatographic analyses were performed on one of the following instruments: F & M Research Chromatograph Model 5750 equipped with thermal and hydrogen flame detectors, a Varian Aerograph Model 90-P, or a Perkin Elmer Model 820.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Ultraviolet Spectra. Ultraviolet spectra were obtained with either a Bausch and Lomb Spectronic 500 or a Perkin-Elmer 402 using one cm quartz cells.

Electron Spin Resonance Spectra. A Varian V-4502 EPR Spectrometer System was used for obtaining esr spectra. Measurements were made on spectra obtained at scans of 100 and 50 gauss in 10 or 5 minutes at a chart speed of 1 in/min.

Melting Points. All melting points were taken on a Fischer-Johns Melting Point Apparatus and are uncorrected.

Elemental Analysis. Elemental analyses were performed by Galbraith Laboratories of Knoxville, Tennessee and Huffman Laboratories of Wheatridge, Colorado.

Constant Temperature Baths. A Precision Scientific Co., Visibility Constant Temperature Bath equipped with a Precision Merc to Merc Thermoregulator was used for high temperature (mineral oil) decomposition: A Sargent Constant Temperature Water Bath equipped with a Sargent Mercurial Thermoregulator was used for low temperature decomposition. Maximum temperature variations were $\pm 1^{o}$.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

A. Ozonolysis Procedure

An Orec O_3V_2 ozone generator was used. The concentration of ozone was about 1% (in oxygen) with a flow rate of 1.5 l./hr. The O_2 was dried prior to entering the generator by passing it through concentrated sulfuric acid. The O_3-O_2 mixture was passed into the reaction system which had been previously cooled to -78° with a Dry Ice-acetone slurry.

Tetraphenylethylene (1.00 g, 3.01 mmol), mp 221-224°, was dissolved in 150 ml of chloroform (distilled) and 100 ml of methyl alcohol (distilled over magnesium) or ethanol, and treated with ozone until the appearance of blue color in the solution indicated excess ozone (ca. 20 min). The excess ozone was then flushed out with nitrogen. The solvent was stripped off (10-20 mm and 10-20°) leaving a clear, colorless oil. Tlc of the oil at -5° on silical gel and developed with $CHCl_3$ indicated two compounds identified as benzophenone and XXIII: yield 0.71 g, 3.90 mmol, of benzophenone and 0.35 g, 1.51 mmol (50%), of bishydroperoxide.

B. Diphenylmethylbishydroperoxide (XXIII)

After recrystallization from hexane, the white needles of (XXIII) had a melting point of 94-96°. A reaction with starch-iodide paper indicated that the compound had active oxygen. The infrared spectrum showed no absorption in the carbonyl region but strong bands were observed at 3450, 1450, 1205, 1040, 781, 741, and 704

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

cm^{-1}. The nmr spectrum in acetonitrile showed two types of protons, a broad singlet at δ 9.70 and a multiplet at δ 7.25-7.73, which integrated 1:5, respectively. The addition of two drops of deuterium oxide to the nmr tube caused the singlet at δ 9.70 to disappear. A low temperature (source at $50^{\circ} \pm 2^{\circ}$) mass spectrum established the parent ion at 232 (1% intensity) with major peaks at 77, 105, 182, and 199. Elemental analysis was not satisfactory due to facile decomposition to benzophenone. However, the diacetyl derivative gave an acceptable analysis.

C. Analysis for Active Oxygen

An analytical technique developed at this laboratory was used to determine active oxygen content. Titrations were carried out in a 125 ml erlenmeyer flask equipped with a gas inlet stem at the bottom. During a titration nitrogen was passed into the titration vessel through a gas washing bottle filled with crushed Dry Ice. A sample (13 mg of XXIII) was added to 25 ml of glacial acetic acid containing 1 g of KI. After 15 min. in the dark (under carbon dioxide-nitrogen), 80 ml of water was added and the iodine titrated with 0.01 N sodium thiosulfate. A blank titration was unnecessary. The titrated solution remained colorless until the gas system was turned off (1 hr later). This technique was very reproducible (equiv wt: 60.41, 61.27) and, based on our results, appears superior to that used by Fliszar and Granger (27), eliminating

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

iodine entrapment by solid ice, air oxidation, and titration at near 0°.

D. Attempted Alternate Preparations of XXIII

Approximately 0.04 moles of 90% hydrogen peroxide was added to 3.64 g (0.02 mole) of benzophenone in 25 ml of methylene chloride. One drop of concentrated sulfuric acid was added as a catalysis (65, 66) (in other reactions no acid was added). The solution was stirred several hours. The methylene chloride solution was washed with saturated ammonium sulfate and dried over magnesium sulfate. After stripping off methylene chloride an ir revealed only benzophenone present. This reaction was run several more times under varying concentrations of acid, temperature (0° to -78°) and contact times. However, only unreacted benzophenone was observed.

E. Kinetic Study of the Thermal Decomposition of XXIII

Ultraviolet kinetic measurements were carried out with 6-10 X 10^{-5} M solutions of XXIII in 2, 2, 4-trimethylpentane (spectral grade). The rate of decomposition of XXIII to benzophenone was followed by the production of benzophenone [uv λ_{max} (cyclohexane) 252 mμ (ϵ = 1.89 X 10^{4}] (44). Two runs were made at each of three different temperatures. A five-place balance was used in the preparation of volumetric solutions. After a solution was prepared it was

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

transferred to a larger volumetric flask to allow for expansion of solvent upon immersion into the hot oil bath.

In a typical run 50 ml of solution was immersed in the oil bath. Periodically, usually between 15 to 90 minutes, a fraction (3-4 ml) was quickly pipetted out of the flask. A new disposable pipette was used for each withdrawal. It was immediately put into a small sample vial immersed in an ice bath. A new sample vial was used for each fraction. After a few minutes the cold fraction was transferred, using a new disposable pipette, to the uv cell. The uv spectrum was then obtained. Recording the uv spectrum at room temperature was a satisfactory procedure since there was no decomposition of XXIII after three hours at 45°--the initial uv spectrum was superimposable on the spectrum taken after three hours at 45°. The uv cell was then washed five to seven times with 1-2 ml of spectral grade cyclohexane and oven dried. The absorptivity and time were recorded. This data was then computer analyzed by a first order kinetic program previously described. Tables I through VI show the observed data used for this analysis.

F. Singlet Oxygen Experiment

To 50 ml of absolute ethanol was added 0.0465 g (0.2 mmol) of XXIII and 0.07 g (0.2 mmol) of tetraphenylcyclopentadienone. The solution was allowed to set at room temperature for 48 hours. No apparent loss of intense rose color due to

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

tetraphenylcyclopentadienone was observed. The solution was gently heated and finally refluxed. There was still no apparent loss of color. The ir spectrum showed only unreacted tetraphenylcyclopentadienone and benzophenone to be present.

G. Other Attempted Syntheses of XV

1. Benzhydryl methyl ether (67)

A solution of 2.75 g (0.015 mole) of benzyhydrol in 25 ml of methyl alcohol with 12 drops of hydrochloric acid was refluxed one hour. Evaporation of the methyl alcohol and vacuum distillation of the benzhydryl methyl ether yielded 2.2 g (82%) of a clear oil: bp $127^{\circ}/5.5$ mm (lit. (67) 270 - 271°); nmr (CCl_4) δ 7.10-7.40 (multiplet), δ 5.10 (singlet), δ 3.25 (singlet) integrating 10:1:3, respectively.

One gram of benzhydryl methyl ether (XXXI) was put in a small flask and placed in an oil bath at 100°. A stream of oxygen was passed through the ether for 2.5 hours. An ir examination of the ether showed a strong carbonyl at 1650 cm^{-1} (benzophenone). The nmr also showed a multiplet at δ 7.63-7.83 which was superimposable on a known spectrum of benzophenone (ortho proton region).

2. p-Nitrobenzhydryl methyl ether (XXXII)

O-Methylation of p-nitrobenzhydrol was accomplished by the general method outlined by Fieser and Fieser (68). A 20 ml ethanoic solution of 1 g (0.004 mole) of p-nitrobenzhydrol was placed in a

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

three neck flask fitted with a condenser and flanked on each side by an addition funnel. Twenty ml of 10 N sodium hydroxide was placed in one additon funnel and 12.6 g (0.1 mole) of dimethyl sulfate was placed in the other funnel. The reagents were added alternately to the stirred ethanol solution over a period of 20 min. After 48 hours the solution turned dark yellow and solid precipitated out. The liquid was decanted out of the reaction vessel and extracted with ether. The ether extract was washed with water and dried over potassium carbonate. The ether was evaporated off leaving 0.4 g (41%) of p-nitrobenzhydryl methyl ether (XXXII). nmr (CCl_4) δ 7.30-8.18 (multiplet), δ 5.28 (singlet), δ 3.33 (singlet) integrating 9:1:3, respectively.

Oxygen was passed into a pyridine solution consisting of 0.4 g (0.0016 mole) p-nitrobenzhydryl methyl ether and 0.125 g (0.0016) acetyl chloride at 100° for two hours. The reaction mixture was chromatographed on silica gel. Infrared examination did not reveal any perester carbonyl band; only the carbonyl band of p-nitrobenzophenone (comparison to authentic sample).

H. Acylation of XXIII

1. Diphenylmethylbisacetylperoxide (XXXIII)

To a pyridine solution of 0.57 g (2.4 mmol) of diphenylmethylbishydroperoxide at 0° was added 0.39 g (5.0 mmol) of acetyl chloride (drop-wise). The mixture was allowed to set for 20 min before

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

placement on a high vacuum rotorary evaporator. The reaction was evaporated to dryness, leaving white crystals. A small amount (2-3 ml) of ether was added to the residue, dissolving the perester and leaving pyridine-hydrochloride behind. The ether solution was pipetted out of the reaction flask and placed in a 15 ml round bottom flask. A second portion of ether was added to the reaction flask and pipetted out into the same 15 ml round bottom flask. Evaporation of the ether left fluffy white crystals behind. The resulting perester was recrystallized from hexane yielding white needles (mp 109.5-111.0°). The nmr spectrum of the perester showed a singlet at δ 1.88 and a multiplet at δ 7.20-7.65 integrating 6:10, respectively. The infrared spectrum had a strong carbonyl band at 1785 cm^{-1} characteristic of peresters (69, 70). A high resolution mass spectrum of the perester with the internal standard, heptacosafluorotributylamine, established the parent ion at 316 (0.3% intensity). Anal. calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10; O, 30.35. Found: C, 64.68; H, 5.23; O, 30.24.

2. Diphenylmethylbisbenzoylperoxide

To a pyridine solution of 0.72 g (3.1 mmol) diphenylmethylbishydroperoxide at 0° was added 0.88 g (6.2 mmol) of benzoyl peroxide (drop-wise). The work-up procedure was the same as above. Recrystallization from hexane gave clear prisms (mp 101-102.5°). The ir spectrum had a strong carbonyl band at

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

1750 cm^{-1}. The uv λ_{max} (methyl alcohol) was at 228 mμ (ϵ = 2.6 X 10^4).

I. Phenyl-N-t-butylnitrone, PBN, (XXXV)

1. Peracetic Acid (71)

To a 100 ml of methlyene chloride, vigorously stirred and cooled in an ice bath, was added 30 ml (1.1 mole) of 90% hydrogen peroxide and two drops of sulfuric acid. To the cooled solution was added 135 g (1.32 mole) of acetic anhydride (drop-wise) over a 30 min period. The solution was then stirred 15 min in the ice bath and 30 min at room temperature.

2. N-Benzylidiene-t-butylamine (72)

To a 50.6 g (0.476 mole) of redistilled t-butylamine was added 34.4 g (0.476 mole) of freshly distilled benzaldehyde at 0^o. The reaction mixture was stirred 30 min; and then allowed to stand 48 hours over a few grams of sodium hydroxide. The aqueous layer which formed in the reaction flask was removed and extracted with ether. The ether extract was combined with the water-insoluble material and dried over potassium hydroxide. After removal of the ether, the product was distilled to give 55.4 g (73%) of N-benzylidene-t-butylamine: bp 51^o/.65 mm (lit. (72) 92^o/8 mm), ir (neat), 1635 cm^{-1} (C=N), (lit. (71) 1638 cm^{-1}).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

3. 2-t-Butyl-3-phenyloxazirane (71)

To a stirred mixture of 55.4 g (0.34 mole) of N-benzylidene-t-butylamine in 100 ml of methylene chloride cooled in an ice bath was added drop-wise 108 g of the peracetic acid solution prepared above. The ice was allowed to melt overnight. The methylene chloride was taken off at reduced pressure yielding 52 g (86%) of the crude oxazirane.

4. Phenyl-N-t-butylnitrone, PBN, (XXXV) (71)

The conversion of 52 g (0.29 mole) of 2-t-butyl-3-phenyl-oxazirane to phenyl t-butyl nitrone was accomplished by refluxing it in 475 ml of dry acetonitrile for three days. Stripping off acetonitrile and recrystallization from petroleum ether yielded 30 g (58%), mp 72-73.5° (lit. (71) 75-76°).

J. ESR Technique

In esr solution work, distilled Skellysolve-H was used. The concentrations were kept very low in order to resolve hyperfine splittings (<0.07 M in PBN). The solution was frozen in liquid nitrogen and placed under vacuum (<1 mm). It was then allowed to thaw; refrozen and placed back on the vacuum line. This freeze-thaw technique was to remove any dissolved oxygen from the solvent. It was found to be a very necessary step. Decomposition of XXXIII was initiated by the thermal control unit on the esr spectrometer.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

The temperature was carefully controlled to avoid boiling the solvent at the reduced pressure in the esr tube.

K. 1,2-Bis-p-nitro-phenyl-1,2-diphenylethylene (XL) (61)

1. p-Nitrobenzhydrol

To 16.8 g (0.074 mole) of p-nitrobenzophenone was added 200 ml of absolute ethanol. All the ketone did not dissolve. However, it all went into solution upon addition of 3.0 g (0.079 mole) of sodium borohydride. Then dilute sulfuric acid was added to the solution until gas evolution ceased. The solution was extracted with ether and dried over $CaCl_2$. Evaporation of the ether and recrystallization from benzene-petroleum ether yielded 10.8 g (64%) mp 72.5-74° (lit. (73) 73-75.7°), ir (KBr) 3480 cm^{-1}.

2. p-Nitrobenzhydrylidenedibromide (61)

A solution of 10.8 g (0.047 mole) of p-nitrobenzhydrol in 153 ml of distilled carbon tetrachloride was mixed with 20 ml (0.206 mole) of phosphorus tribromide. The mixture was allowed to set one day. The next day the mixture was refluxed nine hours. The phosphorus tribromide was vacuum distilled leaving behind approximately 6.2 G of crude product. The solid was recrystallized from benzene, mp 79.5-81.5° (lit. (61) 82-83°).

3. 1,2-Bis-p-nitro-phenyl-1,2-diphenylethylene (XL) (61)

A solution of 18.6 g (0.044 mole) p-nitrobenzhrylidenedibromide in 200 ml of dry carbon disulfide was shaken with 20 g of

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

mercury for 16 hrs. Then an additional 20 g of mercury was added and the mixture shaken for 24 hrs. The solution was filtered with Super Cell, and the carbon disulfide distilled off, leaving a red syrup behind. Yellow crystals formed when ethanol was added to the red syrup and heated. More crystals formed on cooling. The crystals were collected and 1.45 g of the mixture of cis (XLI) and trans (XLII) isomers were placed on 145 g of neutral alumina (Brockmann Activity Grade 1). Separation was accomplished with 30% chloroform in Skellysolve-H. The trans isomer was eluted first. The ir spectra of the cis and trans were superimposable on the literature spectra (61). The region between 900-700 cm^{-1} permitted the identification of the isomer.

4. Ozonation of 1,2-Bis-p-nitro-phenyl-1,2-diphenylethylene

Ozonation of 0.49 g of cis and trans isomers at -78^{o} was attempted in a 50-50 mixture of chloroform and methyl alcohol with two drops of 90% hydrogen peroxide added. After ten minutes of passing ozone through the solution, the reaction mixture was worked up. The ir revealed no change in the reactant. The theoretical ozonation time was approximately ten minutes. The mixture was put back into solution and ozonized an additional 24 minutes; still no change in the ir of the reaction mixture was observed. The mixture was put back into solution and ozonized an additional 49 minutes. The resulting product was not the bishydroperoxide (XXXIX) but

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

p-nitrobenzophenone. This conclusion was reached by nmr and ir examination.

L. Decomposition of Diphenylmethylbisacetyl peroxide (XXXIII)

1. Gas Chromatographic Yield Analysis

A 0.0367 M solution of diphenylmethylbisacetyperoxide (XXXIII) in absolute ethanol was prepared. The perester was decomposed at the injection port (195°). A 5' X 1/4" column packed with 3% SE 30 on 100/120 mesh Varaport 30 at 135° was used to separate benzophenone and phenyl benzoate. The yield data was based on cut and weigh analysis of the area peaks obtained from standard samples. Oxygen and carbon dioxide were identified on a 160/120 mesh Porapak Q column by comparison to authentic samples. The column temperature was 102°.

2. Decomposition Kinetics of XXXIII

Kinetic measurements by nmr were made on 0.008-0.274 M solutions of XXXIII in diphenyl ether. Nitromethane (0.084-0.909 M) was used as the internal standard. Nitromethane was shown experimentally to be inert to hot 30% hydrogen peroxide. The rate of disappearance of methyl carbonyl protons (XXXIII) was followed by periodically measuring the intensity of the nmr signal at δ 1.88. The intensity at δ 4.33 for nitromethane was concurrently measured. The decomposition of XXXIII was accomplished in the nmr tube by a constant temperature water bath. Periodically the nmr tube was

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

removed and quenched in an ice bath. The nmr spectra was then immediately recorded. Since there was no decomposition of XXXIII at 48° for four hours, nmr examination at 40° was a satisfactory procedure. Each peak was integrated five times; the average value was used for the kinetic analysis. The integration values and times were recorded. This data was then computer analyzed by a first order kinetic program previously described. The data is recorded in Tables XI through XIV. In these tables "A_r" refers to the integration of the singlet at δ 1.88 representing the six protons of the reactant (XXXIII). "A_s" refers to the integration of the singlet at δ 4.33 representing the three protons of the standard (nitromethane).

M. Preliminary Investigation of Trifluoroacetic Acid Decomposition of XXXIII

Decomposition of XXXIII by thermal and trifluoroacetic acid was accomplished in the following manner:

The first attempt at thermal decomposition of 28.7 mg of XXXIII in an oil bath at 124° resulted in a violent report. However, 23.3 mg of XXXIII was uneventfully decomposed in a hot water bath. A few drops of trifluoroacetic acid very vigorously decomposed 22.6 mg of XXXIII.

In addition, a 50-50 (weight) mixture of phenyl benzoate and benzophenone in absolute ethanol was prepared. These three

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

samples were individually injected into a gas chromatograph linked to the mass spectrometer. The gc column used was packed with Poly-pak #1. It was at a temperature of 235°.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

SUMMARY

The observation of diphenylmethylbishydroperoxide during the ozonolysis of tetraphenylethylene may be a consequence of the greater stability of the Criegee zwitterion. This stability may be due either to a large delocalization energy via resonance with the π system of the phenyl rings or to the formation of a dioxirane intermediate (XXIV).

The relative stability of diphenylmethylbishydroperoxide (XXIII) is very unusual since most of the aliphatic bishydroperoxides are explosive oils (33). This stability may be due to the phenyl π electron systems and intramolecular hydrogen bonding. The thermal decomposition of XXIII follows very nearly first order kinetics. The somewhat disconcerting fact is the nearly systematic deviation in the point residuals from the least squares line.

The thermal decomposition of diphenylmethylbisacetylperoxide (XXXIII) followed first order kinetics yielding phenyl benzoate. This product requires an aryl migration to oxygen. The migration was found to proceed by a radical mechanism by means of electron spin resonance studies.

Decomposition of XXXIII by trifluoroacetic acid also produces phenyl benzoate. This migration may proceed by an ionic mechanism

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

since an electron spin resonance spectrum was not obtainable during the decomposition.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

LITERATURE CITED

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

LITERATURE CITED

1. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry, A Comprehensive Text", Interscience Publishers, New York, N.Y., 1962, p. 277.

2. R. Trambarulo, S. N. Ghosh, C. A. Burrus, and W. Gordy, J. Chem. Physics, 21, 851 (1953).

3. C. F. Schönbein, J. Prakt. Chem., 66, 282 (1855).

4. A. Houzeau, Compt. Rend., 76, 572 (1873).

5. L. Long, Jr., Chem. Rev., 27, 437 (1940).

6. P. S. Bailey, ibid., 58, 925 (1958).

7. R. Criegee, Record Chem. Progr. (Kresge-Hooker Sci. Lib.), 18, 111 (1957).

8. R. W. Murray, Accounts of Chemical Research, 1, 313 (1968).

9. R. Hisgen, Angew. Chem. Intern. Ed. Engl., 2, 565, 633 (1963).

10. R. Criegee and G. Schröder, Chem. Ber., 93, 689 (1960).

11. P. S. Bailey, J. A. Thompson, and B. A. Shoulders, J. Am. Chem. Soc., 88, 4098 (1966).

12. P. D. Bartlett and M. Stiles, ibid., 77, 2806 (1955).

13. R. Criegee, Advances in Chemistry Series, No. 21, American Chemical Society, Washington, D.C., 1959, p. 133.

14. R. W. Murray, R. D. Youssefyeh, and P. R. Story, J. Am. Chem. Soc., 89, 2429 (1967).

15. P. S. Bailey and A. G. Lane, ibid., 89, 4473 (1967).

16. P. R. Story, R. W. Murray and R. D. Youssefyeh, ibid., 88, 3144 (1966).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

17. R. Criegee and G. Lohaus, Ann. Chem., 583, 6 (1953).

18. R. Criegee in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, New York, N.Y., 1962, p. 29.

19. F. L. Greenwood and H. Rubinstein, J. Org. Chem., 32, 3369 (1967).

20. R. Criegee, Ann., 560, 127 (1948).

21. E. Hedaya and S. Winstein, Tetrahedron Letters, 563, (1962).

22. E. Hedaya and S. Winstein, J. Am. Chem. Soc., 89, 1661 (1967).

23. J. C. Robertson and W. J. Verzino, Jr., J. Org. Chem., 35, 545 (1970).

24. C. Nebel, Chem. Comm., 101 (1968)

25. W. P. Keaveney, M. G. Berger, and J. J. Pappas, J. Org. Chem., 32, 1537 (1967).

26. S. Fliszar, D. Gravel, and E. Cavalieri, Can. J. Chem., 44, 67 (1966).

27. S. Fliszar and M. Granger, J. Am. Chem. Soc., 91, 3330 (1969).

28. C. S. Marvel and V. Nichols, J. Org. Chem., 6, 296 (1941).

29. J. Renard and S. Fliszar, Can. J. Chem., 47, 3333 (1969).

30. R. Criegee, private communication.

31. P. Gunther, Ph.D. Thesis, Technical University, Karlsruhe, Germany (1963).

32. N. A. Milas and A. Goluboric, J. Am. Chem. Soc., 81, 6461 (1959).

33. N. A. Milas and A. Goluboric, ibid., 81, 5824 (1959).

34. N. A. Milas and A. Goluboric, ibid., 81, 3361 (1959).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

35. W. Cooper and W. H. T. Davidson, J. Chem. Soc., 1180 (1952).

36. M. S. Kharasch and G. Sosnovsky, J. Org. Chem., 23, 1322 (1958).

37. A. H. M. Cosijn and M. G. J. Ossewold, Rec. Trav. Chim. Pays-Bas., 87, 1264 (1968).

38. M. C. Whiting, A. J. N. Bolt and J. H. Parish, "Oxidation of Organic Compounds," Vol. III, American Chemical Society, Washington, D.C., 1968, p. 4.

39. L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1948, p. 320.

40. L. P. Kuhn, J. Am. Chem. Soc., 74, 2492 (1952).

41. R. F. Badger, J. Chem. Phys., 8, 288 (1940).

42. L. P. Kuhn, J. Am. Chem. Soc., 76, 4323 (1954).

43. J. I. G. Cadogan, D. H. Hey, and W. A. Sanderson, J. Chem. Soc., 4897 (1960).

44. V. Baliah and P. Subbarayan, J. Org. Chem., 25, 1833 (1960).

45. A. G. Davies, "Organic Peroxides," Butterworth and Company, Ltd., London, 1961, p. 170.

46. C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York 1957, p. 503.

47. C. S. Foote, S. Wexler, W. Ando, and R. Higgins, J. Am. Chem. Soc., 90, 975 (1968).

48. D. B. Sharp and T. M. Patrick, Jr., J. Org. Chem., 26, 1389 (1961).

49. E. G. Janzen and B. J. Blackburn, J. Am. Chem. Soc., 90, 5909 (1968).

50. E. G. Janzen and B. J. Blackburn, ibid., 91, 4481 (1969).

51. E. W. Stone and A. H. Maki, J. Chem. Phys., 37, 1326 (1962).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

52. D. H. Geske, Progr. Phy. Org. Chem., 4, 129 (1967).

53. E. T. Strom, A. L. Bluhm, and J. Weinstein, J. Org. Chem., 32, 3853 (1967).

54. G. Herzberg, "Atomic Spectra and Atomic Structure," Dover Publication, New York, 1944, p. 195.

55. P. D. Bartlett and J. D. Cotman, Jr., J. Am. Chem. Soc., 72, 3095 (1950).

56. P. DeMayo, ed., "Molecular Rearrangements, Part One," Interscience Publishers, New York, 1963, p. 427.

57. E. Hückel, Z. Physik, 70, 207 (1931).

58. N. F. Phelan, H. H. Jaffe, and M. Orchin, J. Chem. Ed., 44, 626 (1967).

59. F. H. Seubold, Jr., J. Am. Chem. Soc., 75, 2532 (1953).

60. J. C. Baird, J. Chem. Phys., 37, 1879 (1962).

61. R. Kuhn and D. Blum, Chem. Ber., 92, 1483 (1959).

62. P. D. Bartlett and R. R. Hiatt, J. Am. Chem. Soc., 80, 1398 (1958).

63. K. Nozaki and P. D. Bartlett, ibid., 68, 1686 (1946).

64. W. Sheehan and W. Carmody, Ind. Eng. Chem., Anal. Ed., 9, 8 (1937).

65. R. C. P. Cubbon and C. Hewlett, J. Chem. Soc., 2983 (1968).

66. R. C. P. Cubbon and C. Hewlett, ibid., 2986 (1968).

67. H. F. Ullmann, Ber., 39, 4014 (1906).

68. L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, 1967, p. 293.

69. L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1964, p. 129.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

70. M. M. Martin and E. B. Sanders, J. Am. Chem. Soc., 89, 3777 (1967).

71. W. D. Emmons, J. Am. Chem. Soc., 79, 5739 (1957).

72. B. L. Emling, R. J. Horyath, A. J. Saraceno, E. F. Ellermeyer, L. Haile, and L. D. Hudac, J. Org. Chem., 24, 657 (1959).

73. B. B. Smith and J. E. Leffler, J. Am. Chem. Soc., 77, 2509 (1955).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

APPENDIX (Spectra)

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

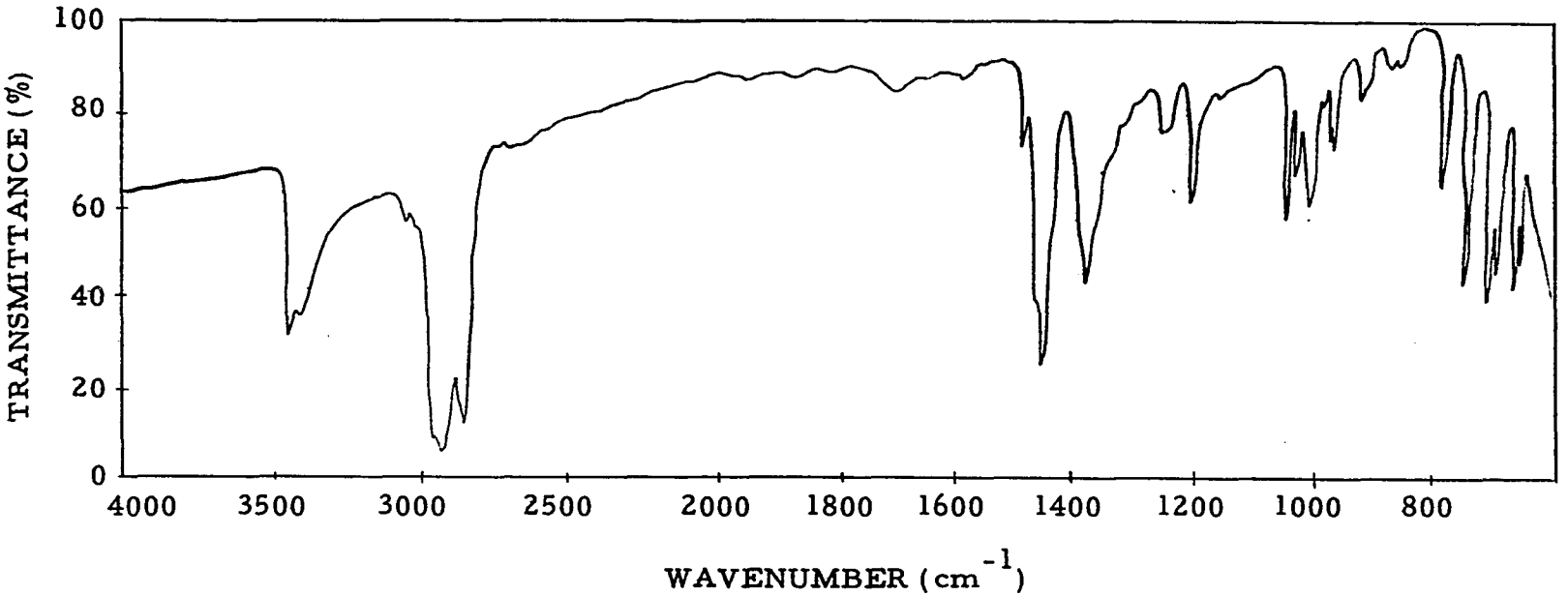


Figure 17. The ir Spectrum of Diphenylmethylbishydroperoxide (XXIII) in Nujol.

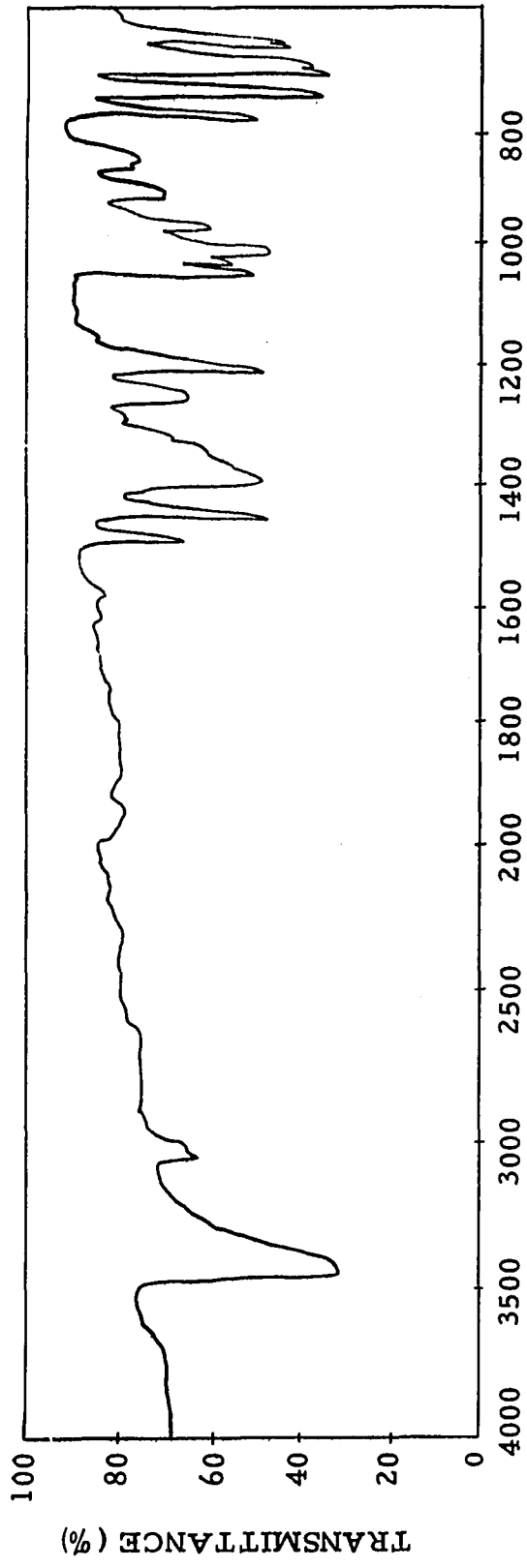


Figure 18. The ir Spectrum of Diphenylmethylbishydroperoxide (XXIII) in KBr.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

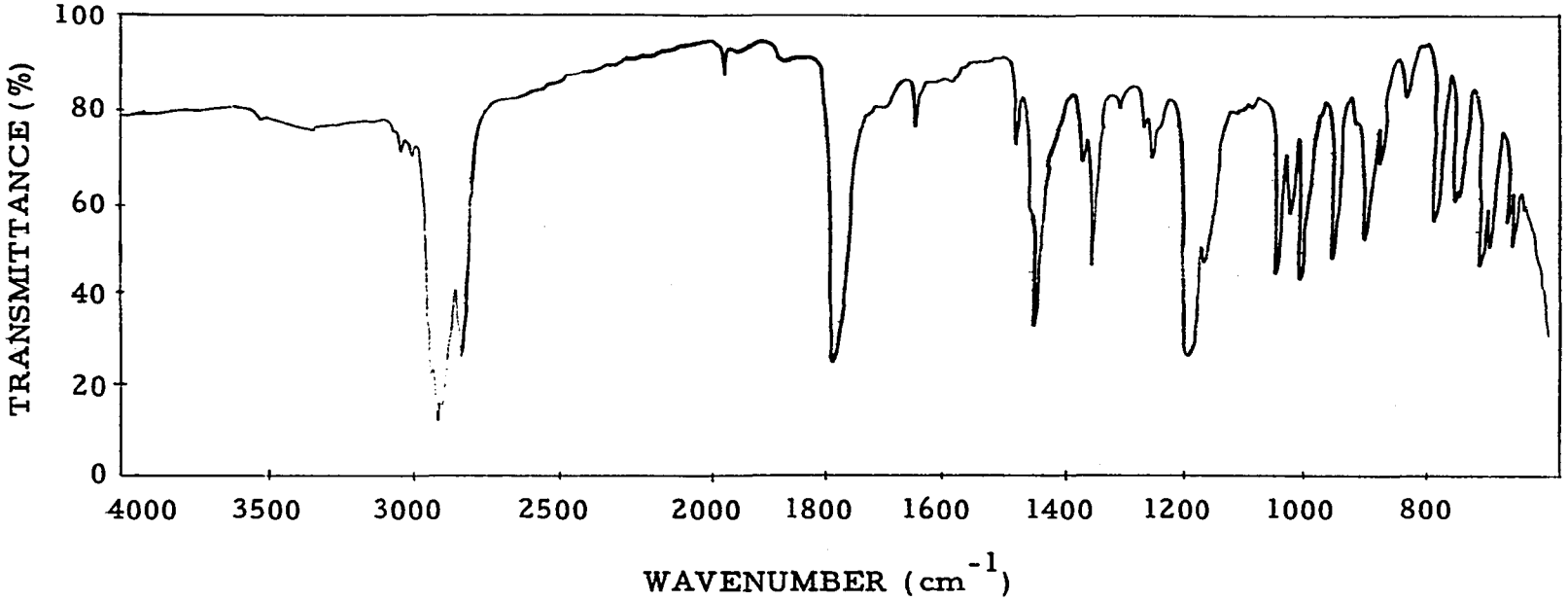


Figure 19. The ir Spectrum of Diphenylmethylbisacetylperoxide (XXXIII) in Nujol.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

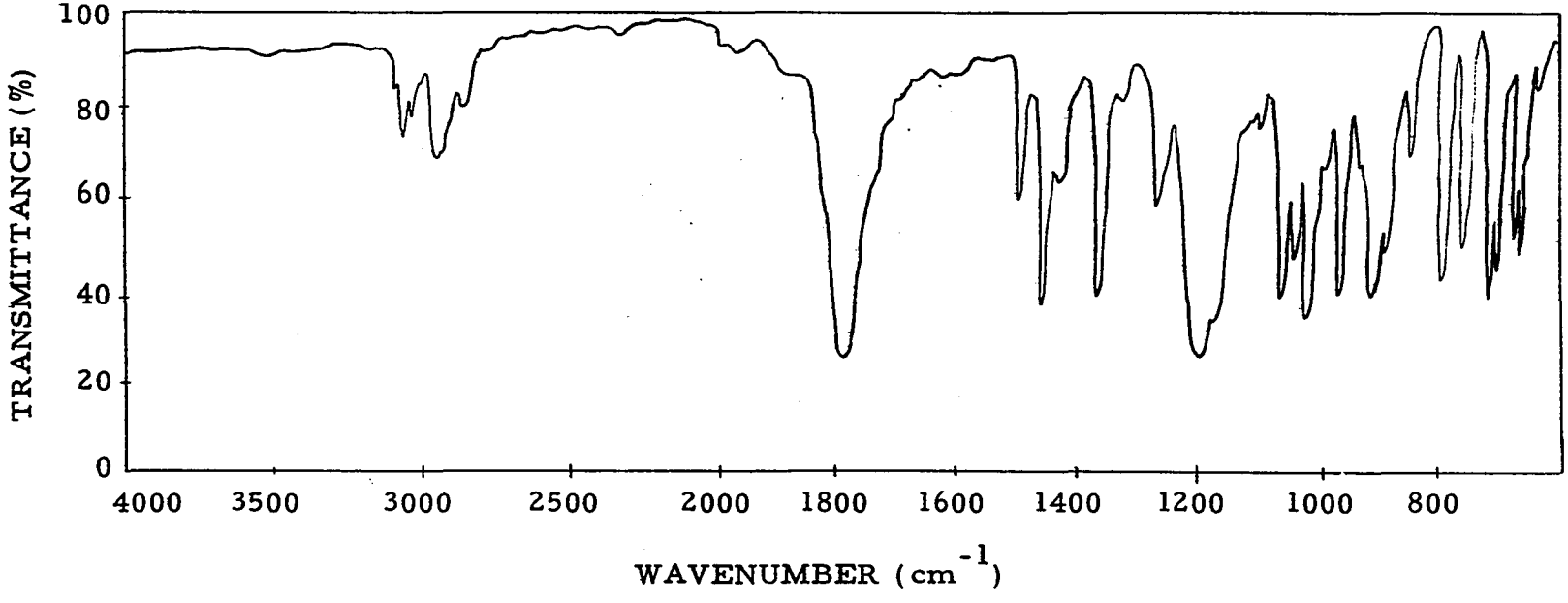


Figure 20. The ir Spectrum of Diphenylmethylbisacetylperoxide (XXXIII) in KBr.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

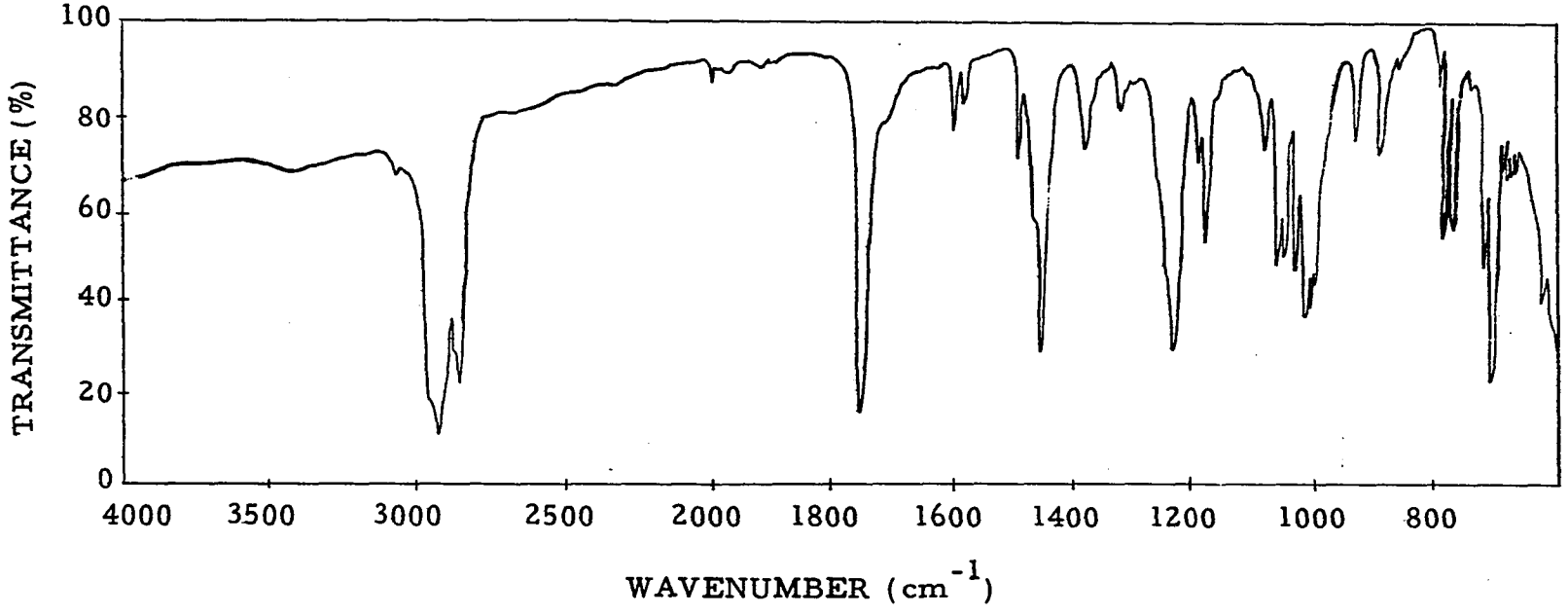


Figure 21. The ir Spectrum of Diphenylmethylbisbenzolyperoxide in Nujol.

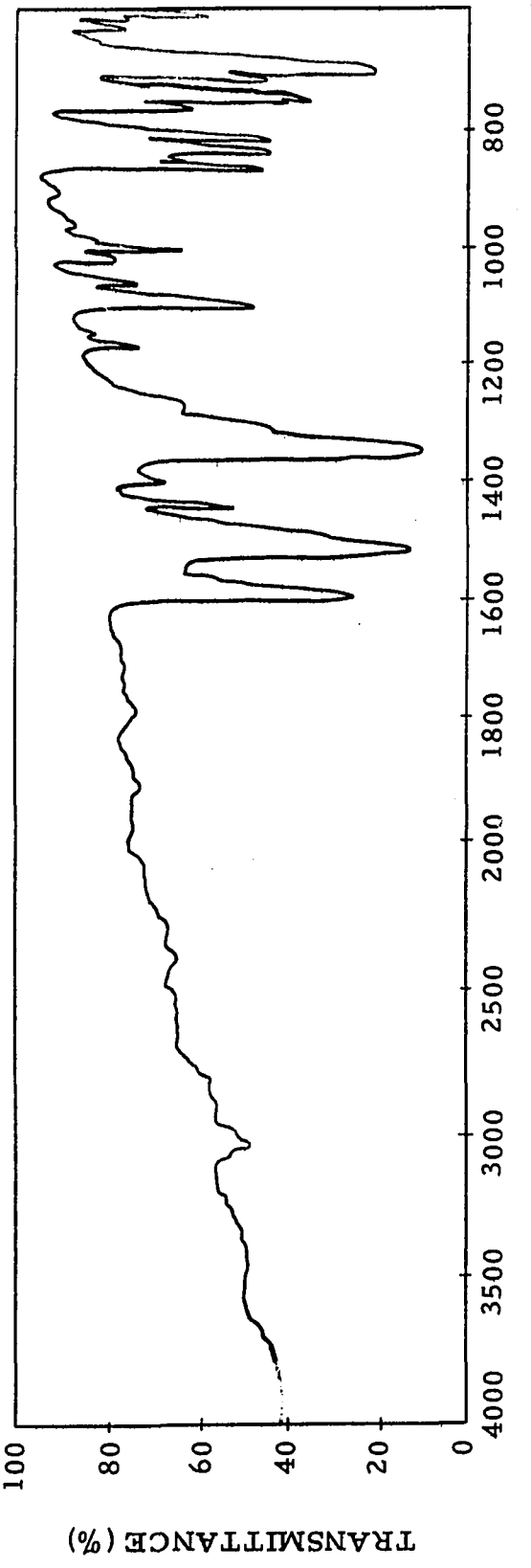


Figure 22. The ir Spectrum of cis, 1,2-Bis-p-nitrophenyl-1,2-diphenylethylene (XLI) in KBr.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

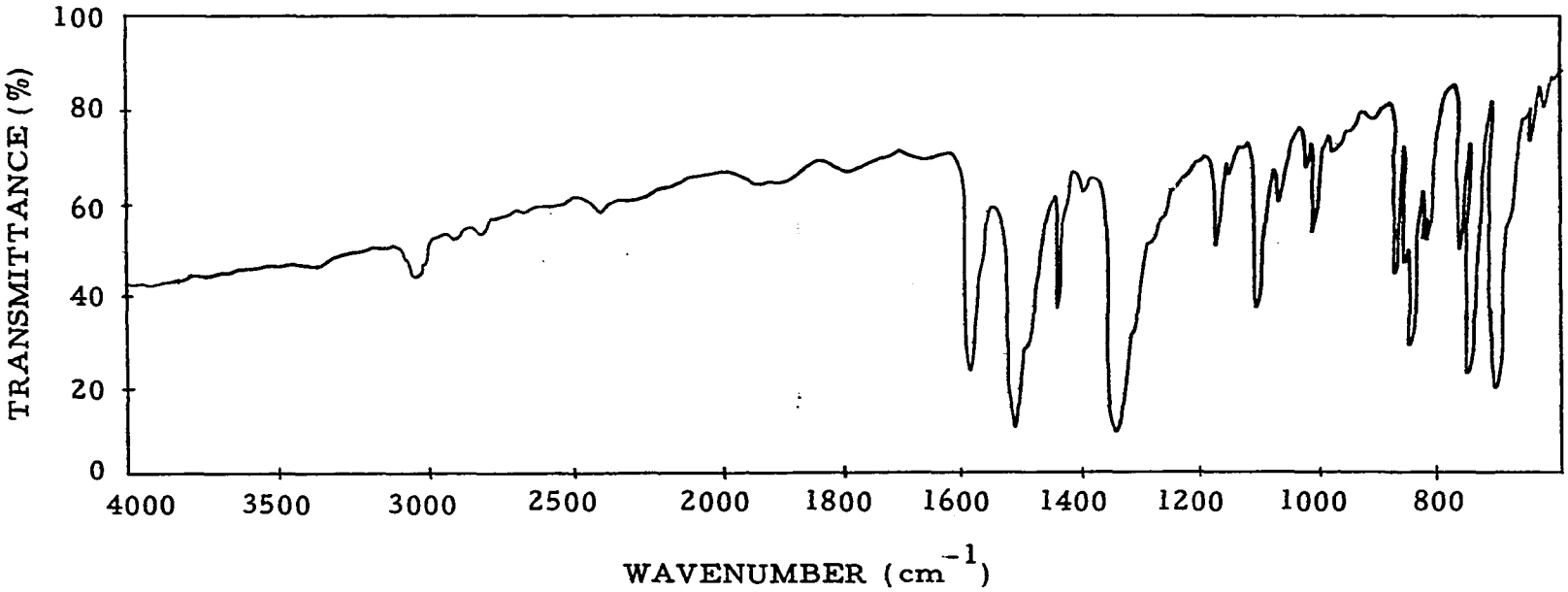


Figure 23. The ir Spectrum of trans, 1,2-Bis-p-nitrophenyl-1,2-diphenylethylene (XLII) in KBr.

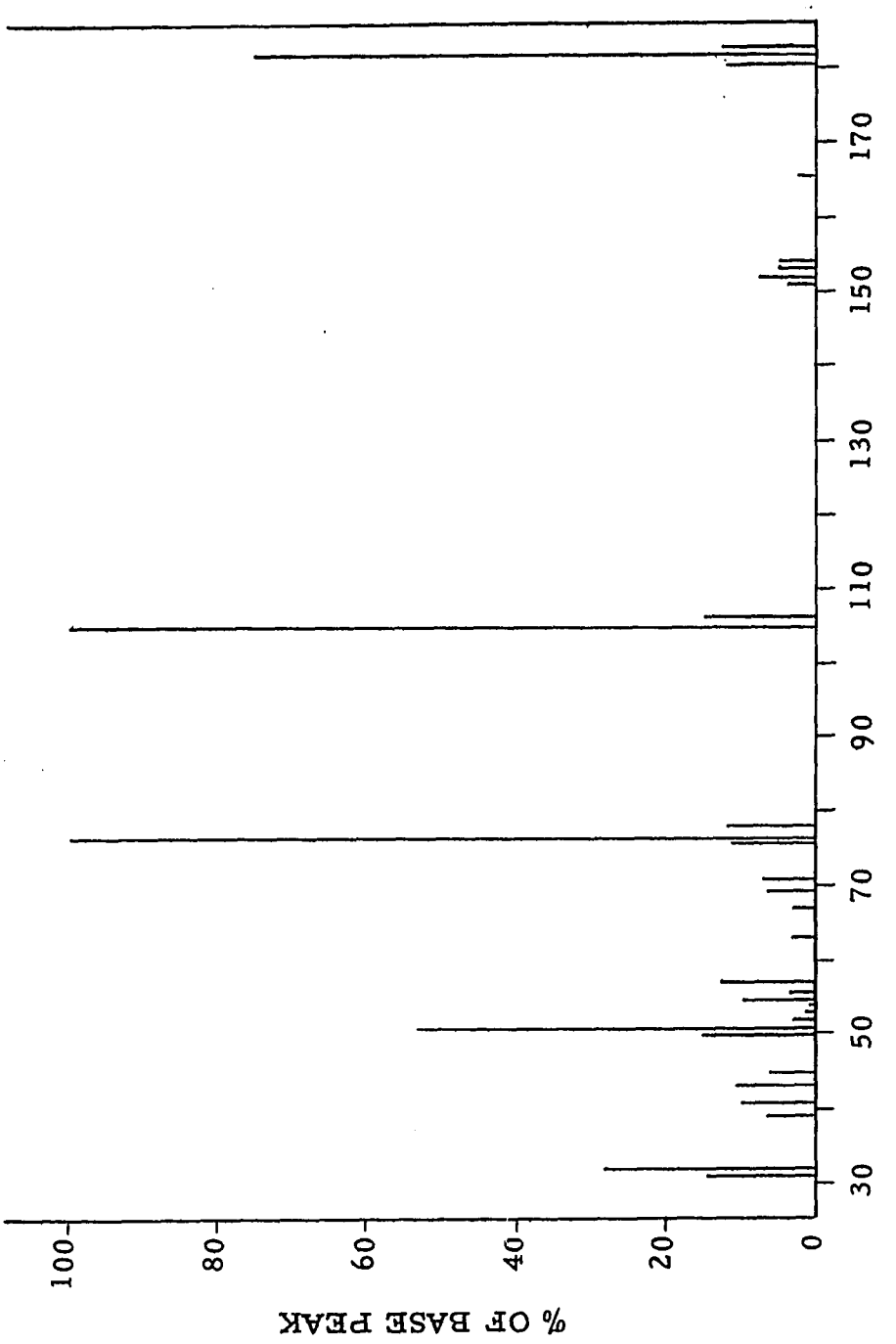


Figure 24. The Mass Spectrum of Diphenylmethylbishydroperoxide (XXIII) with Source at 130°.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

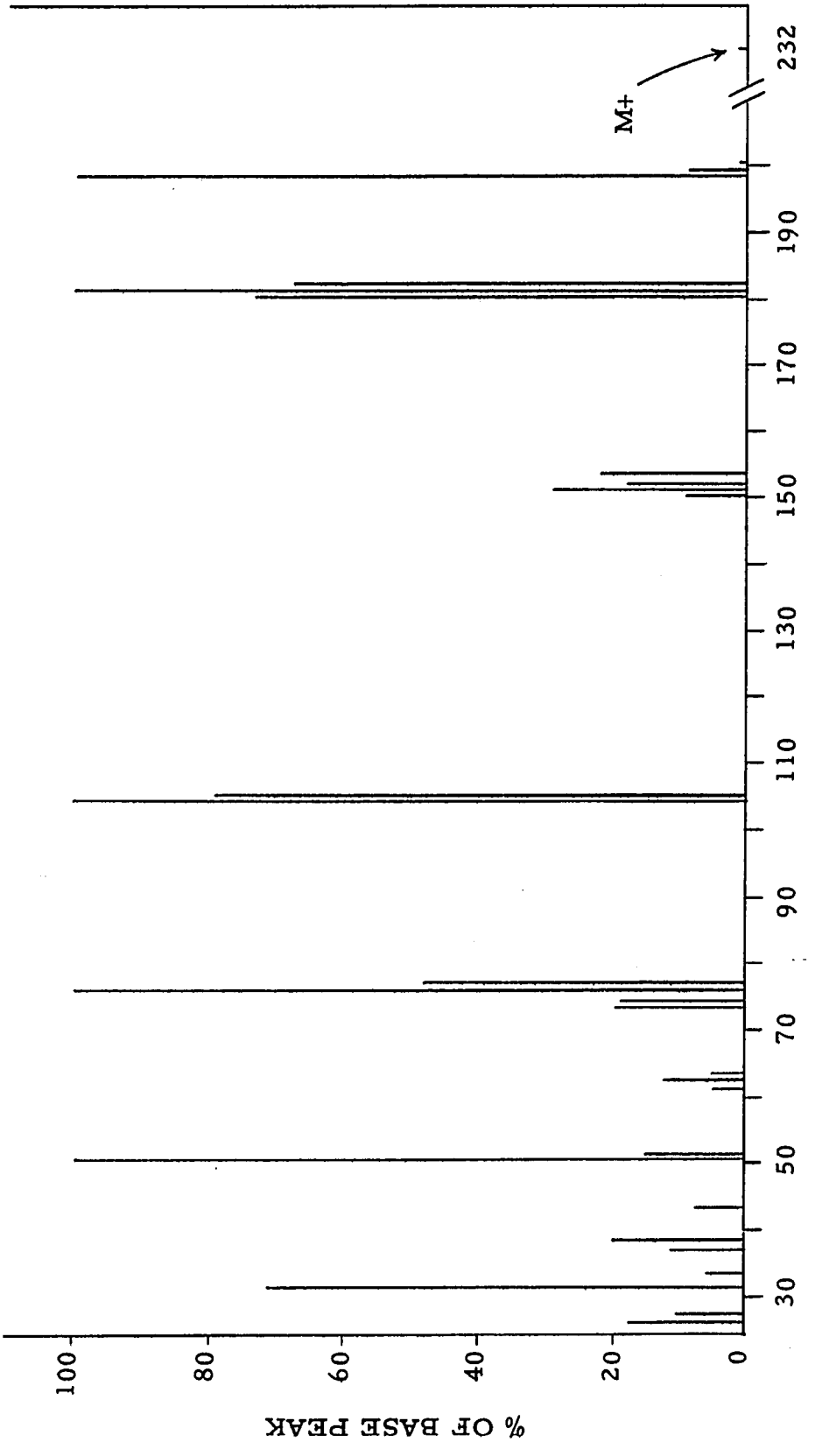


Figure 25. The Mass Spectrum of Diphenylmethylbishydroperoxide (XXIII) with Source at 50°.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

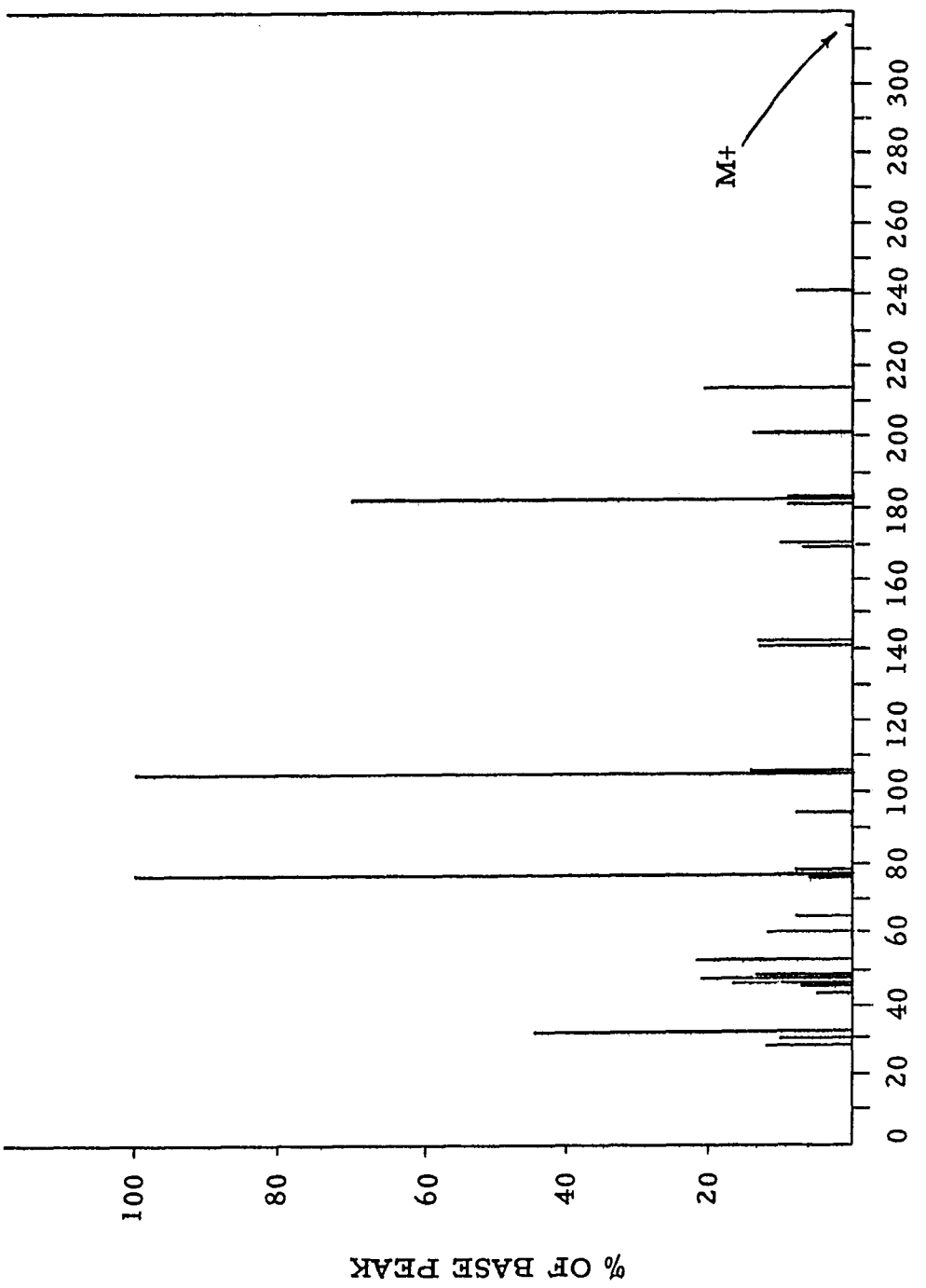


Figure 26. The Mass Spectrum of Diphenylmethylbisacetylperoxide (XXXIII).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

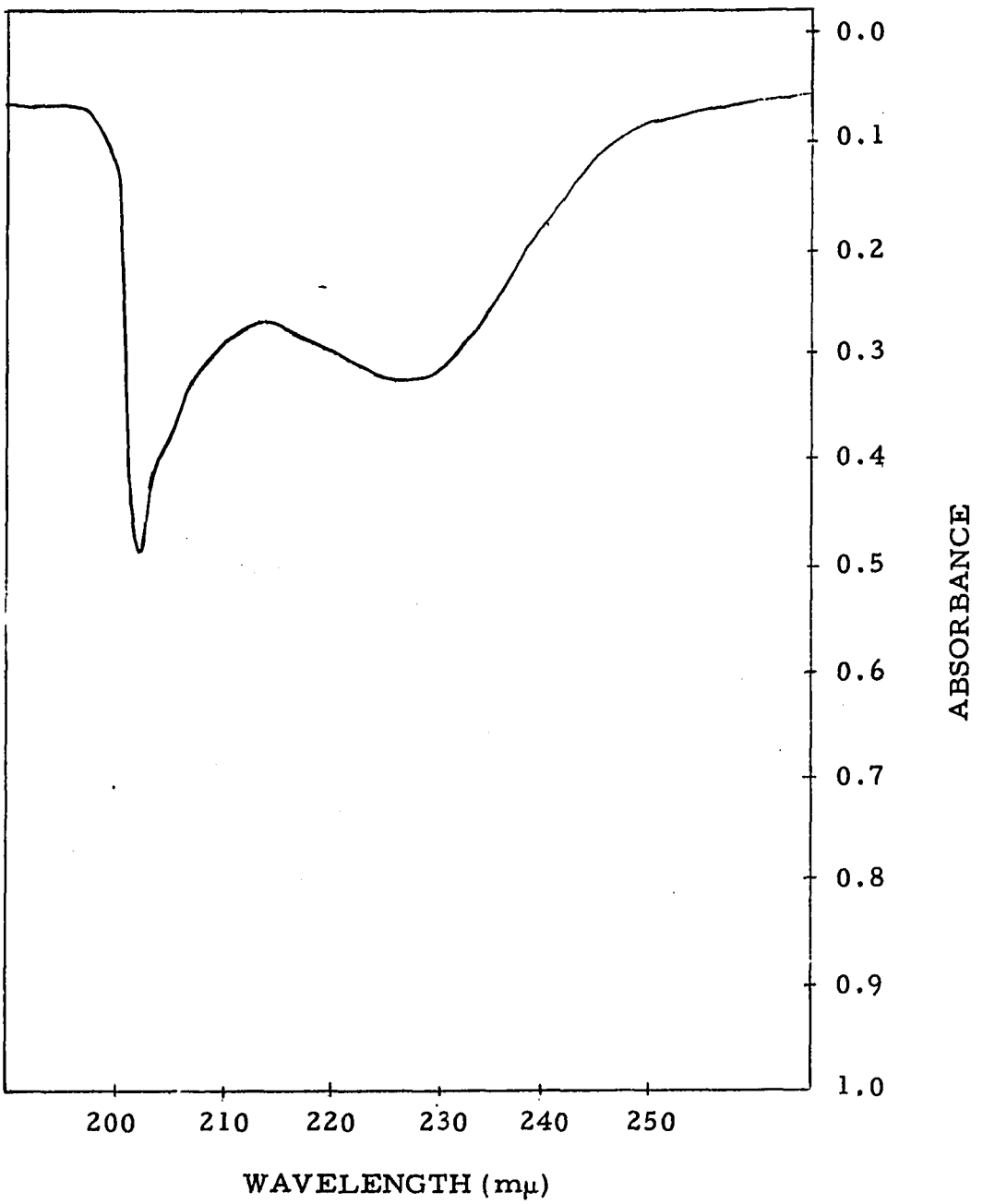


Figure 27. The Ultraviolet Spectrum of Diphenylmethyl-bisbenzolyperoxide in Methyl Alcohol.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

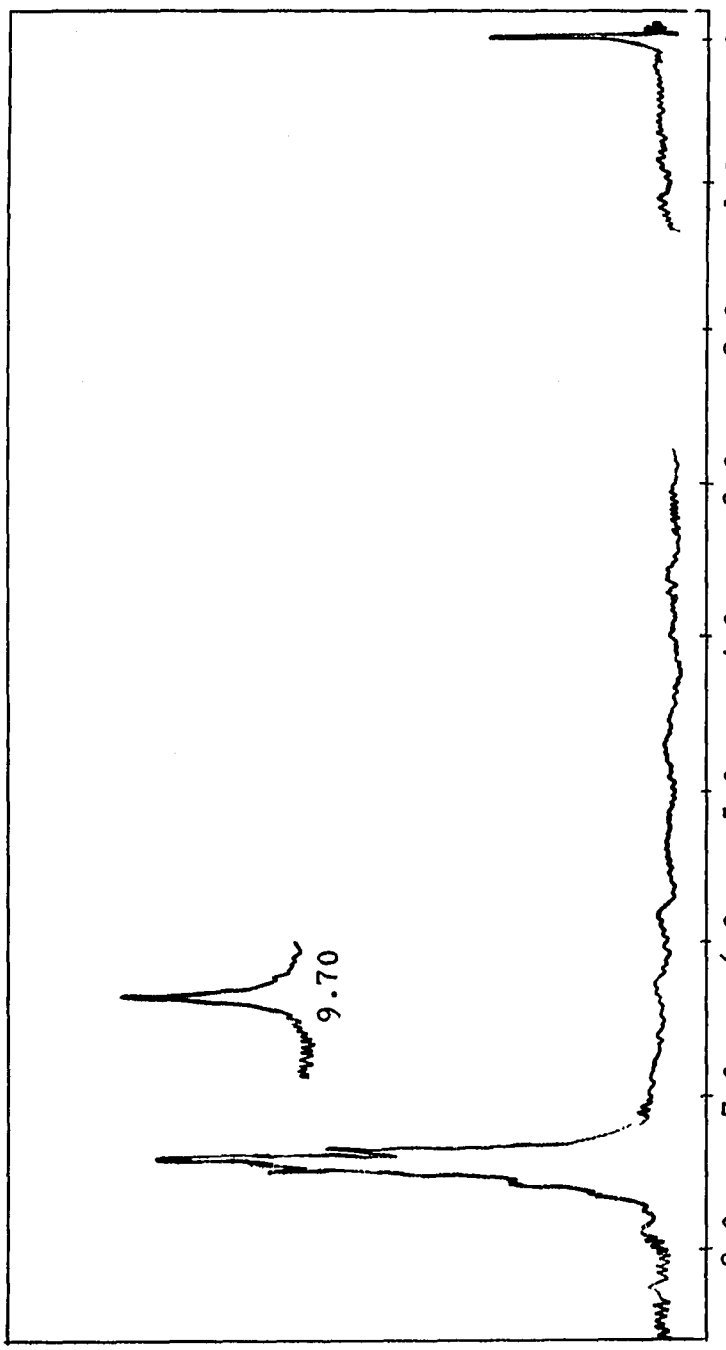


Figure 28. The NMR Spectrum of Diphenylmethylbishydroperoxide (XXIII) in CH_3CN.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

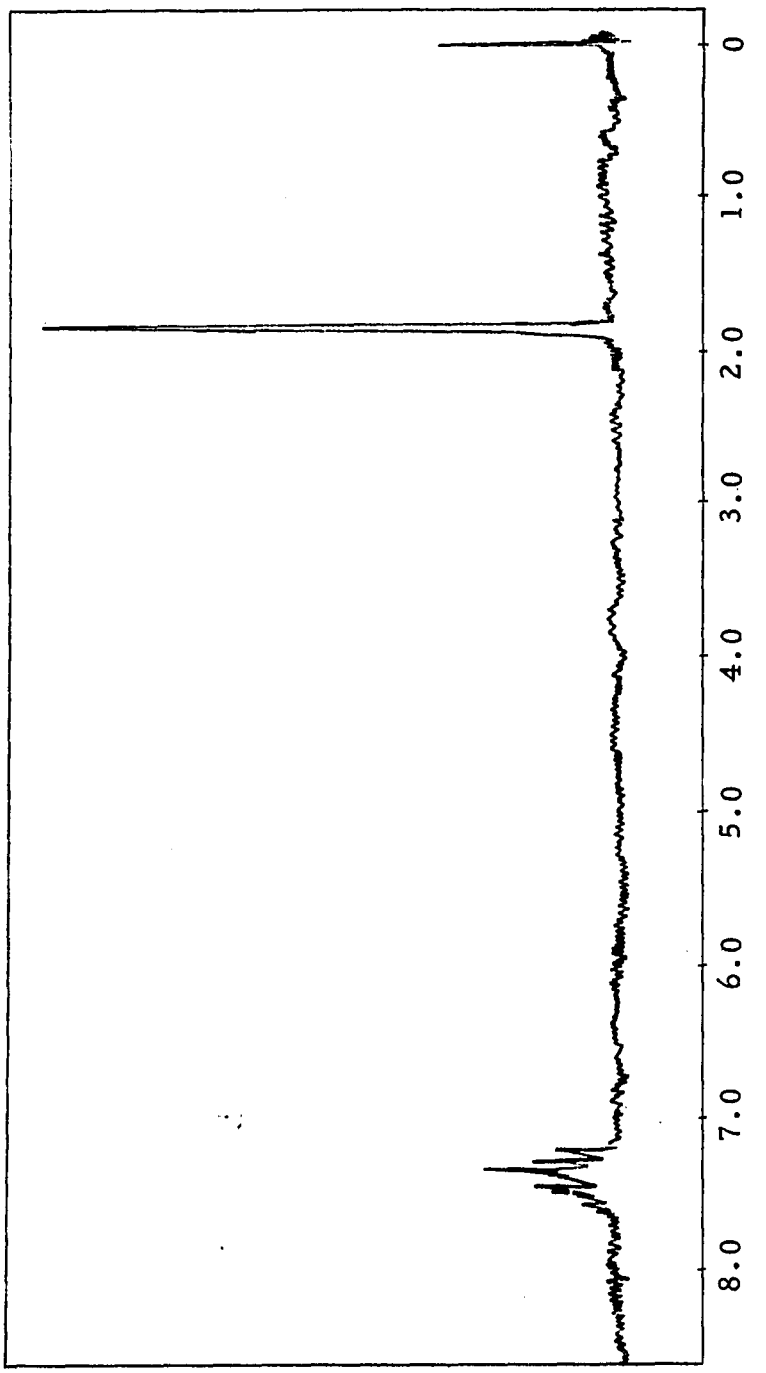


Figure 29. The NMR Spectrum of Diphenylmethylbisacetylperoxide (XXXIII).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.