THE PREPARATION AND PHOTOCHEMISTRY OF SPIRO [1, 2, 3, 4, 5, 6, 7, 8, 9, 10-DECAHYDROANTHRACENE-10-ONE-9, 1'-CYCLOPENTANE]

Thesis for the Degree of M. S. MICHIGAN STATE UNIVERSITY David C. Lankin 1967 THESIS



ABSTRACT

THE PREPARATION AND PHOTOCHEMISTRY OF SPIRO[1,2,3,4,5,6,7.8,9,10-DECAHYDROANTHRACENE-10-ONE-9,1'-CYCLOPENTANE]

by David C. Lankin

The purpose of this study was to investigate the structure of the product or products from the oxidation of s-dodecahydrotriphenylene 34 with peroxytrifluoroacetic acidboron fluoride etherate and further, to study the photochemistry of the dienone products derived from such an oxidation.

When s-dodecahydrotriphenylene 34 was oxidized with a mixture of peroxytrifiluoroacetic acid-boron fluoride etherate in methylene chloride at -3 to +1°, spiro[1,2,3,4,5,6, 7,8,9,10-decahydroanthrace-10-one-9,1'-cyclopentane] 35was produced in 45% yield. When the oxidation was carried out at -67 to -65°, unoxidized hydrocarbon 34, dienone 35, and spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10one-9,1'-cyclopentane] 33 were formed. It was shown that





34



33

David C. Lankin

dienone 33 could be converted into dienone 35 by treatment with either trifluoroacetic acid or boron fluoride etherate in methylene chloride at room temperature. A proposed reaction mechanism accounts for the formation of the dienones.

Irradiation of dienone 35 in ether solution provided dienone 33. Irradiation of dienone 35 in methanol solution produced spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}]tetradec-3-ene-2one-14,1'-cyclopentane], 58, shown to be the primary photoproduct of 35. Further irradiation of 58 in ether afforded dienone 33. The intermediacy of 58, in the production of 33 from photolysis of dienone 35 in ether has been shown and the proposed mechanisms for the various photochemical transformations are consistent with these results.



58

Irradiation of dienone 33 in ether provided ring fission products, but no ketone 58 was formed.

Control experiments showed that none of the irradiated compounds was reactive in the dark in the solvents used for the irradiations.

THE PREPARATION AND PHOTOCHEMISTRY OF SPIRO[1,2,3,4,5,6 7,8,9,10-DECAHYDROANTHRACENE-10-ONE-9,1'-CYCLOPENTANE]

Ву

David C. Lankin

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Chemistry

645737 5/25/07

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor Harold Hart for his encouragement and enthusiasm during the course of this study.

Appreciation is also extended to Mr. Michael Gross for his assistance in operating the HA-100 spectrometer.

Appreciation is also extended to Mr. Roger Murray for many helpful discussions.

Appreciation is extended to Michigan State University for a Graduate Teaching Assistantship from September, 1964 to Spring, 1967.

TABLE OF CONTENTS

		PAGE
INTRODUC	CTION	1
RESULTS	AND DISCUSSION	11
Α.	The Oxidation of s-Dodecahydrotriphenylene	11
в.	The Photochemistry of Spiro[1,2,3,4,5,6,7,8, 9,10-decahydroanthracene-10-one-9,1'-cyclo- pentane]	20
c.	The Photochemistry of Spiro[tetracyclo [7.4.1.0 ^{1,@03,8}]tetradec-3-ene-2-one-14,1'- cyclopentane]	30
D.	The Photochemistry of Spiro[1,2,3,4,5,6,7,8, 9,10-decahydrophenanthrene-10-one-9,1'- cyclopentane]	37
EXPERIM	ENTAL	40
Α.	General Procedures	40
в.	Preparation of s-Dodecahydrotriphenylene	41
c.	The Oxidation of s-Dodecahydrotriphenylene	42
	1. The Reaction with 110% Excess Oxidant at -3 to +1°	42
	2. The Reaction with 110% Excess Oxidant at -67 to -65°	43
D.	The Rearrangement of Spiro[1,2,3,4,5,6,7,8,9, 10-decahydrophenanthrene-10-one-9,1'-cyclo- pentane] with Boron Fluoride Etherate	45
E.	The Rearrangement of Spiro[1,2,3,4,5,6,7,8,9, 10-decahydrophenanthrene-10-one-9,1'-cyclo- pentane] with Trifluoroacetic Acid	46
F.	General Photolysis Procedures	46

PAGE

G.	<pre>Irradiation of Spiro]1,2,3,4,5,6,7,8,9,10- decahydroanthracene-10-one-9,1'-cyclo- pentane] in Anhydrous Ether</pre>	47
н.	The Dark Reaction of Spiro[1,2,3,4,5,6,7,8,9, 10-decahydroanthracene-10-one-9,1'-cyclo- pentane] in Anhydrous Ether	48
I.	<pre>Irradiation of Spiro[1,2,3,4,5,6,7,8,9,10- decahydroanthracene-10-one-9,1'-cyclo- pentane] in Methanol</pre>	49
J.	The Dark Reaction of Spiro[1,2,3,4,5,6,7,8,9, 10-decahydroanthracene-10-one-9,1'-cyclo- pentane] in Methanol	49
К.	<pre>Irradiation of Spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}] tetradec-3-ene-2-one-14,1'-cyclopentane] in Anhydrous Ether</pre>	50
L.	The Dark Reaction of Spiro[tetracyclo [7.4.1.0 ^{1,9} 0 ^{3,8}]tetradec-3-ene-2-one-14,1'- cyclopentane] in Anhydrous Ether	50
М.	<pre>Irradiation of Spiro[1,2,3,4,5,6,7,8,9,10- decahydrophenanthrene-10-one-9,1'-cyclo- pentane] in Anhydrous Ether</pre>	51
N.	The Dark Reaction of Spiro[1,2,3,4,5,6,7,8,9, 10-decahydrophenanthrene-10-one-9,1'-cyclo- pentane] in Anhydrous Ether	51
SUMMARY		52
LITERATU	E CITED	54
APPENDIX		57
1.	a) IR Spectrum of Spiro[1,2,3,4,5,6,7,8,9,10- decahydroanthracene-10-one-9,1'-cyclo- pentanel	58
	b) UV Spectrum of Spiro[1,2,3,4,5,6,7,8,9,10- decahydroanthracene-10-one-9,1'-cyclo- pontanol	5.9
		00

TABLE OF CONTENTS (Cont.)

2.	a) IR Spectrum of Spiro[1,2,3,4,5,6,7,8,9,10- decahydrophenanthrene-10-one-9,1'-cyclo- pentane]	59
	<pre>b) UV Spectrum of Spiro[1,2,3,4,5,6,7,8,9,10- decahydrophenanthrene-10-one-9,1'-cyclo- pentane]</pre>	59
3.	a) IR Spectrum of Spiro[tetracyclo[7.4.1.0 ^{1,9} 0 ^{3,8} tetradec-3-ene-2-one-14,1'-cyclopentane].	⁸] 60
	<pre>b) UV Spectrum of Spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8} tetradec-3-3n3-2-one-14,1'-cyclopentane].</pre>	⁸] 60
4.	<pre>NMR Spectrum of Spiro[1,2,3,4,5,6,7,8,9,10- decahydroanthracene-10-one-9,1'-cyclo- pentane]</pre>	61
5.	NMR Spectrum of Spiro[1,2,3,4,5,6,7,8,9,10- decahydrophenanthrene-10-one-9,1'-cyclo- pentane]	62
6.	NMR Spectrum of Spiro[tetracyclo[7.4.1.0 ^{1,9} 0 ^{3,8}] tetradec-3-ene-2-one-14,1'-cyclopentane]	63

LIST OF FIGURES

FIGURE		
 General mode of photochemical reaction of 6,6-disubstituted-2,4-cyclohexadienones 	•	6
2. A mechanism for the oxidation of s-dodeca- hydrotriphenylene	•	18
 A mechanistic scheme depicting principle modes of rearrangement of 2,5-cyclohexadienones 	•	21
4. The photolysis of spiro[1,2,3,4,5,6,7,8,9,10- decahydroanthracene-10-one-9,1'-cyclopentane] in ether as monitored by uv spectroscopy	•	25
5. The photolysis of spiro[1,2,3,4,5,6,7,8,9,10- decahydroanthracene-10-one-9,1'-cyclopentane] in methanol as monitored by uv spectroscopy .	•	26
6. A mechanistic scheme depicting principle modes of photorearrangement of bicyclo[3.1.0] hexenones	•	31
7. The photolysis of spiro[tetracyclo[7.4.1.0 ^{1,9} 0 ³ tetradec-3-ene-2-one-14,1'-cyclopentane] in ether as monitored by uv spectroscopy	, 8]	34

INTRODUCTION

It has been established that organic peracids are very good sources of electrophilic hydroxyl, particularly in their reaction with aromatic hydrocarbons(1). Peroxytrifluoroacetic acid provides a very efficient source of positive hydroxyl, as trifluoroacetate ion is a good leaving group(2). However, while peroxytrifluoroacetic acid hydroxylations of aromatic compounds result in good yields, the conversions are generally low. It was therefore considered that oxidation efficiency could be greatly enhanced by the presence of a Lewis acid, such as boron fluoride, which could coordinate with one of the oxygens of the trifluoroacetate group, thus facilitating heterolytic cleavage of the peroxide oxygen-oxygen bond(3).



When mesitylene 1 was oxidized with a mixture of peroxytrifluoroacetic acid and boron fluoride in methylene chloride at $0^{0}(3,4)$, mesitol 2 was formed in 88% yield. When the oxidation was carried out at -40^{0} , the yield was quantitative.



The peroxytrifluoroacetic acid-boron fluoride oxidation of prehnitene 3 proceeded equally well producing the expected prehnitol, plus other products, one of which was identified as 4,5,6,6-tetramethyl-2,4-cyclohexadienone 4(3,4,5).



Dienone <u>4</u> is presumed to arise from attack of electrophilic hydroxyl at a substituted carbon atom followed by a Wagner-Meerwein methyl shift and loss of a proton. This was a particularly important observation, since the direct synthesis of alkyl substituted 2,4-cyclohexadienones might be achieved from the corresponding alkyl substituted benzene.

It seemed likely that if the benzene were totally substituted with alkyl groups, peroxytrifluoroacetic acidboron fluoride oxidation might render only dienone products. This was shown to be the case when hexamethylbenzene 5 was oxidized with peroxytrifluoroacetic acid-boron fluoride etherate in methylene chloride at 0°; 2,3,4,5,6,6-hexamethyl-2,4-cyclohexadienone 6 was formed in greater than 90% yield (6,7). Oxidation of hexaethylbenzene $\frac{7}{2}$ results in the formation of the corresponding hexaethyldienone $\frac{8}{2}$ in $\frac{82\%}{100}$ yield (6).



Oxidation of durene 9 gave 3,4,6,6-tetramethyl-2,4-cyclo-hexadienone 10 in over 50% yield (8).



Oxidation of pentamethylbenzene gives predominantly dienone products (9).

Recently, the oxidation of 1, 2, 3, 4-tetramethylnaphthalene $\underbrace{11}$ has provided naphthaleneones(benzocyclohexadienones) $\underbrace{12}$ and $\underbrace{13}$, as the major products (10).



The photochemistry of 6,6-disubstituted-2,4-cyclohexadienones was first studied by Barton and Quinkert (14) and has been extensively reviewed (11,12,13). Figure 1 depicts the reaction alternatives of 2,4-cyclohexadienones.

In general, three primary processes of 2,4-cyclohexadienones have been elucidated: a) ring fission of 14 to give a <u>cis</u> ketene 15 which can undergo 1,2 addition of a nucleophile H-X to give the $\beta\gamma$: $\delta\epsilon$ unsaturated diene acid derivative 16, having the <u>cis</u> geometry, which can be subsequently photoisomerized to the <u>trans</u> $\beta\gamma$: $\delta\epsilon$ unsaturated diene acid derivative 17 or the <u>cis</u> ketene can undergo 1,6 addition of H-X to give the diene acid derivative 18, which is much rarer; b) loss of a group Y from C₆, either by homolytic cleavage of the C-Y bond or by migration of Y to C₅, provided it is unsubstituted (R₂ = H) followed by aromatization to the phenols 19 or 20; c) rearrangement to a bicyclo[3.1.0]hexenone 21. Which pathway the cyclohexadienone takes depends on the number and position of the substituents on the cyclohexadienone ring. Pathways <u>a</u> and <u>b</u> were first elucidated by Barton and Quinkert (14). Route <u>a</u>, however, is considerably different than as first proposed by Barton (11). It was first suggested that the <u>cis</u> ketene <u>15</u> isomerized to a <u>trans</u> ketene <u>15</u>a which added the nucleophilic species H-X 1,2 or 1,4 to give $\beta\gamma:\delta\epsilon$ and $\alpha\beta:\delta\epsilon$ diene acid derivatives respectively. Whether H-X added 1,2 or 1,4 was presumed to be determined by the 1,3-steric interactions in the <u>trans</u> ketene <u>15</u>a.



However, Hart and Collins (9) have shown that cyclohexadienones which undergo ring fission do so to give a <u>cis</u> ketene which reacts with H-X to give a $\beta\gamma:\delta\epsilon$ <u>cis</u> diene acid derivative (1,2 addition) which can be photoisomerized to the $\beta\gamma:\delta\epsilon$ <u>trans</u> diene acid derivative. For example, irradiation of a methanol solution of 22 through Pyrex gave dienoate 23 having the <u>cis</u> geometry. Irradiation of 22 through Vycor gave the isomerized dienoate 24 having the <u>trans</u> geometry, as well as 23. Only in one case was a small amount of $\alpha\beta:\gamma\delta$ unsaturated dienoate detected. Irradiation of a methanol solution of dienone 10 gave, in addition to





the major product $\beta\gamma:\delta\epsilon$ unsaturated dienoate 26, about 15% of 27, arising from 1,6 addition of the methanol to the <u>cis</u> ketene 25 (8,9). No diene acid derivatives arising from 1,4 addition of the nucleophile were observed.



Reaction alternative <u>c</u>, recently elucidated by Hart, Collins and Waring (6,15), involves rearrangement to a bicyclo[3.1.0]hexenone. Irradiations of 1% ether solutions of 2,3,4,5,6,6-hexamethyl-2,4-cyclohexadienone, <u>6</u> or the hexaethyl analog, <u>8</u> through Pyrex, resulted in the formation of the corresponding bicyclo[3.1.0]hexenones, <u>28</u> and <u>29</u>. The mechanism has been shown, by suitable labelling experiments, to involve "bond crossing" rather than alkyl



migration (6). This is a radical departure from the more familiar ring fission reaction which had previously been observed. There is however, a relationship between ring fission and bicyclic ketone formation, in that they are competing reactions. Evidence to support this idea has been presented by Hart and Collins (9). Irradiation of a methanol solution of 2,4,5,6,6-pentamethyl-2,4-cyclohexadienone <u>30</u> provided both bicyclic ketone <u>31</u> and diene ester <u>32</u> (9).



The course of the reaction seems to be controlled by the position of the hydrogen on the ring. In the pentamethyl series, if the hydrogen is at C_2 , photolysis gives exclusively the ring fission product. When the hydrogen is

at C₅, photolysis gives exclusively the bicyclic ketone.

Since the photochemistry of 2,4-cyclohexadienones depends on the number and position of substituents and as has been shown, photolysis of hexaalkylsubstituted-2,4-cyclohexadienones results in the formation of bicyclic ketones, it seemed that a subtle structural modification in dienones 6 or 8 might alter the photochemical behavior of the dienone. An investigation into the photochemistry of spiro-[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,1'cyclopentane] 33 (16) was undertaken, since it is structurally similar to dienone 8. The ethyl groups have effectively been prevented from rotating, by incorporating them into rings.



It was visualized that the synthesis of dienone 33 could be accomplished by peroxytrifluoroacetic acid-boron fluoride etherate oxidation of s-dodecahydrotriphenylene 34 (17). Attack of electrophilic peroxytrifluoroacetic acid on 34 followed by a 1,2-Wagner-Meerwein alkyl shift and loss of a proton should provide a reasonable synthetic route to dienone 33.



<u>34</u>

The oxidation of hydrocarbon $\underbrace{34}_{\sim}$ and the photochemistry of the products will be the subject of this thesis.

RESULTS AND DISCUSSION

A. The Oxidation of s-Dodecahydrotriphenylene

The preparation of s-dodecahydrotriphenylene 34 was carried out according to the procedure by Mannich (17). Cyclohexanone, dissolved in methanol, was condensed with itself in the presence of concentrated sulfuric acid. After refluxing and stirring for 24-36 hrs, work-up afforded the literature yield of 34.

s-Dodecahydrotriphenylene was oxidized at -3 to $+1^{0}$ with 110% excess peroxytrifluoroacetic acid in methylene chloride and distilled 47% boron fluoride etherate, both of which were added at equal rates over a 1.5 hr period. Under these conditions, a 100% conversion of the starting material resulted, as determined by tlc analysis of the reaction mixture before hydrolysis and after work-up, and the product, formed in 45% yield after recrystallization from methanol, mp 115-117⁰, was shown by analysis on tlc to consist of a single compound, free of starting material. The compound was assigned the structure spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane], 35 (16), on spectroscopic evidence and mode of formation.



 $\frac{CF_3CO_2OH-BF_3\cdot Et_2O}{CH_2Cl_2, -3 \text{ to } 1^0}$

34

Compound $\underline{35}$, a colorless crystalline solid, analyzed well for $C_{18}H_{24}O$. The mass spectrum indicated a parent peak at m/e 256, showing this to be the molecular formula. The ir spectrum of $\underline{35}$ in CCl₄ solution showed principle absorptions at 1655 and 1627 cm⁻¹ (C=O and C=C, conjugated). Dienone $\underline{35}$ had a uv absorption maximum at 253 mµ(ϵ 18,300) with a shoulder at 280 mµ(ϵ 6800). The nmr spectrum of $\underline{35}$ consisted of three broad absorptions, centered at 7.79 τ , 8.17 τ and 8.40 τ , with areas in the ratio of 1:1:1. The three absorptions are assigned to the allylic methylene protons (8H), the spirocyclopentane protons (8H), and the non-allylic protons in the six-membered rings (8H).

The spectroscopic evidence supports the structure for 35. The ir and uv data are typical for 2,5-cyclohexadienones (18). Garbisch (19) has reported the uv absorption maximum for dienone 36 to be 234.5 mµ(ϵ 14,500). Hart and Swatton (20) have reported the uv absorption maximum for the completely methylated dienone 37 at 246 mµ(ϵ 14,800). The uv absorption maximum for spiro dienone 38, reported by Winstein and Baird (21), appears at 242 mµ(ϵ 16,000). These

uv data compare very favorably with that obtained for 35. From the spectra of these three dienones, 36, 37 and 38, it is possible to arrive at a predicted uv absorption maximum for a dienone of the general formula 39, where R is alkyl. Enchancement of the uv absorption maximum due to the presence of the five membered spiro ring is about 7.5 mµ (the difference between the absorption maxima of dienones 36 and 38).



If this difference is added to the absorption maximum of dienone 37, a predicted value of 253.5 mµ, for the absorption maximum of 39, is obtained. This agrees very nicely



39

with the value of 253 m μ observed for dienone 35.

The ir values obtained for 35 are also in good agreement with the values reported for dienone 37 (20). Dienone 37 has absorptions in its ir spectrum at 1653 and 1624 cm⁻¹ (C=0 and C=C, conjugated).

The proton assignments in the nmr are also consistent with structure $\underline{35}$. The low field absorption at 7.79τ is typical of allylic methylene protons in a six membered ring (35). The absorption at 8.17τ was assigned to the spiro cyclopentane ring protons on the basis of the spiro cyclopentane ring proton assignment in dienone $\underline{38}$. These protons appear at 8.17τ as a slightly split singlet (60 Mc) (21a). These exact absorption characteristics are observed in the nmr spectrum of $\underline{35}$ at 60 Mc. The remaining absorption at 8.40τ is assigned to the non-allylic protons in the six membered ring by process of elimination.

Since the oxidations of hexamethyl- and hexaethylbenzene yielded only linearly conjugated dienones, it seemed rather strange that a cross-conjugated dienone should be formed in the present case. In the oxidation of pentamethyl benzene (9), dienone 40a, formed in 7% yield, was presumed to arise from rearrangement of the 2,4-cyclohexadienone 40, also formed in the reaction.



Oxidation of s-dodecahydrotriphyenylene 34 using the same conditions as already described, but lowering the reaction temperature to -67 to -65⁰ and immediately hydrolyzing

with saturated sodium bicarbonate solution gave, after work-up and subsequent separation of the reaction mixture by preparative thin layer chromatography, three products: a) unreacted s-dodecahydrotriphenylene 34; b) cross-conjugated dienone 35; and c) a new compound assigned the structure spiro[1,2,3, 4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane] 33 (16), on spectroscopic evidence, mode of formation and chemical reactivity.



The identity of the first two products was demonstrated by comparison of their ir spectra and their R_{f} 's on tlc with pure samples.

Compound, 33, a pale yellow solid, mp 69-71°, analyzed well for $C_{18}H_{24}O$. The mass spectrum showed a parent peak at m/e 256, indicating this to be the molecular formula; thus 33 was an isomer of dienone 35. The ir spectrum of 33 in CCl₄ solution showed principle bands at 1644 and 1580 cm⁻¹ (C=O and C=C, conjugated). The uv spectrum of 33 had an absorption maximum in methanol at 332 mµ(ϵ 5100). The nmr spectrum in CCl₄ showed two broad complex, absorptions centered at 7.78 τ and 8.37 τ , which integrated with an approximate relative ratio of 1:2. It was tentatively presumed that the low field absorption was due to the allylic methylene protons (8H) and that the rest of the nmr spectrum accounted for the remaining protons (16H). Further spectrum-structure correlation, using nmr, was not possible.

The ir and uv spectral data are typical for a 2,4cyclohexadienone (18) and compare very favorably with other hexaalkyl-substituted-2,4-cyclohexadienones obtained by this synthetic route (6,7). The uv absorption maximum of dienones $\underline{6}$ and $\underline{8}$ occur at 330 mµ(ϵ 4500) and 339 mµ(ϵ 11,000), respectively, which is in good agreement with that obtained for 33. The principle absorptions in the ir spectra of dienones $\underline{6}$ and $\underline{8}$ occur at 1647 and 1567 cm⁻¹ (C=0 and C=C conjugated) and 1635 and 1560 cm⁻¹ (C=0 and C=C conjugated), respectively, which compare favorably with the values obtained for 33.

Treatment of 33 with either trifluoroacetic acid or boron fluoride etherate in methylene chloride at room temperature converts it into dienone 35. The structure of the rearrangement product follows from comparison of its ir spectrum and R_f on tlc with that of pure dienone 35. The rearrangement carried out with trifluoroacetic acid was observed to be about 9 times faster than when carried out with boron fluoride etherate under the same conditions. This same type of rearrangement has been shown to occur with dienone 6, but requires more vigorous conditions (20).



33

35

Treatment of 6 with fuming sulfuric acid converts it quantitatively to dienone, 37. The mechanism is presumed to



involve a series of methyl migrations.

With the facts that have been presented, a mechanism which is consistent with the results may be formulated. The course of oxidation is depicted in Figure 2. The oxidizing species is written OH^+ , although it is recognized that this is probably not the true oxidant and that it may be complexed to trifluoroacetate ions or other ligands in solution. Evidence for the cationic nature of the oxidant, however, has been presented (2).

The oxidation presumably involves initial attack of electrophilic peroxytrifluoroacetic acid on 34 to give carbonium 34a, which undergoes a 1,2-Wagner-Meerwein shift





of an alkyl group, to give carbonium ion 34b. Carbonium ion 34b undergoes another 1,2-shift, through its resonance hybrid 34c to give carbonium ion 34d. The carbonium ion 34d then undergoes a subsequent 1,2-shift, through its resonance hybrid 34efollowed by loss of a proton. The last two processes can probably be written in either a stepwise or concerted fashion. It is written in a stepwise fashion here for clarity.

It is interesting to note that in formulating the mechanism, dienone 33 is not involved. However the protonated form of 33, carbonium ion 34b, is involved. It has been observed, qualitatively, that the reaction leading to the formation of 35 is facile even at -67° . It is therefore felt that any equilibrium between protonated and unprotonated dienone favors the protonated form. When the alkyl substitutents are methyl or ethyl, the equilibrium is



shifted toward the unprotonated form, as is evidenced from the formation of the corresponding linearly conjugated dienones from such oxidations. The fact that dienone 33 is obtained from the hydrolysis of the low temperature oxidation probably involves hydrolysis of the protonated form of the dienone.

B. <u>The Photochemistry of Spiro[1,2,3,4,5,6,7,8,9,10-</u> decahydroanthracene-10-one-9,1'-cyclopentane]

The photochemistry of 2,5-cyclohexadienones has been extensively investigated (12,13,22,23,24,25) In general, 2,5-cyclohexadienones undergo two primary photochemical processes: a) loss of a substituent from C₄ carbon followed by aromatization and b) rearrangement to a bicyclo-[3.1.0]hexenone (lumiproduct). Figure 3 depicts the possible reaction routes.

The principle steps involved in the photolysis of 2,5-cyclohexadienones are: a) excitation followed by intersystem crossion to n, π^* triplet $(41 \rightarrow 42)$; b) bond alteration, 3,5-bonding $(42 \rightarrow 43)$ and d) skeletal rearrangement $(44 \rightarrow 45)$. The competition of rearrangements of type $(41 \rightarrow 45)$ in suitably 4-substituted 2,5-cyclohexadienones by a radical fragmentation has been explained with homolytic cleavage in the excited state of 42 and expulsion of a substituent (e.g., R) in radical form. The resulting phenoxy radical 46 would then abstract a hydrogen from the solvent to give phenol 47.

Recently, Schuster (26) has demonstrated that radical fragmentation does compete with bicyclic ketone formation. Irradiation of dienone $\underbrace{48}_{\sim}$ in benzene solution provides a mixture of <u>p</u>-cresol, $\underbrace{49}_{\sim}$, and the corresponding bicyclic ketone.





48 49 50

However, irradiation of spirodienone 51 in ether solution gives only radical fragmentation products, <u>p</u>-ethylphenol 52 being the major one (27).



The most interesting photoreaction of 2,5-cyclohexadienones is the formation of bicyclo[3.1.0]hexenones. Zimmerman has studied the photochemistry of 4,4-diphenyl-2,5cyclohexadienone 53 in great detail (23,28). Irradiation of 53 in aqueous dioxane solution afforded bicyclic ketone 54 as the major product. Side products, shown to arise from subsequent photolysis of the bicyclic ketone, were also observed.



Kropp has investigated the photochemistry of 2,5-cyclohexadienones (24,25), one of which was spirodienone 55. Irradiation of a methanolic solution of 55 gave the corresponding bicyclic ketone 56 (25).



Recently, it has been shown that irradiation of dienone, 57 in ether provided the expected bicyclic ketone 28 (20).



Irradiation of spiro[1,2,3,4,5,6,7,8,9,10-decahydroantracene-10-one-9,1'-cyclopentane] 35 in anhydrous ether

through Vycor with a 200-watt Hanovia Type S lamp resulted in formation of dienone 33. The reaction, followed by uv spectroscopy (Figure 4), was completed when the absorption intensity at 332 m μ due to 33 reached a maximum, in about 4.9 hr.

The photoproduct of dienone 35, a pale yellow solid, mp 69-71⁰ from methanol, was shown to be identical to dienone 33 by comparison of its ir and uv spectrum with that of 33 obtained from the low temperature oxidation of s-dodecahydrotriphenylene 34. Also comparison of the R_f of the photoproduct with the R_f of a pure sample of 33 on the showed them to be identical. The photoproduct could also be converted back to 35 by treatment with trifluoroacetic acid in methylene chloride at room temperature, which is consistent with the chemical reactivity of 33 under these conditions.



Irradiation of spiro dienone 35 in methanol solution, through Vycor provided a very smooth conversion to a new compound. The reaction, followed by uv spectroscopy (Figure 5), was completed in 50 minutes when no further








change in the uv was observed. Evaporation of the solvent produced a slightly colored transparent oil in quantitative yield. It was shown to be spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}]-tetradec-3-ene-2-one-14,1'-cyclopentane], 58 (16), based on spectroscopic evidence and mode of formation.

Compound <u>58</u> analyzed for $C_{18}H_{24}O$, the carbon content, however, being slightly low. The mass spectrum indicated a parent peak at m/e 256, showing this to be the molecular formula. The compound was therefore isomeric with dienone <u>35</u>. The ir spectrum (liquid film) had absorptions at 1685 and 1639 cm⁻¹ (C=O and C=C, conjugated). The uv spectrum in methanol had an absorption maximum at 240 mµ (ϵ 6440), a shoulder at 275 mµ (ϵ 2735) and another maximum at 325-340 mµ (ϵ 580). The nmr spectrum (CCl₄ solution) consisted of broad complex absorptions between 7-9 τ , with principle peaks centered at 8.02 τ , 8.43 τ (with a shoulder at 8.38 τ) and 8.72 τ . Accurate integration of the nmr spectrum was not possible as the peaks overlapped too much to obtain any useful information. Any kind of spectrum structure correlation using the nmr data was not possible.





35

The ir and uv data are consistent with the structural assignment to 58, by comparison with the spectral data of compounds having similar structural features.



56

28

29

The uv spectrum of 56 (25) showed absorption maxima at 233 mµ (ϵ 4200) and 265 mµ (ϵ 3290). The uv spectra of bicyclic ketones 28 and 29 (6,15) in 95% ethanol have absorption maxima at 235 mµ (ϵ 6270), 274 mµ (ϵ 3240), shoulder at 320 mµ (ϵ 605) and 239 mµ (ϵ 5300), 270 mµ (ϵ 2660), 332 mµ (ϵ 850), respectively. The uv data for 56, 28 and 29 compare very favorably with that obtained for 58. The ir spectrum of 56 has absorptions at 1689 and 1608 cm⁻¹ (C=0 and C=C, conjugated). Bicyclic ketones 28 and 29 have similar absorptions in their ir spectra at 1690 and 1640 cm⁻¹ and 1680 and 1638 cm⁻¹, respectively. These data also give very favorable support to structure 58.

The photoproduct of 35 in methanol, assigned structure 58, is the primary photoproduct of dienone 35. The structure of the photoproduct is consistent with the spectral data and its mode of formation is consistent with the general mechanistic scheme described in Figure 3. The proposed mechanism for the formation of ketone 58 from dienone 35 may



therefore be formulated as below. The ionic intermediate

35a is used for convenience and clarity.

If ketone 58 is the primary photoproduct from dienone 35, then how does dienone 33 arise when 35 is photolyzed in ether? A tentative answer can be obtained by examining the uv spectra obtained from following the photolyses in ether and methanol, Figures 4 and 5, respectively. Figure 4 shows a steady decrease in the absorption of the uv spectrum due to dienone 35. It appears to decay to a uv spectrum which is very similar to the uv spectrum for ketone 58. This intermediate uv spectrum then appears to decay to the uv spectrum of dienone 33. The same sort of decrease in absorption is observed in Figure 5, except that further photolysis either does not occur or is so slow that a significant change in the uv spectrum is not detectable and the photolysis stops at the intermediate uv spectrum. This therefore suggests that ketone 58 is the probable intermediate in the formation of dienone 33 from the photolysis of dienone 35 in ether.

C. The Photochemistry of Spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}] tetradec-3-ene-2-one-14,1'-cyclopentane]

The photochemistry of bicyclo[3.1.0]hexenones has received much attention (22). In general, the photolysis of bicyclo[3.1.0]hexenones can proceed to give three kinds of products: a) phenols; b) 2,4-cyclohexadienones and c) 2,5-cyclohexadienones. Figure 6 describes the reaction alternatives.

The photolysis of 59 may be described in the following way: a) excitation followed by intersystem crossing to n, π^* triplet (59 -> 60); b) 1,5-bond fission (60 -> 61); c) intersystem crossing to the dipolar ground state singlet (61 -> 62) and skeletal rearrangements leading to 63, 64 and 65. The nature of the substituents directs the route of rearrangement. For example, irradiation of bicyclic ketone 56 in methanol leads to a 2,4-cyclohexadienone, 66 (24,25).



<u>56</u>

66

Irradiation of umbellone, $\underline{67}$ (29), affords thymol as the photoproduct, $\underline{68}$.





67

68

Recently, Hart and Swatton (20) have shown that the intermediate corresponding to $\underline{62}$ can be trapped. Irradiation of the hexamethyl bicyclic ketone $\underline{28}$ in acid-free methanol produced photoproduct $\underline{69}$, resulting from addition of the solvent to $\underline{28a}$.



Several years ago, Matsuura (30) and more recently Miller (31,32) have shown another alternative in the photolysis of bicyclo[3.1.0] hexenones. As depicted in Figure 6, 1,5-bond cleavage of the bicyclic ketone is most common. However, cleavage of the 5,6-bond can also occur. Irradiation of bicyclic ketone 70 in cyclohexane solution (32)produced dienone 71. The mechanism is presumed to involve cleavage of the C₅-C₆ bond, giving 70a as an intermediate, which can then undergo acyl migration and double bond formation to give 71. The mechanism has many characteristics of



carbonium ion reactions and the acyl migration has a close analogy in carbonium ion chemistry. However, the fine points to the mechanism have not been elucidated.

Irradiation of an ether solution of spiro[tetracyclo [7.4.1.0^{1,9}0^{3,8}]tetradec-3-ene-2-one-14,1'-cyclopentane], 58, through Vycor with a 200 watt Hanovia lamp provided a smooth conversion to dienone 33 as the only product. The photolysis, followed by uv spectroscopy (Figure 7), showed a steady decay of the band at 240 m μ due to 58, and a gradual increase in the band at 332 m μ due to dienone 33. The reaction was completed in about 2 hr when the band at 332 m μ had reached maximum intensity. Evaporation of the solvent and crystal-lization from methanol provided dienone 33. The structure of the photoproduct follows from its ir spectrum and comparison of R_f 's on the with a pure sample of dienone 33.

This result tends to substantiate the tentative suggestion that ketone 58 is the intermediate in the production of dienone 33 from the photolysis of dienone 35 in ether. Therefore, the sequence of photoreactions to describe this system may be written as follows:







A tentative mechanism for the conversion of ketone <u>58</u> to <u>33</u> may be proposed which is totally consistent with Miller's mechanism (32). Also, the notation used by Miller, depicting 5,6-bond cleavage and subsequent acyl migration and double bond formation, will be used here since the exact nature of the excited state is not known.



33

The question now arises, why should this process occur at all in this particular system? Miller (32) has postulated the following explanation to account for the 5,6-bond cleavage in his <u>t</u>-butyl bicyclic ketones. In the ground state, 72, there is severe steric interaction between the <u>t</u>-butyl



72

73

group at C_1 and the <u>exo</u> substituent at C_6 . Weakening the C_5-C_6 bond to allow the <u>exo</u> substituent at C_6 to rotate slightly toward the carbonyl, as in 73, would markedly relieve the crowding while at the same time bring the geometry at C_6 into a more favorable arrangement for migration of the carbonyl group.

Therefore, a tentative explanation accounting for the formation of dienone 33 from the photolysis can be proposed. An examination of models of structure 58 shows some steric interaction between the protons on the <u>exo</u> side of the spiro cyclopentane ring and the protons of the bridging cyclohexane ring. These interactions may be minimized in two ways: a) the bridging cyclohexane ring can assume a particular conformation so as to minimize interactions and, applying Miller's argument, b) the C_5-C_6 bond can weaken slightly, rotating the spiro cyclopentane ring so that the <u>exo</u> protons are pointed toward the carbonyl. The degree of importance of the steric effect is probably less than in the case of the <u>t</u>-butyl bicyclic ketones. However, an over-riding factor greatly magnifies the steric importance in the

photolysis of 58. Examination of the excited state of ketone 58, corresponding to the ground state singlet 62 in Figure 6,



58b

58c

shows the presence of double bonds and positive charges at bridgehead carbons, which violates the Bredt rule (33). Therefore, photolysis by the 'normal' route becomes less important and the alternative route, cleavage of the C_5-C_6 bond becomes more important.

D. The Photochemistry of Spiro[1,2,3,4,5,6,7,8,9,10decahydrophenanthrene-10-one-9,1'-cyclopentane]

The photochemistry of 2,4-cyclohexadienones has been previously described (See introduction). The two important photoreactions of 2,4-cyclohexadienones are: a) ring fission to give a <u>cis</u> ketene; and b) rearrangement to a bicyclo[3.1.0]hexenone. As has been described (11), the pathway taken by the cyclohexadienone depends on the size, number and position of the substituents on the cyclohexadienone ring as well as the nucleophilic character of the solvent. Subtle structural changes in 2,4-cyclohexadienones are known to influence the photochemical course of the reaction. Such a structural change was made in dienone §. The ethyl groups were effectively pinned back into a ring system, resulting in dienone 33.



Irradiation of an ether solution of 33 through Pyrex using a Hanovia 200-watt Type S lamp was followed by uv spectroscopy and resulted in a gradual decay of the band at 332 mµ due to dienone 33. The only band that remained appeared at an absorption maximum of 205 mµ. Upon completion of the reaction, in about 6.2 hr, evaporation of the solvent afforded a slightly colored oil having a mildly pungent odor. The ir spectrum of the oil in CCl₄ solution showed principle absorptions at 3500, 1720 and 1705 cm⁻¹. Comparison of the R_f of the oil with the R_f of a sample of ketone 58, also an oil, on tlc showed them to be different.

The ir data strongly suggest that the photoproduct has a carboxylic acid function (34). This fact alone suggests that dienone 33 has undergone ring fission to the ketene, which has reacted with the small quantity of water, (about .01%) present in commercially available anhydrous ether. This is purely supposition, however, and requires further proof. It is clear that dienone 33 did not react to give ketone 58. The structure of the photoproduct and an explanation to account for this photochemical behavior are subjects for further research.

EXPERIMENTAL

A. General Procedures

Unless otherwise stated, all ultraviolet spectra were measured in methanol solution with a Unicam Model SP-800 untraviolet spectrophotometer. Infrared spectra were measured in carbon tetrachloride with a Unicam Model SP-200 infrared spectrophotometer and were calibrated against polystyrene. All nmr spectra were measured in carbon tetrachloride with a Varian Associates HA-100 spectrometer. Chemical shifts are in τ values, measured from tetramethylsilane as an internal reference. Mass spectra were carried out by Dr. L. B. Sims and Mr. John Wettaw of this department with a Consolidated Electrodynamics Corporation 21-103C instrument, operating at an ionizing potential of 70 v. Analyses by thin layer chromatorgraphy were carried out using 1" x 4" microscope slides coated with Brinkmann Silica Gel-H as the adsorbent, eluted with chloroform and developed with iodine vapor. Separations by preparative thin layer chromatography were carried out using 8" x 8" glass plates coated with Brinkmann Silica Gel-PF₂₅₄, of 2 mm thickness, as the adsorbent and eluted with chloroform. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan. All melting points are uncorrected.

40

B. **Preparation of s-Dodecahydrotriphenylene** (17)

To a stirred solution of cyclohexanone (100 g, 94 ml, 1.02 mole) in 300 ml of methanol was added concentrated sulfuric acid (100 g, 55.5 ml, 1.02 mole) in a dropwise fashion. When addition of the sulfuric acid was completed, the solution was stirred and refluxed for 24-36 hours. After about 5 hours of refluxing, a tan colored oil began to separate.

When the reflux period was completed, the reaction mixture was allowed to cool to room temperature for 24 hours while still being stirred. The dark green reaction mixture was decanted, leaving the tan oil. The oil was dissolved in 400 ml of benzene and the benzene layer extracted with water $(3 \times 250 \text{ ml})$ which turned the benzene layer yellow. After drying the organic layer over anhydrous sodium sulfate, the benzene was concentrated to 150 ml and cooled for 24-36hours, which induced crystallization. The crystals were filtered and gently rinsed with cold benzene and then cold methanol. The crystals were suction dried on a Büchner funnel and provided 5.9 g $(2.5 \times 10^{-2} \text{ mole})$ of s-dodecahydrotriphenylene 34, mp 232-2330 (lit. value (17) 232-2330), as colorless needles. The yield was 7.4% (lit. yield 6.0 g, 7.5%). The nmr spectrum showed two broad singlets centered at 7.55τ and $8.3\tau_{1}$ corresponding to the benzylic and alicyclic methylenes respectively. The areas were in the ratio of 1:1.

41

C. The Oxidation of s-Dodecahydrotriphenylene

1. The Reaction with 110% Excess Oxidant at -3 to +1°

To a cooled, vigorously stirred solution of s-dodecahydrotriphenylene $(4.59q, 1.9 \times 10^{-2} \text{ mole})$ in 200 ml of methylene chloride was simultaneously added: 1) a solution of peroxytrifluoroacetic acid, made by dissolving trifluoroacetic anhydride (9.0 g, 4.3 x 10^{-2} mole) in 15 ml of methylene chloride, cooling to 0^{0} , and with vigorous stirring adding 98% hydrogen peroxide (1.1 ml, 4.3 x 10^{-2} mole) until a homogeneous solution was obtained; 2) distilled 47%boron fluoride etherate (20 ml). The temperature was maintained at -3 to $+1^{\circ}$. Slow addition of the oxidant and acid catalyst (found to be important in oxidizing this compound) was completed after 1.5 hr. After an additional 1.5 hr of stirring, during which time the temperature was allowed to rise to 20⁰, the reaction mixture was analyzed by thin layer chromatography and it was determined that all of the starting hydrocarbon had reacted. The reaction mixture was then hydrolyzed with 200 ml of water and the organic layer was successively extracted with water (2 x 200 ml), saturated sodium bicarbonate solution (2 x 300 ml), water (2 x 200 ml) and dried over anhydrous sodium sulfate. The methylene chloride was evaporated and the residue dissolved in 20 ml of methanol. The methanol was concentrated to 5-10 ml and cooled overnight. Crystallization afforded 2.21 g (8.65 x 10⁻³ mole) of colorless crystals which were shown to be

spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'cyclopentane], 35,mp 114-117°. Recrystallization from methanol provided 1.75 g, mp 115-117°. The yield of the dienone before recrystallization was 45%, based on the hydrocarbon consumed. The colorless crystalline dienone had major bands in its ir spectrum (CCl₄ solution) at 1655 and 1627 cm⁻¹ (C=0 and C=C, conjugated). The uv spectrum showed bands at λ_{max}^{MeOH} 253 mµ (ϵ 18,300) and 280 mµ (shoulder on main band) (ϵ 6800). The mass spectrum indicated a parent peak at m/e 256. The nmr spectrum consisted of three broad peaks centered at 7.79 τ , 8.17 τ , 8.40 τ with relative areas in the approximate ratio of 1:1:1. The three peaks were assigned to the 8 allylic methylene protons, 8 methylene protons in the 5-membered spiro ring, and the remaining 8 methylene protons in the two 6-membered rings.

Anal. Calcd for $C_{18}H_{24}O$: C, 84.32; H, 9.43. Found: C, 84.26; H, 9.26.

2. The Reaction With 110% Excess Oxidant at -67 to -65°

To a cooled, vigorously stirred solution of s-dodecahydrotriphenylene (4.74 g, 1.97×10^{-2} mole) in 175 ml of methylene chloride was simultaneously added: 1) a solution of peroxytrifluoroacetic acid, made by dissolving trifluoroacetic anhydride (8.7 g, 4.15 x 10^{-2} mole) in 15 ml of methylene chloride, cooling to 0^{0} , and with vigorous stirring adding 98% hydrogen peroxide (2.9 g, 8.3 x 10^{-2} mole) until a homogeneous solution was obtained; 2) distilled 47% boron fluoride etherate (15 ml). The temperature was maintained at -67 to -65° using a dry ice-acetone bath. Addition of the oxidant and acid catalyst was completed in 35 minutes and the reaction was hydrolyzed by pouring the reaction mixture into 750 ml of ice cold saturated sodium bicarbonate solution. The organic layer was washed with water (2 x 300 ml), saturated sodium bicarbonate (2 x 200 ml), water (2 x 200 ml) and dried over anhydrous sodium sulfate. The reaction mixture was analyzed by thin layer chromatography and shown to contain 3 components. The reaction mixture was then separated by preparative thin layer chromatography and the 3 components were identified.

The least polar material was identified as unreacted s-dodecahydrotriphenylene by its ir and nmr spectra and by comparison of its R_f with that of a pure sample of the hydrocarbon on tlc. The most polar component was identified as spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'cyclopentane] by its ir and nmr spectra and by comparison of its R_f value with that of a pure sample on tlc. The third component, whose R_f was slightly greater than the R_f of spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane], was shown to be <u>spiro[1,2,3,4,5,6,7,8</u>, <u>9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane],33</u>,mp 69-71°. The pale yellow solid displayed major bands in the ir (CCl₄ solution) at 1644 and 1580 cm⁻¹ (C=0 and C=C, conjugated). The uv spectrum consisted of a broad band λ_{max}^{MeOH} 332 mµ (ϵ 5100). The mass spectrum indicated a parent peak at m/e 256. The nmr spectrum (CCl₄ solution) showed 2 broad peaks centered at 7.78_{τ} and 8.37_{τ} with an approximate relative area ratio of 1:2, corresponding to 8 allylic methylene protons and 16 alicyclic protons (the 5-membered spiro ring and the 6-membered rings combined).

Anal. Calcd for
$$C_{18}H_{24}O$$
: C, 84.32; H, 9.43.
Found: C, 84.35; H, 9.44.

D. <u>The Rearrangement of Spiro[1,2,3,4,5,6,7,8,9,10-deca-hydrophenanthrene-10-one-9,1'-cyclopentane]</u> with Boron Fluoride Etherate

To a solution of spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane], 33, (100 mg, 3.9 x 10^{-4} mole) in 30 ml of methylene chloride was added 3 ml of 47%boron fluoride etherate and the mixture was allowed to stir at room temperature. The reaction was monitored by thin layer chromatography and after 3 hours, there was no detectable amount of the starting conjugated dienone. The reaction mixture was then hydrolyzed with 150 ml of ice water and further extracted with water $(2 \times 50 \text{ ml})$ and the organic layer dried over anhydrous sodium sulfate. The methylene chloride was evaporated and the residue dissolved in methanol. Crystallization from methanol afforded 56.9 mg of spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'cyclopentane], 35, as the only product formed (tlc), mp 114-117⁰. Comparison with a pure sample (tlc and ir) of the crossconjugated dienone 25 showed the two to be identical.

E. <u>The Rearrangement of Spiro[1,2,3,4,5,6,7,8,9,10-decahydro-phenanthrene-10-one-9,1'-cyclopentane]</u> with Trifluoroacetic Acid

To a stirred solution of spiro[1,2,3,4,5,6,7,8,9,10decahydrophenanthrene-10-one-9,1'-cyclopentane],33,(100 mg, 3.9×10^{-4} mole) in 30 ml of methylene chloride was added 2 ml of trifluoroacetic acid. The reaction mixture was allowed to stir at room temperature for 45 minutes. The reaction was monitored by tlc, by sampling the reaction mixture after 5, 10 and 20 minutes. It was determined that after 20 minutes, all of the starting dienone had reacted. The reaction mixture was then hydrolyzed with 150 ml of water, extracted with saturated sodium bicarbonate solution $(2 \times 50 \text{ ml})$, water $(2 \times 50 \text{ ml})$ and dried over anhydrous sodium sulfate. The methylene chloride was evaporated and the residue dissolved in methanol. Analysis of the methanol solution by tlc indicated that only one product had been formed. Crystallization provided 71.4 mg $(2.8 \times 10^{-4} \text{ mole})$ or spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane] 33 mp 114-117°. Comparison of the rearrangement product (tlc, ir) with a pure sample of the crossconjugated dienone 25 showed them to be the same.

F. General Photolysis Procedures

Unless otherwise stated, all irradiations were conducted using a Hanovia Type S200 watt Mercury vapor lamp. This was placed in a quartz water jacket which was fitted into a Pyrex well of slightly larger diameter. The effective volume of the Pyrex well could hold up to 450 ml of solution which could be agitated with a flow of nitrogen gas. Also unless otherwise stated, irradiations were carried out using a Vycor filter, which was fitted between the lamp and the quartz water jacket. The entire flask assembly was immersed in a Dewar flask filled with cold water, which was used as a cooling bath.

G. Irradiation of Spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane] in Anhydrous Ether

A solution of spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane], 35, (770.7 mg, 3.0 x 10^{-3} mole) in 400 ml of anhydrous ether was irradiated. The photolysis, followed by disappearance of the ultraviolet band at 253 mµ and appearance of an ultraviolet band at 332 mµ, was completed in 4.9 hours (at which time the band at 331 mµ reached a maximum). The ether was evaporated and the yellow residue dissolved in 15 ml of methanol. Analysis (tlc) of the methanol solution showed that no starting material was present and that only one component was present. It was therefore concluded that a quantitative conversion occurred. The methanol solution was concentrated to 5 ml or less and cooled. Crystallization afforded 438.4 mg, 1.71 x 10^{-3} mole (57% yield) of spiro[1,2,3,4,5,6,7,8,-9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane], 33, mp $69-71^{\circ}$. This was shown to be the same conjugated dienone as that obtained from the oxidation of s-dodecahydrotriphenylene at -67 to -65°, by comparison of their R_{f} 's on tlc and infrared and nmr spectra.

H. The Dark Reaction of Spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane] in Anhydrous Ether

A solution of spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane], 35, (13.9 mg, 5.3 x 10^{-5} mole) in 3 ml of anhydrous ether in a Pyrex test tube was sealed with a cork and placed in the dark. Analysis of the solution after 36 days by thin layer chromatography and infrared spectroscopy showed that no reaction had taken place. Evaporation of the ether afforded a quantitative recovery of the starting dienone.

I. Irradiation of Spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane] in Methanol

A solution of spiro[1,2,3,4,5,6,7,8,9,10-decahydroantracene-10-one-9,1'-cyclopentane], 35_{\star} (691.6 mg, 2.7 x 10^{-3} mole) in 400 ml of methanol was irradiated. The photolysis, followed by the disappearance of the ultraviolet band at 253 mµ, was completed after 50 minutes. The methanol was evaporated affording 672 mg (2.62 x 10^{-3} mole) of a slightly colored transparent oil which was shown to be <u>spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}]tetradec-3-ene-2-one,14,1'-</u> <u>cyclopentane], 58</u>. The oil was analyzed by tlc and compared to the starting dienone and was found to be free of starting dienone and consist of a single component.

The oil had predominent bands in the ir spectrum (liquid film) at 1685 and 1639 cm⁻¹ (C=O and C=C, conjugated). The uv spectrum consisted of bands at λ_{max}^{MeOH} 240 mµ (ϵ 6440), 275 mµ (shoulder) (ϵ 2735) and 325-340 mµ (ϵ 580). The mass spectrum indicated a parent peak at m/e 256. The nmr spectrum (CCl₄ solution) consisted of broad complex peaks between 7-9 τ , with principle peaks centered at 7.7 τ , 8.02 τ , 8.43 τ (shoulder at 8.38 τ), and 8.72 τ . Accurate integrations of the peaks were virtually impossible, due to their complexity.

<u>Anal</u>. Calcd for C₁₈H₂₄O: C, 84.32; H, 9.43. Found: C, 82.35; H, 9.34.

J. <u>The Dark Reaction of Spiro[1,2,3,4,5,6,7,8,9,10-deca-</u> hydroanthracene-10-one-9,1'-cyclopentane] in Methanol

A solution of spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane],35,(14.0 mg, 5.6 x 10^{-5} mole) in 5 ml of methanol was placed in a Pyrex test tube, sealed with a cork and placed in the dark. Analysis of the solution after 27 days by tlc and infrared spectroscopy showed that no reaction had taken place. Evaporation of methanol gave a quantitative recovery of the starting dienone.

K. <u>Irradiation of Spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}]tetradec-</u> <u>3-ene-2-one-14,1'-cyclopentane]</u> in Anhydrous Ether

A solution of spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}]tetradec-3-ene-2-one-14,1'-cyclopentane], 58,(448.9 mg, 1.78 x 10⁻³ mole) in 350 ml of ether was irradiated. The photolysis, followed by the appearance of an untraviolet band at 332 mµ, was completed after about 2 hours (at which time the band at 332 mµ had reached a maximum). The ether was evaporated and the residue dissolved in methanol. Crystallization provided 347 mg of spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane], 33. Analysis by tlc and infrared spectroscopy showed the photoproduct to be identical to the conjugated dienone obtained from the oxidation of s-dodecahydrotriphenylene at -67 to -65°.

L. <u>The Dark Reaction of Spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}]</u> <u>tetradec-3-ene-2-one-14,1'-cyclopentane] in Anhydrous</u> Ether

A solution of spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}]tetradec-3-ene-2-one-14,1'-cyclopentane], 58, (15 mg, 5.85 x 10^{-5} mole) in 3 ml of anhydrous ether was placed in a Pyrex test tube, sealed with a cork and placed in the dark. No reaction could be detected after 15 days by analysis of the solution by tlc and by infrared specroscopy. Evaporation of the ether gave a quantitative recovery of starting material.

M. Irradiation of Spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane] in Anhydrous Ether

A solution of spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane] 33 (107 mg, 4.2 x 10^{-4} mole) in 300 ml of anhydrous ether was irradiated through a Pyrex filter using a 200 watt Hanovia Type S mercury lamp. The photolysis, followed by the disappearance of the ultraviolet band at 332 mµ, was completed in 6.2 hours. The ether was evaporated yielding 110 mg of a slightly colored oil. Comparison of this oil with spiro[tetracyclo [7.4.1.0^{1,9}0^{3,8}]tetradec-3-ene-2-one-14,1'-cyclopentane] 58 by infrared and uv spectroscopy and tlc showed them to be different. The oil had characteristic bands in the ir at 3500, 1720, 1705 and 1452 cm⁻¹. The uv spectrum had a band at λ_{max}^{MeOH} 205 (ϵ 12,300). The photoproduct was not further investigated at this time.

N. <u>The Dark Reaction of Spiro[1,2,3,4,5,6,7,8,9,10-decahydro-</u> phenanthrene-10-one-9,1'-cyclopentane] in Anhydrous Ether

A solution of spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane] 33 (13.9 mg, 5.3 x 10^{-5} mole) in 3 ml of anhydrous ether in a Pyrex test tube was sealed with a cork and placed in the dark. Analysis of the solution after 39 days by ir and tlc indicated that no reaction had taken place. Evaporation of the ether afforded a quantitative recovery of the starting dienone.

SUMMARY

1. The oxidation product of s-dodecahydrotriphenylene with 110% excess peroxytrifluoroacetic acid-boron fluoride etherate at -3 to +1° was spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane] in 45% yield after recrystallization from methanol based on a 100% conversion of the hydrocarbon.

2. Oxidation of s-dodecahydrotriphenylene under the same conditions but at -67 to -65° followed by immediate hydrolysis gave unreacted s-dodecahydrotriphenylene, spiro-[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane] and spiro[1,2,3,4,5,6,7,8,9,10-decahydro-phenanthrene-10-one-9,1'-cyclopentane].

3. Treatment of spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane] with either trifluoroacetic acid or boron fluoride etherate in methylene chloride rearranged it to spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane]. The reaction with trifluoroacetic acid was about nine times faster than with boron fluoride etherate.

4. Irradiation of spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane] in ether through Vycor gave spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane].

52

5. Irradiation of spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane] in methanol through Vycor gave spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}]tetradec-3-ene-2-one-14,1'-cyclopentane] as the primary photoproduct.

6. Irradiation of spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}] tetradec-3-ene-2-one-14,1'-cyclopentane] in ether through Vycor gave spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane].

7. Irradiation of spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane] in ether through Pyrex gave a product which is presumed to be a ring fission product. No spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}]tetradec-3ene-2-one-14,1'-cyclopentane] was formed.

8. Control experiments showed that none of the irradiated compounds were reactive in the dark in the solvents used for the irradiations.

LITERATURE CITED

- 1. Waters, W. S. and D. H. Derbyshire, <u>Nature</u>, <u>165</u>, 401 (1950).
- Norman, R. O. C. and A. J. Davidson, <u>J. Chem. Soc</u>., 5404 (1964).
- 3. Hart, H. and C. A. Buehler, <u>J. Org. Chem.</u>, <u>29</u>, 2397 (1964).
- 4. Hart, H., C. A. Buehler and A. J. Waring in "Selective Oxidation Processes", Advances in Chemistry Series, American Chemical Society, Washington, D.C., 1965, p. 1.
- 5. Hart, H. and C. A. Buehler, <u>J. Am. Chem. Soc</u>., <u>85</u>, 2177 (1963).
- Hart, H., P. M. Collins and A. J. Waring, <u>J. Am. Chem</u>. <u>Soc.</u>, <u>88</u>, 1005 (1966).
- 7. Hart, H. and A. J. Waring, <u>J. Am. Chem. Soc.</u>, <u>86</u>, 1454 (1964).
- 8. Hart, H. and R. M. Lange, <u>J. Org. Chem</u>., <u>31</u>, 3776 (1966).
- 9. Collins, P. M. and H. Hart, J. Chem. Soc., in press.
- 10. Hart, H. and R. K. Murray, Jr., J. Org. Chem., in press.
- 11. Quinkert, G., <u>Angew. Chem., Intern. Ed. Engl.</u>, <u>4</u>, 211 (1965).
- 12. deMayo, P. and S. T. Reid, <u>Quart. Rev</u>. (London), <u>15</u>, 393 (1961).
- 13. Chapman, O. L. in "Advances in Photochemistry", edited by W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., Interscience Publishers, New York, Vol. 1, 1963, pp. 330-351.
- 14. Barton, D. H. R. and G. Quinkert, <u>J. Chem. Soc</u>., 1 (1960).
- 15. Hart, H. and A. J. Waring, <u>Tetrahedron Letters</u>, 325 (1965).

- 16. "Definitive Rules for Nomenclature of Organic Chemistry", J. Am. Chem. Soc., 82, 5545 (1960).
- 17. Mannich, C., <u>Ber</u>., <u>40</u>, 153 (1906).
- 18. Waring, A. J. in "Advances in Alicyclic Chemistry", edited by H. Hart and G. J. Karabatsos, Academic Press, New York, Vol. 1, 1966, pp. 184-193.
- 19. Garbisch, E. W., <u>J. Org. Chem.</u>, <u>30</u>, 2109 (1963).
- 20. Hart, H. and D. W. Swatton, <u>J. Am. Chem. Soc</u>., <u>89</u>, 1874 (1967).
- 21. a) Winstein, S. and R. Baird, <u>J. Am. Chem. Soc.</u>, <u>84</u>, 788 (1962); b) Winstein, S., private communication.
- 22. Schaffner, K. in "Advances in Photochemistry", edited by W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., Interscience Publishers, New York, Vol. 4, 1966, pp. 81-112.
- 23. Zimmerman, H. E. and D. I. Schuster, <u>J. Am. Chem. Soc</u>., <u>84</u>, 4527 (1962).
- 24. Kropp, P. J., <u>J. Am. Chem. Soc.</u>, <u>86</u>, 4053 (1964).
- 25. Kropp, P. J., <u>Tetrahedron</u>, <u>21</u>, 2183 (1965).
- 26. Schuster, D. I. and D. J. Patel, <u>J. Am. Chem. Soc</u>., <u>88</u>, 1825 (1966).
- 27. Schuster, D. I. and C. J. Polowczyk, <u>J. Am. Chem. Soc.</u>, <u>88</u>, 1722 (1966).
- 28. Zimmerman, H. E. and J. S. Swenton, <u>J. Am. Chem. Soc</u>., <u>89</u>, 906 (1967).
- 29. Wheeler, J. W. and R. H. Eastman, <u>J. Am. Chem. Soc</u>., <u>81</u>, 236 (1959).
- 30. Matsuura, T., <u>Bull. Chem. Soc. Japan</u>, <u>37</u>, 564 (1964).
- 31. Miller, B. and H. Margulies, Chem. Comm., 314 (1965).
- 32. Miller, B. and H. Margulies, <u>J. Am. Chem. Soc</u>., <u>89</u>, 1678 (1967.
- 33. Eliel, E., "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, p. 300.

- 34. Nakanishi, K., "Practical Infrared Absorption Spectroscopy", Holden-Day, San Francisco, 1964, p. 43.
- 35. Mathieson, D. W., "Interpretation of Organic Spectra", Academic Press, New York, 1965, pp. 51-58.

APPENDIX



1. a) IR Spectrum of Spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane].



1. b) UV Spectrum of Spiro[1,2,3,4,5,6,7,8,9,10-decahydroanthracene-10-one-9,1'-cyclopentane].



2. a) IR Spectrum of Spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane].



2. b) UV Spectrum of Spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthrene-10-one-9,1'-cyclopentane].



3. a) IR Spectrum of Spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}]tetradec-3-ene-2-one-14,1'-cyclopentane].



3. b) UV Spectrum of Spiro[tetracyclo[7.4.1.0^{1,9}0^{3,8}]tetradec-3-ene-2-one-14,1'-cyclopentane].












