Synthesis and Structure Proof of Cis-6,6-Dichloro-2-Diphenylmethylene- Bicyclo [3.2.0] Hept-3-Ene-7-One and Cis-2,2- Dichloro- 1,2,2a,7a-Tetrahydro- 7-Diphenylmethylene-Cyclobut (a) Inden-1-0ne

William Douglas Barta

Follow this and additional works at: https://scholarworks.wmich.edu/masters_theses

Part of the Chemistry Commons

Recommended Citation
Barta, William Douglas, "Synthesis and Structure Proof of Cis-6,6-Dichloro-2-Diphenylmethylene- Bicyclo [3.2.0] Hept-3-Ene-7-One and Cis-2,2- Dichloro- 1,2,2a,7a-Tetrahydro- 7-Diphenylmethylene-Cyclobut (a) Inden-1-0ne" (1970). Master's Theses. 4373.
https://scholarworks.wmich.edu/masters_theses/4373
SYNTHESIS AND STRUCTURE PROOF OF 
cis-6,6-DICHLORO-2-DIPHENYL METHYLENE-
BICYCLO [3.2.0] HEPT-3-ENE-7-ONE
AND
cis-2,2-DICHLORO-1,2,2a,7a-TETRAHYDRO-
7-DIPHENYL METHYLENE-CYCLOBUT (a) INDEN-1-ONE

by

William Douglas Barta

A Thesis
Submitted to the
Faculty of the Graduate College
in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
December 1970
ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. Robert E. Harmon for his inspiration and many helpful suggestions. Thanks are also extended to Drs. Robert E. Earl, S. K. Gupta, and H. N. Subbarao for their practical assistance.

The author extends his gratitude to Dr. George Slomp of The Upjohn Company for his interpretation of the nmr spectra of compounds II, XI, and XII.

The author also thanks the Department of Chemistry of Western Michigan University and the National Institute of Health for their financial support.

In conclusion the author wishes to thank his wife, Patti, whose steadfastness served as a rock of hope in a sea of despair.

William Douglas Barta
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acknowledgements</td>
<td>ii</td>
</tr>
<tr>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>Historical</td>
<td>2</td>
</tr>
<tr>
<td>The Addition of Ketenes to Olefins</td>
<td>2</td>
</tr>
<tr>
<td>Mechanism</td>
<td>2</td>
</tr>
<tr>
<td>Stereochemistry</td>
<td>3</td>
</tr>
<tr>
<td>Mode of Addition</td>
<td>4</td>
</tr>
<tr>
<td>The Reactions of Fulvenes with Dienophiles</td>
<td>4</td>
</tr>
<tr>
<td>Experimental</td>
<td>7</td>
</tr>
<tr>
<td>Preparation of the Dichloroketene Adducts</td>
<td>7</td>
</tr>
<tr>
<td>Diphenylfulvene (I)</td>
<td>7</td>
</tr>
<tr>
<td>cis-6,6-Dichloro-2-diphenylmethylene-bicyclo [3.2.0] hept-3-ene-7-one (II)</td>
<td>8</td>
</tr>
<tr>
<td>Benzodiphenylfulvene (III)</td>
<td>9</td>
</tr>
<tr>
<td>cis-2,2-Dichloro-1,2,2a,7a-tetrahydro-7-diphenylmethylene-cyclobut (a) inden-1-one (IV)</td>
<td>9</td>
</tr>
<tr>
<td>Degradation of Compound II</td>
<td>10</td>
</tr>
<tr>
<td>2-Diphenylmethylene bicyclo [3.2.0] hept-3-ene-7-one (V)</td>
<td>10</td>
</tr>
<tr>
<td>Methyl-(4-diphenylmethylene-cyclopent-2-ene)-acetate (VI)</td>
<td>11</td>
</tr>
<tr>
<td>Methyl-(3-diphenylmethylene-cyclopentane)-acetate (VII)</td>
<td>12</td>
</tr>
<tr>
<td>Derivatives of VI and VII</td>
<td>12</td>
</tr>
<tr>
<td>Methyl-(3-oxo-cyclopentane)-acetate (VIII)</td>
<td>14</td>
</tr>
</tbody>
</table>
Synthesis of an Authentic Sample ............... 15
(3-Oxo-cyclopentane)-acetic acid (IX) ........... 15
Methyl-(3-oxo-cyclopentane)-acetate (X) .......... 16
Synthesis of Compounds for NMR Studies .......... 18
cis-6-Chloro-2-diphenylmethylene bicyclo[3.2.0]hept-3-ene-7-one (XI) ........ 18
cis-2-Chloro-1,2,2a,7a-tetrahydro-7-diphenylmethylene-cyclobut(a)inden-1-one (XII) . 18
Figure 1. NMR Spectrum of VI ................... 20
Figure 2. NMR Spectrum of VII .................... 21
Discussion ........................................ 22
Interpretation of NMR Spectra .................... 22
Diphenylfulvene Adduct ............................ 22
Table 1. NMR Spectral Data for Compound II .... 23
Table 2. NMR Spectral Data for Compound XI .... 24
Benzodiphenylfulvene Adduct ...................... 24
Table 3. NMR Spectral Data for Compound XII ... 25
Table 4. Results from Computer Analysis of OPQRS . 26
Degradation of II ................................ 26
Summary ........................................... 30
Bibliography ...................................... 31
Vita .............................................. 34
INTRODUCTION

The purpose of this research endeavor was to determine the structures of the adducts of dichloroketene with diphenylfulvene and benzodiphenylfulvene. Structure elucidation was attempted by chemical degradation and nmr analysis.

The structures of the adducts of dichloroketene with cyclopentadiene\textsuperscript{1, 2} and indene\textsuperscript{3, 4} have been determined by previous workers. The influence of the exocyclic double bond on the mode of cycloaddition is unknown.
HISTORICAL

The Addition of Ketenes to Olefins

Mechanism

The additions of ketenes to conjugated dienes characteristically yield 1,2 addition products. The formation of 1,4 Diels-Alder type adducts have not been observed. J. D. Roberts has suggested the following two possible reaction mechanisms for the reactions of ketenes with olefins: a diradical and an ionic mechanism. Therefore, the reaction of dichloroketene and cyclopentadiene can also proceed by the following two routes:

\[
\begin{align*}
\text{Cyclopentadiene} & + \text{Cl}_2\text{C}≡\text{C}=\text{O} \\
\text{Diradical intermediate} & \rightarrow \text{Product} \\
\text{Ionic intermediate} & \rightarrow \text{Product}
\end{align*}
\]

However, subsequent data indicated the reaction rate to be nearly independent of solvent effects and, thus, rendered a formal ionic mechanism questionable. Several workers have suggested that a concerted mechanism may be operative. According to them the high stereoelectivity of the reaction, the greater reactivity of
the cis olefin over the trans, and a high negative entropy support a concerted mechanism.\(^7\)

The data reported by some other workers questions the validity of a true concerted mechanism. For example Frey and Isaacs\(^8\) reported that the reaction of dimethylketene and trans-but-2-ene yielded 65-80% trans adduct. The authors reasoned that a diradical mechanism would allow limited rotation to relieve steric strain before the ring closes. Katz and Dessau\(^9\) reacted 1-deuterio-cyclohexene with diphenylketene and obtained two deuterium labeled isomers. The authors found an isotope effect of 1.13 and concluded the bonds were not formed simultaneously.

**Stereochemistry**

The stereochemistry at the ring juncture of the adduct is cis\(^10\) and, therefore, it permits the substituents on the cyclo- butanone ring to reside in an exo or an endo position. Thus, the adduct of chloroketene and cyclopentadiene may have the chlorine atom in an exo or an endo position.

Brady compared this adduct with an authentic sample of endo
isomer and was amazed to find them identical. His findings have been verified by X-ray and nmr studies.\textsuperscript{11} In fact the \textit{endo} position of the chlorine can be predicted by the Woodward-Hoffmann orbital symmetry conservation rule.\textsuperscript{12} DoMinh and Strausz also suggested a concerted mechanism favored the bulkier substituent in the \textit{endo} position.

\textbf{Mode of Addition}

The additions of ketenes to indene produce adducts analogous to the cyclopentadiene adducts. The structures of the adducts have been elucidated by chemical degradation and nmr studies.\textsuperscript{4, 13}

\[
\begin{align*}
\text{R} & \quad \text{C}=\text{C}=\text{O} \\
\text{R} & \quad = \quad -\phi, \text{-Cl}, \text{-CH}_3
\end{align*}
\]

The Reactions of Fulvenes with Dienophiles

Fulvenes react with dienophiles to product 1,4 Diels-Alder type adducts. The reaction of maleic anhydride with fulvenes is well known. Alder\textsuperscript{14} was the first to note that this reaction afforded two isomers. Woodward\textsuperscript{15} confirmed this report by isolating the \textit{exo} and \textit{endo} isomers of the adduct of pentamethylene-fulvene with maleic anhydride. However, diphenylfulvene yielded exclusively an \textit{exo} adduct with maleic anhydride,\textsuperscript{16} whereas maleimide
afforded only the endo adduct.\textsuperscript{17}

Diazomethane and benzonitrile oxide react with fulvenes to yield 1,2 addition products. Alder and coworkers\textsuperscript{18} reported the addition of one mole of diazomethane to dimethylfulvene. They suggested the resulting adduct could be either 1 or 2. After the compound was stored several days at room temperature, the infrared spectrum indicated a new absorption peak in the N-H region. The authors suggested that the adduct rearranges to a fulvene system, structure 3 or 4.

In 1963 Paul and coworkers\textsuperscript{19} reported the reaction of two moles of diazomethane with diphenylfulvene. Surprisingly, the
second mole of diazomethane reacted with the exocyclic double bond to produce a spiro pyrazoline.

Quilico and coworkers $^{20}$ described the addition of benzonitrile oxide to various fulvenes. In each case mixtures of compounds 5 and 6 were obtained.

$$R = -\text{CH}_3; -\text{CH}_2\text{, -C}_2\text{H}_5; -\phi$$
EXPERIMENTAL

All melting and boiling points reported are corrected and expressed in degrees centigrade. Infrared spectra (ir) were obtained employing a Beckman IR-8 spectrophotometer and assignments were made according to Rao. The ultraviolet spectra (uv) were obtained with a Cary Model 14 spectrophotometer. Nuclear magnetic resonance spectra (nmr) were obtained with a Varian A-60 spectrophotometer employing deuterated chloroform as a solvent and tetramethylsilane as an internal standard. The integration values were rounded to the nearest whole number. The nmr spectra of compounds II, XI, and XII were obtained and interpreted by Dr. George Slomp of The Upjohn Company. Derivatives were prepared as described by Shriner, Fuson, and Curtin. Cyclopentenone was purchased from Pfaltz and Bauer and employed as received.

Preparation of the Dichloroketene Adducts

Diphenylfulvene (I)

A solution of sodium ethoxide was prepared by dissolving 14.7 g (0.615 mol) of sodium metal in 250 ml of absolute ethanol. The solution was cooled in an ice bath. The subsequent reaction was carried out in a nitrogen atmosphere. Then 40.0 g (0.615 mol) of freshly distilled cyclopentadiene was added and the resulting dark solution was stirred at ice bath temperature for 2 hours. The addition of a solution of 120 g (0.615 mol) of benzophenone in
200 ml of absolute ethanol was achieved in 30 minutes. The re-
action mixture was refluxed for 15 minutes, allowed to cool slowly
to room temperature, and then placed in the refrigerator overnight.
Filtration yielded 89.0 g (63%) of diphenylfulvene as orange
crystals: mp 79-81° (lit. 23 mp 82°).

\textbf{cis-6,6-Dichloro-2-diphenylmethylene-
bicyclo [3.2.0] hept-3-ene-7-one (II)}

A solution of 25.7 g (0.174 mol) of dichloroacetyl chloride
in 20 ml of anhydrous hexane was added dropwise to a hot solution
of 40.0 g (0.174 mol) of diphenylfulvene and 19.3 g (0.190 mol) of
freshly distilled triethylamine in 800 ml of anhydrous hexane.
Addition was completed in 40 minutes and the reaction mixture was
refluxed for 4 hours. An additional 25.7 g (0.174 mol) of dichloro-
acetyl chloride and 19.3 g (0.190 mol) of triethylamine were added
to the reaction mixture. Reflux was resumed for 4 hours and then
the reaction mixture was cooled in an ice bath. The solid was
filtered and washed with ether. The ether-hexane solution was
washed with water, 5% sodium bicarbonate solution, and saturated
sodium chloride solution and dried over anhydrous magnesium sulfate.
The drying agent was separated by filtration and evaporation of the
solvents gave 41.1 g (70%) of a tan solid: mp 135-137.5°. Three
recrystallizations from acetone-water gave an analytical sample
of compound II: mp 137.5-138°; ir (nujol) 1804, s (ketone C=O);
778, m: 767, s; 753, s; 726, s; 707, s (Ar and/or C-Cl); 692, s;
648 cm$^{-1}$, s (C-Cl); nmr (CDCl$_3$) δ 7.28 (m, 10H, ArH); 6.52 (m,
1H, CH=CH); 6.02 (m, 1H, CH=CH); 4.73 (m, 1H, CH-C=O); 4.22 (m, 1H, CH-C-Cl).

Anal. calcd for C_{20}H_{12}Cl_{2}O:  C, 70.81;  H, 3.57;  Cl, 20.90.
Found:  C, 70.69;  H, 3.71;  Cl, 20.75.

Benzodiphenylfulvene (III)

A solution of sodium ethoxide was prepared by dissolving 3.9 g (0.172 mol) of sodium metal in 200 ml of absolute ethanol. Then 20.0 g (0.172 mol) of indene and 24.0 g (0.132 mol) of benzophenone were added rapidly to the sodium ethoxide solution and the reaction mixture was refluxed for 12 hours. The reaction mixture was cooled in the refrigerator and subsequent filtration gave 17.2 g (48%) of benzodiphenylfulvene: mp 112-114° (lit. 24, mp 114-115°).

cis-2,2-Dichloro-1,2,2a,7a-tetrahydro-7-diphenylmethylene-cyclobut (a)
inden-1-one (IV)

A solution of 4.5 g (0.03 mol) of dichloroacetyl chloride in 20 ml of anhydrous hexane was added rapidly to a hot solution of 8.2 g (0.03 mol) of benzodiphenylfulvene and 3.0 g (0.03 mol) of freshly distilled triethylamine in 250 ml of anhydrous hexane. The reaction mixture was heated to reflux. An additional 0.45 mol of dichloroacetyl chloride and triethylamine were added in 0.03 mol portions over a 24 hour period. After 80 hours of reflux, the reaction mixture was cooled in an ice bath. The resulting solid was filtered and washed with ether. The filtrate was evaporated and the black tan was triturated with petroleum ether (30-60).
Evaporation of the petroleum ether washings gave 2.5 g (22%) of yellow solid: mp 167-168°. Three recrystallizations from benzene-hexane gave an analytical sample of IV: mp 170-171°; ir (nujol) 1802, s (ketone C=O); 1495, m; 1460, m; 1447, m (Ar); 794, m; 774, s; 765, s; 753, s; 700, s (Ar and/or C-Cl); 656, m; 649, m; 632 cm\(^{-1}\), m (C-Cl); nmr (CDCl\(_3\)) \(\delta\) 7.70-6.20 (m, 14H, ArH); 4.96 (d, 1H, Ar-CH); 4.46 (m, 1H, CH-C=O).

**Anal. calcd for C\(_{24}\)H\(_{16}\)Cl\(_2\)O:** C, 73.67; H, 4.12; Cl, 18.12.

**Found:** C, 73.43; H, 4.21; Cl, 17.98.

Degradation of Compound II

2-Dipenylmethylene bicyclo [3.2.0] hept-3-ene-7-one (V)

A slurry of 12.8 g (0.0378 mol) of II, 12.3 g (0.189 mol) of powdered zinc, 80 ml of methanol, and 80 ml of glacial acetic acid was refluxed for 4 hours. The reaction mixture was filtered while hot and the filtrate cooled in the refrigerator. Filtration gave 8.6 g (84%) of beautiful needle crystals: mp 123-124°. Three recrystallizations from hot methanol yielded an analytical sample of V: mp 125-126°; ir (nujol) 1765, s (ketone C=O); 1585, w; 1560, w (C=C); 773, s; 752, s; 700 cm\(^{-1}\), s (Ar); uv max (95% C\(_2\)H\(_5\)OH) 280 m\(\mu\) (\(\epsilon\) 2.1 \(\times\) 10\(^6\)); nmr (CDCl\(_3\)) \(\delta\) 7.33 (m, 1OH, ArH); 6.38 (d, 1H, (CH=CH); 6.15 (m, 1H, CH=CH); 4.49 (m, 1H, CH-C=O); 3.69 (m, 1H, CH-CH\(_2\)); 2.92 (m, 2H, CH\(_2\)).

**Anal. calcd for C\(_{20}\)H\(_{14}\)O:** C, 88.20; H, 5.92; 0, 5.87.

**Found:** C, 87.98; H, 6.01; 0, 6.11.
Methyl-(4-diphenylmethylene-cyclopent-2-ene)-acetate (VI)

A solution of 1.0 g (0.018 mol) of sodium methoxide in 10 ml of anhydrous methanol was added dropwise to a solution of 4.0 g (0.015 mol) of V in 40 ml of anhydrous tetrahydrofuran at -10° under a nitrogen atmosphere. The addition was complete in 20 minutes and then the solution was stirred for 1 hour at -10°. The solution was allowed to warm to 0° and acidified to pH 4 with glacial acetic acid. The solution was diluted with an equal amount of water and extracted with methylene chloride. The extract was washed with water, 5% sodium bicarbonate solution, and saturated sodium chloride solution and dried over anhydrous sodium sulfate. Filtration of the drying agent and evaporation of the solvent yielded a yellow oil. The oil was chromatographed on 475 g of silica gel. Elution with benzene yielded 3.7 g (67%) of VI. However, the compound is unstable in the presence of air and could be isolated in about 95% purity; ir (neat) 1600, m; 1575, m (C=C); 2955, s; 2925, s; 2855, s; 1460, m; 1380, m (alkane); 1725, s (ester C=O); 1275, s; 1122, s; 1072, s; 1040, m (OCH$_3$); 741, m; 704 cm$^{-1}$, m (Ar); uv max (95% C$_2$H$_5$OH) 280 m$i$ (ε 2.6 X 10$^5$); nmr (CDCl$_3$) δ 7.19 (s, 10H, ArH); 6.25 (m, 2H, CH-CH); 3.61 (s, 3H, OCH$_3$); 3.39-2.13 (m, 5H, CH$_2$-CH-CH$_2$).

Anal. calcd for C$_{21}$H$_{20}$O$_2$: C, 82.85; H, 6.64. Found: C, 81.28; H, 6.58.
Methyl-(3-diphenylmethylenecyclopentane)-acetate (VII)

A slurry of 2.0 g (0.0069 mol) of freshly prepared VI and 0.167 g of prereduced 10% palladium on carbon in 30 ml of ethyl acetate was hydrogenated at atmospheric pressure. The reaction consumed 170 ml of hydrogen in one hour and then stopped (uptake of hydrogen calcd at 155 ml). The catalyst was removed by filtration and the solvent evaporated. The resulting colorless oil was chromatographed on 170 g of silica gel. Elution with 5:1 benzene-chloroform gave 1.8 g (85%) of VII. This compound is also unstable in air. Although more stable than VI, an unacceptable analysis was obtained with the chromatographed material; ir (neat) 1600, m (C=C); 3010, m; 1490, m; 757, m; 746, m; 700, s (Ar); 2950, m; 1440, m (alkane); 1255, m; 1200, m; 1170, m; 1030 cm\(^{-1}\), m (OCH\(_3\)); nmr (CDCl\(_3\)) \(\delta\) 7.23 (s, 10H, ArH); 3.62 (s, 3H, OCH\(_3\)); 2.32 (m, 9H, CH\(_2\), CH).


Derivatives of VI and VII

The reactions were performed with both VI and VII in an attempt to form a solid derivative. It was hoped a solid derivative could be purified to give an acceptable analysis. Identical results were obtained for both compounds. All reactions were done with freshly chromatographed material in a nitrogen atmosphere to retard possible oxidation.
The ester was reacted with hydrazine in an effort to form an acid hydrazide. A solution containing 0.200 g (0.00067 mol) of ester and 2 ml of 95% hydrazine was heated at 130° in an oil bath for 15 minutes. The solution was cooled to 80° and diluted with 1 ml of 95% ethanol. The reaction mixture was refluxed 2 hours. Thin layer chromatography indicated the reaction was complete. The solvent was evaporated and excess hydrazine was removed in vacuo. A melting point determination of the resulting tan substance suggested the material was a glass. An attempted crystallization from ether-petroleum ether (30-60) gave an oil which turned dark on standing.

The second reaction was the hydrolysis of the ester with potassium hydroxide. A solution was prepared which contained 0.100 g. (0.00033 mol) of ester, 2 ml of dioxane, and 3 ml of IM aqueous potassium hydroxide. Distilled water was added to the solution until it turned cloudy. After 5 minutes, tlc indicated the starting material had reacted completely. The dioxane was evaporated and the water was washed with ether. The water layer was acidified, extracted with ether, and the ether extract was dried over anhydrous magnesium sulfate. Concentration of the extract gave an oil whose tlc had 3 spots. Attempts to induce crystallization were unsuccessful.

The third reaction was an attempt to synthesize a N-benzylamide. A mixture of 0.300 g (0.001 mol) of ester, 0.200 g (0.001 mol) of benzylamine, and 0.014 g of ammonium chloride was refluxed one hour. The solution was cooled to room temperature and
washed with water. A dark oil was isolated which could not be
induced to crystallize.

**Methyl-(3-oxo-cyclopentane)-acetate (VIII)**

A solution of 0.907 g (0.00335 mol) of VII in 110 ml of
acetone was prepared. The flask was flushed with nitrogen and a
ground (glass) stopper was in place during the reaction. A mix-
ture of 0.350 g (0.00265 mol) of freshly prepared ruthenium
tetroxide in 7 ml of carbon tetrachloride and 2.0 g (0.0094 mol)
of sodium meta-periodate in 50 ml of distilled water was added to
the acetone solution at room temperature. The resulting mixture
darkened rapidly and became warm. The flask was cooled with cold
water for 2 minutes and stirring was resumed. Sodium meta-
periodate was added to the reaction mixture in 2.0 g portions as
the black ruthenium dioxide precipitate was formed until a total
of 10.0 g (0.0467 mol) of sodium meta-periodate had been added.
The excess ruthenium tetroxide was destroyed after 24 hours by
adding 20 ml of methanol. The precipitate was filtered and washed
with acetone. The acetone was evaporated and the water was
extracted with ether. The extract was washed with saturated
sodium chloride solution and dried over anhydrous magnesium sul-
fate. The drying agent was separated by filtration and the ether
was carefully evaporated in vacuo below 30° to yield a yellow oil.
The oil was chromatographed over 170 g of silica gel. Elution with
chloroform gave 0.350 g (67%) of VIII. Its infrared spectrum was
nearly identical with an authentic sample; ir (neat) 2950, m, 1440, m, 1405, m, 1375, m, 1340, m (alkane), 1740, s (ester C=O), 1710, s (ketone C=O), 1200, m, 1160 cm⁻¹, m (OCH₃).

A solid derivative was prepared by adding 3 ml of a freshly prepared solution of 0.4 g of 2,4-dinitrophenylhydrazine, 2 ml of concd sulfuric acid, 3 ml of distilled water, and 10 ml of methanol to 0.093 g of VIII in 2 ml of methanol. Crystallization began immediately after mixing and was allowed to proceed at room temperature for 2 hours. The flask was placed in the refrigerator overnight. An analytical sample of [methyl-3(oxo-cyclopentane)-acetate]-2,4 dinitro phenyl hydrazone was prepared by two recrystallizations from ethyl acetate: mp 135-136° (lit. 26 mp 134-135°); ir (nujol) 3300, s (N-H); 1730, s (ester C=O); 1335, s (Ar-NO₂); 1500, m; 841, m; 833, m; 743, m; 720, m (Ar); 1455, s; 1415, m (alkane); 1270, m; 1210, m; 1175, m; 1130, m; 1070, m (OCH₃).

Anal. calcd for C₁₄H₁₄N₄O₆: C, 50.00; H, 4.80; N, 16.66. Found: C, 50.30; H, 4.82; N, 16.41

A mixed melting point with an authentic sample was undepressed and the infrared spectrum was identical to an authentic sample.

Synthesis of an Authentic Sample

(3-Oxo-cyclopentane)-acetic acid (IX)

A solution of 0.3 g (0.013 mol) of sodium metal and 20.8 g (0.130 mol) of diethylmalonate in 20 ml of absolute ethanol was
refluxed 10 minutes. The solution was cooled to -5° and a nitrogen atmosphere maintained while 10.0 g (0.122 mol) of cyclopentenone was added in 25 minutes. When addition was complete, 2 ml of glacial acetic acid was added and the solution was allowed to warm to room temperature. The ethanol was evaporated and the water solution was extracted with ether. The extract was washed with water, 5% sodium bicarbonate solution, and saturated sodium chloride solution and dried over anhydrous sodium sulfate. The drying agent was separated by filtration and the ether was evaporated. The resulting liquid was refluxed with 45 ml of concd hydrochloric acid and 160 ml of distilled water for 24 hours. The water solution was extracted with ether. The ether was evaporated and the product distilled in vacuo to yield 3.4 g (32%) of IX: bp 127-132° (0.15 mm) [lit.27 bp 127-128° (0.2 mm)].

Methyl-(3-oxo-cyclopentane)-acetate (X)

A distillation set-up was prepared with rubber stoppers replacing glass ground joints. Both the distillation flask and the receiving flask were cooled in ice-salt baths. A slurry of 170 ml of ether, 26 ml of diglyme, and 34 ml of 30% aqueous potassium hydroxide was placed in the distillation flask. Then 6.3 g (0.032 mol) of bis-(N-methyl-N-nitroso)-terephthalamide was added to the slurry and the characteristic yellow color of diazomethane appeared. The ice-salt bath was removed and the distillation flask was warmed to 40° with a water bath. The ether-
diazomethane mixture distilled into a receiving flask containing 2.0 g (0.014 mol) of IX in ether. The receiving flask was swirled until a permanent yellow color was perceived. Distillation was halted immediately and the excess diazomethane was destroyed with glacial acetic acid. The ether solution in the receiving flask was washed with water, 5% sodium bicarbonate solution, and saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration and the ether was evaporated to yield 2.1 g (95%) of X; ir (neat) 2960, m; 1445, m; 1400, m; 1380, m; 1340, m (alkane); 1200, m; 1160, m (OCH₃); 1740, s (ester C=O); 1710 cm⁻¹, s (ketone C=O).

A solid derivative was prepared by adding a solution containing 0.4 g of 2,4-dinitrophenylhydrazine, 2 ml of concd sulfuric acid, 3 ml of distilled water, and 10 ml of methanol to 0.5 g of X in 10 ml of methanol. The product was allowed to crystallize at room temperature and then placed in the refrigerator overnight. Recrystallization from ethyl acetate realized yellow crystals of [methyl-(3-oxo-cyclopentane)-acetate]-2,4-dinitro phenyl hydrazone: mp 135-136° (lit. ²⁶ mp 134-135°); ir (nujol) 3300, s (N-H); 1730, s, (ester C=O); 1335, s (Ar-NO₂); 1500, m; 841, m; 833, m; 743, m; 720, m (Ar); 1455, s; 1415, m (alkane); 1270, m; 1210, m; 1175, m; 1130, m; 1070 cm⁻¹, m (OCH₃).
Synthesis of Compounds for NMR Studies

cis-6-Chloro-2-diphenylmethylene bicyclo [3.2.0] hept-3-ene-7-one (XI)

A slurry containing 32.6 g (0.0962 mol) of II, 7.1 g (0.109 mol) of powdered zinc, 100 ml of methanol, and 100 ml of glacial acetic acid was refluxed for 17 hours. The reaction mixture was filtered hot and allowed to cool in the refrigerator. Filtration gave a white solid, 16.7 g (57%) of XI: mp 157-162°. An analytical sample was prepared by three recrystallizations from hot methanol: mp 163-164°; ir (nujol) 1790, s (ketone C=O), 776, m, 762, s, 748, s, 702, s (Ar and/or C-Cl), 666, m, 638 cm\(^{-1}\), s (C-Cl); nmr (CDCl\(_3\)) \(\delta\) 7.30 (m, 1OH, Ar), 6.48 (m, 1H, CH=CH), 6.09 (m, 1H, CH=CH), 5.07 (m, 1H, CH-Cl), 4.36 (m, 1H, CH-C=O), 4.08 (m, 1H, CH-CHCl).

Anal. calcd for C\(_{20}\)H\(_{13}\)ClO: C, 78.29; H, 4.93; Cl, 11.55.

Found: C, 77.99; H, 5.21; Cl, 11.84.

cis-2-Chloro-1,2,2a,7a-tetrahydro-7-diphenylmethyl-cyclobut (a) inden-1-one (XII)

A slurry of 0.500 g (0.00128 mol) of IV and 0.500 g of 5% palladium on barium sulfate in 50 ml of ethanol was hydrogenated at 60 p.s.i. at 25° for 4 hours. The catalyst was filtered and washed with chloroform. The filtrate was evaporated to dryness to yield 0.450 g (90%) of XII: mp 208-210°. The white solid was recrystallized twice from benzene-ligroin (60-110) to give an
analytical sample: mp 210-211°; ir (KBr) 1802, s (ketone C=O), 3062, m; 1495, m; 1465, m; 1448, m (Ar); 762, s; 754, s; 748, s; 741, s; 730, s; 700, s (Ar and/or C-Cl); 689, s, (C-Cl); 2930 cm⁻¹, m (alkane); nmr (CDCl₃) δ 7.58-6.15 (m, 14H, ArH); 4.97 (m, 1H, CH-CI); 4.57 (m, 1H, Ar-CH); 4.52 (m, 1H, Ar-CH); 4.05 (m, 1H, CH-C=O); 3.78 (m, 1H, CH-CH-CI).

Anal. calcd for C₂₄H₁₉ClO: C, 80.33; H, 5.34; Cl, 9.88.
Found: C, 80.26; H, 5.42; Cl, 9.97.
FIGURE 1. NMR SPECTRUM OF VI
FIGURE 2. NMR SPECTRUM OF VII
DISCUSSION

Interpretation of NMR Spectra

**Diphenylfulvene Adduct**

The cycloaddition of dichloroketene to diphenylfulvene may form two isomers, IIa or IIb. The Diels-Alder adduct was rejected on the basis of the infrared spectrum. The carbonyl absorption at 1804 cm\(^{-1}\) is reasonable for a cyclobutanone ring\(^{28}\) but not representative of a cyclopentanone ring. A nmr spectrum was obtained and the chemical shifts and coupling constants are listed in Table 1. The values for Jsx and Jrx were measured as 0.9 and 2.9 Hz, respectively. The value for Jrx is too large for long range coupling as depicted in structure IIb. The value of 0.9 Hz for Jsx is acceptable for the system represented in IIa. A Dreiding model of IIa was constructed. The Barfield relationships\(^{29}\) for allylic and saturated systems were used as approximations and gave as results, respectively, Jry calcd = -1.75 Hz (Jry = -1.8)
and Jsx calcd = 0.6 Hz. Therefore, structure IIa was designated as the isomer formed.

Table 1. NMR Spectral Data for Compound II

<table>
<thead>
<tr>
<th>Chemical Shift</th>
<th>Number of Protons</th>
<th>Coupling Constant (cps)</th>
<th>Proton Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.28</td>
<td>10</td>
<td>Jyx 5.7</td>
<td>ArH</td>
</tr>
<tr>
<td>6.52</td>
<td>1</td>
<td>Jyr 1.8</td>
<td>Hy</td>
</tr>
<tr>
<td>6.02</td>
<td>1</td>
<td>Jxy 5.7</td>
<td>Hx</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jxr 2.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jxs 0.9</td>
<td></td>
</tr>
<tr>
<td>4.73</td>
<td>1</td>
<td>Jsr 6.6</td>
<td>Hs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jsx 0.9</td>
<td></td>
</tr>
<tr>
<td>4.22</td>
<td>1</td>
<td>Jrs 6.6</td>
<td>Hr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jrx 2.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jry 1.8</td>
<td></td>
</tr>
</tbody>
</table>

Verification of this assignment was obtained by reducing one of the chlorine atoms and studying the nmr spectrum of the monochloro adduct. The adduct could be formed as structure XIa or XIb. The carbonyl absorption of the infrared spectrum was consistent for a cyclobutanone ring. The chemical shifts and coupling constants are listed in Table 2. The values of Jsx = 1.0 Hz and Jrx = 2.5 Hz indicate that Hr and Hx are vicinal protons. In addition the value for Jsx is more reasonable for long range
coupling than the value for $J_{rx}$. Similarly, $J_{or} = 9.0$ Hz and $J_{os} = 3.0$ Hz indicate that $H_o$ and $H_r$ are also vicinal protons. Only structure XIa meets these criteria.

Table 2. NMR Spectral Data for Compound XI

<table>
<thead>
<tr>
<th>Chemical Shift</th>
<th>Number of Protons</th>
<th>Coupling Constant (cps)</th>
<th>Proton Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.30</td>
<td>10</td>
<td>$J_{yx}$ 6.0</td>
<td>$ArH$</td>
</tr>
<tr>
<td>6.48</td>
<td>1</td>
<td>$J_{yr}$ 1.5</td>
<td>$Hy$</td>
</tr>
<tr>
<td>6.09</td>
<td>1</td>
<td>$J_{yx}$ 0.5</td>
<td></td>
</tr>
<tr>
<td>6.09</td>
<td>1</td>
<td>$J_{xy}$ 6.0</td>
<td>$Hx$</td>
</tr>
<tr>
<td>5.07</td>
<td>1</td>
<td>$J_{or}$ 9.0</td>
<td>$Ho$</td>
</tr>
<tr>
<td>4.36</td>
<td>1</td>
<td>$J_{os}$ 7.0</td>
<td>$Hs$</td>
</tr>
<tr>
<td>4.08</td>
<td>1</td>
<td>$J_{ro}$ 9.0</td>
<td>$Hr$</td>
</tr>
</tbody>
</table>

Benzodiphenylfulvene Adduct

The adduct of benzodiphenylfulvene and dichloroketene may be formed as isomer IVa or IVb. However, the correct structure could

![IVa](image1)

![IVb](image2)
not be deduced from the nmr spectrum. Therefore, the adduct was hydrogenated and the product scrutinized via nmr spectroscopy. The reduction product may be isomer XIIa or XIIb. The nmr data are listed in Table 3. Analysis of the spectrum indicated that

Table 3. NMR Spectral Data for Compound XII

<table>
<thead>
<tr>
<th>Chemical Shift</th>
<th>Number of Protons</th>
<th>Coupling Constant (cps)</th>
<th>Proton Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.33</td>
<td>12</td>
<td></td>
<td>ArH</td>
</tr>
<tr>
<td>6.92</td>
<td>1</td>
<td></td>
<td>ArH</td>
</tr>
<tr>
<td>6.22</td>
<td>1</td>
<td></td>
<td>ArH</td>
</tr>
<tr>
<td>4.97</td>
<td>1</td>
<td>Jor 8.7</td>
<td>Ho</td>
</tr>
<tr>
<td>4.57</td>
<td>1</td>
<td>Jos 2.3</td>
<td></td>
</tr>
<tr>
<td>4.52</td>
<td>1</td>
<td>Jpq 12.3</td>
<td>Hp</td>
</tr>
<tr>
<td>4.05</td>
<td>1</td>
<td>Jps -0.4</td>
<td></td>
</tr>
<tr>
<td>3.78</td>
<td>1</td>
<td>Jps 7.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jro 8.7</td>
<td>Hr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jrs 7.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jso 2.3</td>
<td>Hs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jsp -0.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jsq 7.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jsr 7.4</td>
<td></td>
</tr>
</tbody>
</table>

XIIa was the correct structure. The coupling constants obtained from a Dreiding model gave reasonable results (Jrq calcd = -0.1 Hz, Jrq = -0.15 Hz). The PQ coupling constant was satisfactory when Hp was placed trans to Hq.
Confirmation of the OPQRS interpretation was obtained by computer using the LAOCN-3 program. The computer results are listed in Table 4. The establishment of structure XIIa defines the initial adduct as IVa.

Table 4. Results from Computer Analysis of OPQRS

<table>
<thead>
<tr>
<th>Proton Assignment</th>
<th>Chemical Shift</th>
<th>Coupling</th>
<th>Coupling Constant (cps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho</td>
<td>4.96612</td>
<td>OP</td>
<td>0</td>
</tr>
<tr>
<td>Hp</td>
<td>4.56609</td>
<td>OQ</td>
<td>0</td>
</tr>
<tr>
<td>Hq</td>
<td>4.52081</td>
<td>OR</td>
<td>8.671</td>
</tr>
<tr>
<td>Hr</td>
<td>4.04953</td>
<td>OS</td>
<td>2.321</td>
</tr>
<tr>
<td>Hs</td>
<td>3.77501</td>
<td>PQ</td>
<td>12.272</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PR</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PS</td>
<td>-0.443</td>
</tr>
<tr>
<td></td>
<td></td>
<td>QR</td>
<td>-0.149</td>
</tr>
<tr>
<td></td>
<td></td>
<td>QS</td>
<td>7.647</td>
</tr>
<tr>
<td></td>
<td></td>
<td>RS</td>
<td>7.414</td>
</tr>
</tbody>
</table>

RMS error of fit = 0.310

Degradation of II

The key to the degradation scheme was the ring cleavage reaction with sodium methoxide. This type of reaction had been previously performed by Ghosez and coworkers$^1$ with the adduct of cyclopentadiene and dichloroketene. It was hoped that the same reaction would hold for the analogous diphenylfulvene adduct.
Initial experiments indicated the reaction was not efficient. Thin layer chromatography gave three major and two minor spots. Removal of the chlorine atoms on the adduct and subsequent cleavage with methoxide ion gave a cleaner reaction. In this case the tlc showed one major and four minor spots. Isolation of the major compound via column chromatography and subsequent appraisal of the nmr spectrum suggested the ring cleavage product was not analagous to the cyclopentadiene ring cleavage product. Apparently after attack by methoxide ion, the carbanion moves into conjugation with the double bonds and the benzene rings.

Complications ensued when VI was found to be unstable in air. Storage of freshly chromatographed VI under nitrogen, covered with foil, and placed in the refrigerator only succeeded in retarding
the decomposition. The conditions favorable to decomposition suggested an oxidation reaction might be occurring. The cyclic double bonds of 2,3,4,5-tetraphenylfulvene and dimethylfulvene oxidize photochemically to form epoxides. Also possible is the oxidation of VI to a fulvene system. It was hoped the selective reduction of the cyclic double bond would avoid these difficulties. However, the reduction product VII was also unstable in air. Data regarding the decomposition products are lacking. Therefore, the suggestion that the compounds are being oxidized is pure speculation.

Since it was impossible to obtain a pure sample of VI or VII for an analytical sample, an effort was made to secure a solid derivative. Attempts were made to synthesize a hydrazide, an acid or a N-benzylamide of VI and VII. However, the reactions gave only oils which could not be crystallized. Thin layer chromatography indicated the ester reacted completely with the desired reagents. Exposure of the oils to air caused them to darken slowly.

The selective reduction of the cyclic double bond of fulvenes has been effected by palladium on charcoal and palladium on silicon dioxide. However, palladium on charcoal reduced all the double bonds of a benzofulvene. Selective reduction of this system occurred with rhodium on alumina as a catalyst. The attempted selective hydrogenation of V only succeeded in reducing both double bonds. The ease of reduction of the exocyclic double bond in this case may be due to the relief of steric strain.
The subsequent oxidation of the exocyclic double bond proved to be dependent on the proper oxidizing agent. The oxidation of olefins with potassium permanganate and sodium meta-periodate was ineffective. The infrared spectrum indicated benzophenone was formed; however, column chromatography of the reaction products indicated the desired product was not present. Therefore, another oxidation system was sought. The desired experimental result was achieved employing ruthenium tetroxide and sodium meta-periodate. The literature stated this reagent combination was more potent than osmium tetroxide and sodium meta-periodate. Ruthenium tetroxide has been used to cleave diphenylmethylene groups on steroid molecules. These examples seemed analogous to the molecule of interest and this was verified experimentally.

A 2,4 dinitrophenylhydrazone was prepared from the ketone and compared with an authentic sample. Comparison of the infrared spectra and a mixed melting point indicated the derivative and the authentic sample were identical.
SUMMARY

The reaction of dichloroketene with diphenylfulvene yielded a cycloadduct. The structure was elucidated from the nmr spectrum. The structure was also determined with a chemical degradation scheme. The end product and an authentic sample were identical as determined by the infrared spectrum and a mixed melting point.

The adduct of dichloroketene and benzodiphenylfulvene was prepared and then catalytically hydrogenated. The structure of the adduct was determined from the nmr spectrum of the reduction product.

The dichloroketene adducts of diphenylfulvene and benzodiphenylfulvene are analogous to the ketene adducts of cyclopentadiene and indene.


VITA

The author was born on September 16, 1943 in Hamtramck, Michigan. He attended Cass Technical High School in Detroit and graduated in June, 1961. In September, 1961 he began his studies at Wayne State University and received his Bachelor of Science in Chemistry in June, 1966. He was employed with Ash-Stevens, Inc. from June, 1965 to November, 1966 as an organic chemist and with the Ford Motor Company as a polymer chemist from November, 1966 to July, 1968. In August, 1968 he married the former Patricia Potocki and began graduate work at Western Michigan University. He has been financially supported by a teaching assistantship and a research fellowship. He is a member of the American Chemical Society.