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

William Douglas Barta

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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-ONE

by

William Douglas Barta

A Thesis  
Submitted to the  
Faculty of the Graduate College  
in partial fulfillment  
of the  
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Kalamazoo, Michigan  
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William Douglas Barta

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## 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.

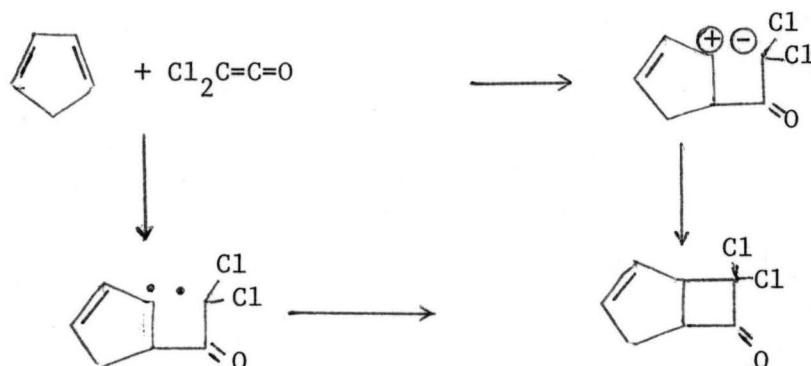
The structures of the adducts of dichloroketene with cyclopentadiene<sup>1, 2</sup> and indene<sup>3, 4</sup> have been determined by previous workers. The influence of the exocyclic double bond on the mode of cycloaddition is unknown.

## 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.<sup>5</sup> J. D. Roberts has suggested the following two possible reaction mechanisms for the reactions of ketenes with olefins: a diradical and an ionic mechanism.<sup>6</sup> Therefore, the reaction of dichloroketene and cyclopentadiene can also proceed by the following two routes:<sup>1</sup>



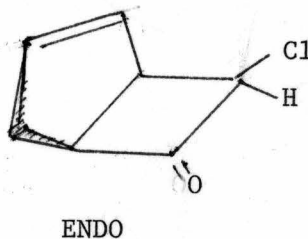
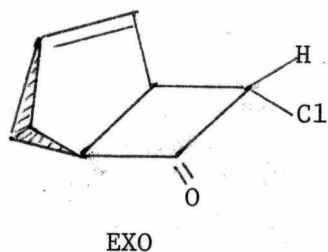
However, subsequent data indicated the reaction rate to be nearly independent of solvent effects and, thus, rendered a formal ionic mechanism questionable. Several workers have suggested that a concerted mechanism may be operative. According to them the high stereoelectivity of the reaction, the greater reactivity of

the cis olefin over the trans, and a high negative entropy support a concerted mechanism.<sup>7</sup>

The data reported by some other workers questions the validity of a true concerted mechanism. For example Frey and Isaacs<sup>8</sup> 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<sup>9</sup> 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<sup>10</sup> and, therefore, it permits the substituents on the cyclobutanone 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.



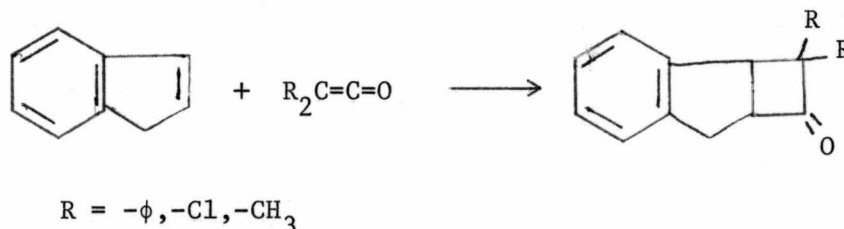
Brady compared this adduct with an authentic sample of endo



isomer and was amazed to find them identical. His findings have been verified by X-ray and nmr studies.<sup>11</sup> In fact the endo position of the chlorine can be predicted by the Woodward-Hoffmann orbital symmetry conservation rule.<sup>12</sup> DoMinh and Strausz also suggested a concerted mechanism favored the bulkier substituent in the endo position.

#### Mode of Addition

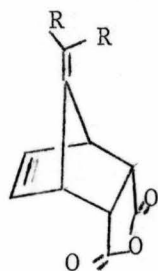
The additions of ketenes to indene produce adducts analogous to the cyclopentadiene adducts. The structures of the adducts have been elucidated by chemical degradation and nmr studies.<sup>4, 13</sup>



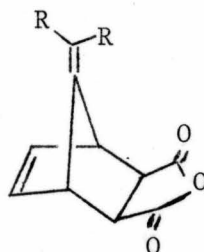
#### The Reactions of Fulvenes with Dienophiles

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

afforded only the endo adduct.<sup>17</sup>

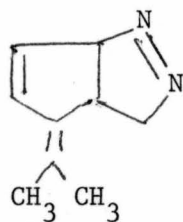


ENDO

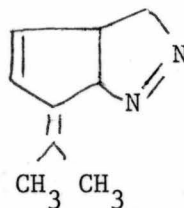


EXO

Diazomethane and benzonitrile oxide react with fulvenes to yield 1,2 addition products. Alder and coworkers<sup>18</sup> 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



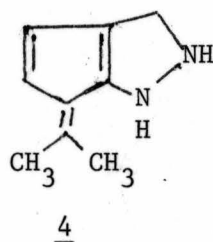
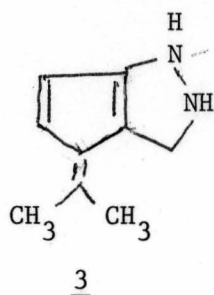
1



2

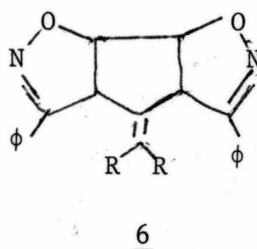
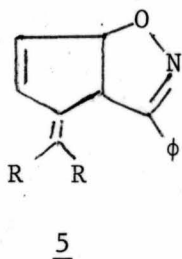
spectrum indicated a new absorption peak in the N-H region. The authors suggested that the adduct rearranges to a fulvene system, structure 3 or 4.

In 1963 Paul and coworkers<sup>19</sup> 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<sup>20</sup> described the addition of benzonitrile oxide to various fulvenes. In each case mixtures of compounds 5 and 6 were obtained.



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

## 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.<sup>21</sup> 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.<sup>22</sup> 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 reaction 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.<sup>23</sup> mp 82°).

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 dichloroacetyl 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<sup>-1</sup>, s (C-Cl); nmr (CDCl<sub>3</sub>) δ 7.28 (m, 10H, ArH); 6.52 (m,

1H,  $\underline{\text{CH}}=\text{CH}$ ); 6.02 (m, 1H,  $\text{CH}=\underline{\text{CH}}$ ); 4.73 (m, 1H,  $\underline{\text{CH}}-\text{C}=\text{O}$ ); 4.22 (m, 1H,  $\underline{\text{CH}}-\text{C}-\text{Cl}$ ).

Anal. calcd for  $\text{C}_{20}\text{H}_{12}\text{Cl}_2\text{O}$ : 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.<sup>24</sup>, 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  $\text{cm}^{-1}$ , m (C-Cl); nmr ( $\text{CDCl}_3$ )  $\delta$  7.70-6.20 (m, 14H, ArH); 4.96 (d, 1H, Ar-CH); 4.46 (m, 1H, CH-C=O).

Anal. calcd for  $\text{C}_{24}\text{H}_{16}\text{Cl}_2\text{O}$ : 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  $\text{cm}^{-1}$ , s (Ar); uv max (95%  $\text{C}_2\text{H}_5\text{OH}$ ) 280 m $\mu$  ( $\epsilon$   $2.1 \times 10^6$ ); nmr ( $\text{CDCl}_3$ )  $\delta$  7.33 (m, 10H, 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<sub>2</sub>); 2.92 (m, 2H, CH<sub>2</sub>).

Anal. calcd for  $\text{C}_{20}\text{H}_{14}\text{O}$ : C, 88.20; H, 5.92; O, 5.87.  
Found: C, 87.98; H, 6.01; O, 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  $-10^{\circ}$  under a nitrogen atmosphere. The addition was complete in 20 minutes and then the solution was stirred for 1 hour at  $-10^{\circ}$ . The solution was allowed to warm to  $0^{\circ}$  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 ( $\text{OCH}_3$ ); 741, m;  $704\text{ cm}^{-1}$ , m (Ar); uv max (95%  $\text{C}_2\text{H}_5\text{OH}$ ) 280 m $\mu$  ( $\epsilon\ 2.6 \times 10^5$ ); nmr ( $\text{CDCl}_3$ )  $\delta$  7.19 (s, 10H, ArH); 6.25 (m, 2H,  $\text{CH}=\text{CH}$ ); 3.61 (s, 3H,  $\text{OCH}_3$ ); 3.39-2.13 (m, 5H,  $\text{CH}_2-\text{CH}=\text{CH}_2$ ).

Anal. calcd for  $\text{C}_{21}\text{H}_{20}\text{O}_2$ : 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  $\text{cm}^{-1}$ , m ( $\text{OCH}_3$ ); nmr ( $\text{CDCl}_3$ )  $\delta$  7.23 (s, 10H,  $\text{ArH}$ ); 3.62 (s, 3H,  $\text{OCH}_3$ ); 2.32 (m, 9H,  $\text{CH}_2$ ,  $\text{CH}$ ).

Anal. calcd for  $\text{C}_{21}\text{H}_{22}\text{O}_2$ : C, 82.32; H, 7.24. Found: C, 81.45, H, 7.60.

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 1M 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 mixture of 0.350 g (0.00265 mol) of freshly prepared ruthenium tetroxide<sup>25</sup> 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 sulfate. 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  $\text{cm}^{-1}$ , m ( $\text{OCH}_3$ ).

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.<sup>26</sup> mp 134-135°); ir (nujol) 3300, s (N-H); 1730, s (ester C=O); 1335, s (Ar- $\text{NO}_2$ ); 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 ( $\text{OCH}_3$ ).

Anal. calcd for  $\text{C}_{14}\text{H}_{16}\text{N}_4\text{O}_6$ : 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  $-5^{\circ}$  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  $127-132^{\circ}$  (0.15 mm) [lit.<sup>27</sup> bp  $127-128^{\circ}$  (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  $40^{\circ}$  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 ( $\text{OCH}_3$ ); 1740, s (ester  $\text{C}=\text{O}$ );  $1710\text{ cm}^{-1}$ , s (ketone  $\text{C}=\text{O}$ ).

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  $135\text{--}136^\circ$  (lit.<sup>26</sup> mp  $134\text{--}135^\circ$ ); ir (nujol) 3300, s (N-H); 1730, s, (ester  $\text{C}=\text{O}$ ); 1335, s ( $\text{Ar-NO}_2$ ); 1500, m; 841, m; 833, m; 743, m; 720, m (Ar); 1455, s; 1415, m (alkane); 1270, m; 1210, m; 1175, m; 1130, m;  $1070\text{ cm}^{-1}$ , m ( $\text{OCH}_3$ ).

## 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  $\text{cm}^{-1}$ , s (C-Cl); nmr ( $\text{CDCl}_3$ )  $\delta$  7.30 (m, 10H, ArH), 6.48 (m, 1H,  $\text{CH}=\text{CH}$ ), 6.09 (m, 1H,  $\text{CH}=\text{CH}$ ), 5.07 (m, 1H,  $\text{CH}-\text{Cl}$ ), 4.36 (m, 1H,  $\text{CH}-\text{C}=\text{O}$ ), 4.08 (m, 1H,  $\text{CH}-\text{CHCl}$ ).

Anal. calcd for  $\text{C}_{20}\text{H}_{13}\text{ClO}$ : 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  $\text{cm}^{-1}$ , m (alkane); nmr ( $\text{CDCl}_3$ )  $\delta$  7.58-6.15 (m, 14H, ArH); 4.97 (m, 1H,  $\text{CH-Cl}$ ); 4.57 (m, 1H, Ar- $\text{CH}$ ); 4.52 (m, 1H, Ar- $\text{CH}$ ); 4.05 (m, 1H,  $\text{CH-C=O}$ ); 3.78 (m, 1H,  $\text{CH-CH-Cl}$ ).

Anal. calcd for  $\text{C}_{24}\text{H}_{19}\text{ClO}$ : C, 80.33; H, 5.34; Cl, 9.88.

Found: C, 80.26; H, 5.42; Cl, 9.97.



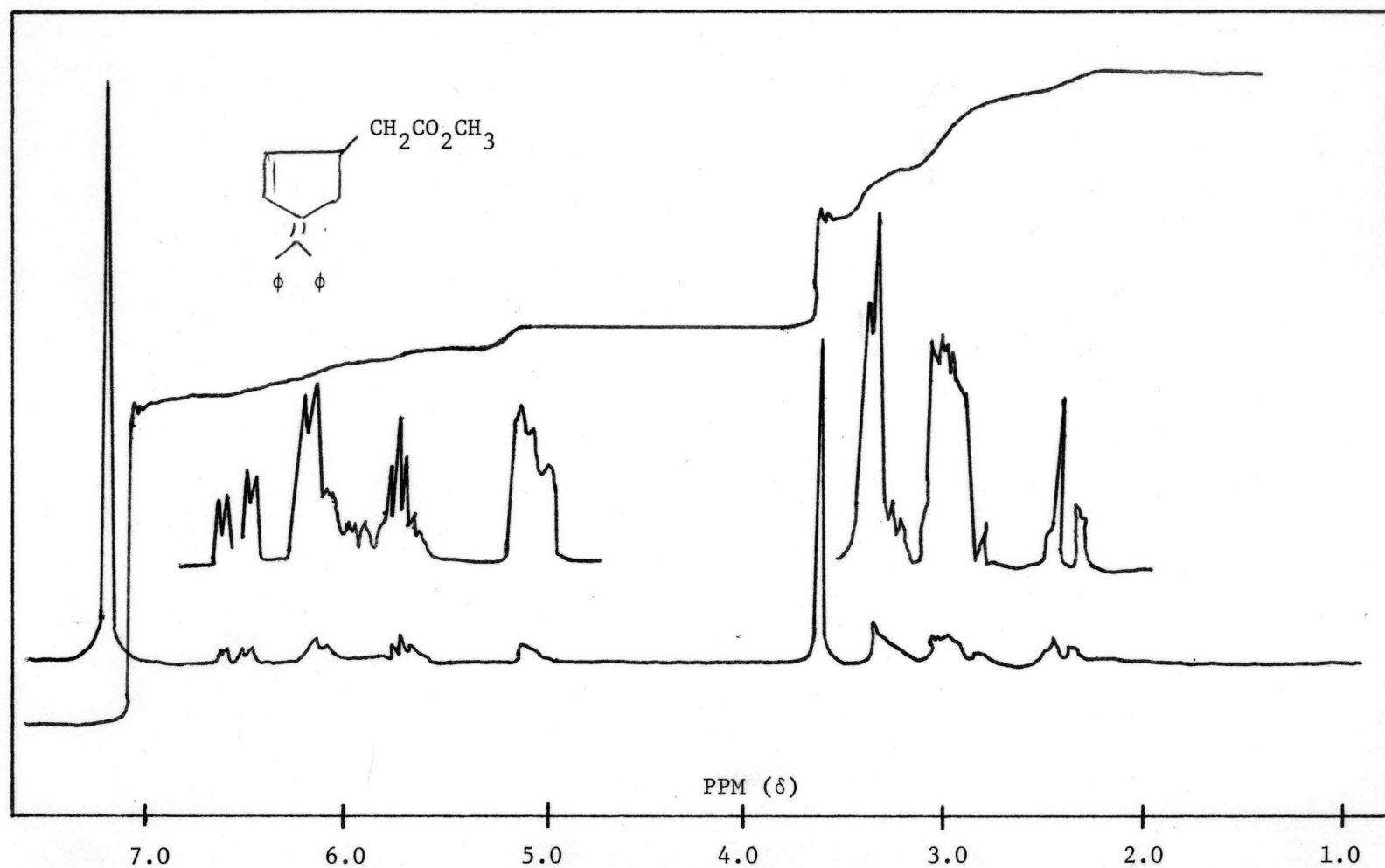


FIGURE 1. NMR SPECTRUM OF VI

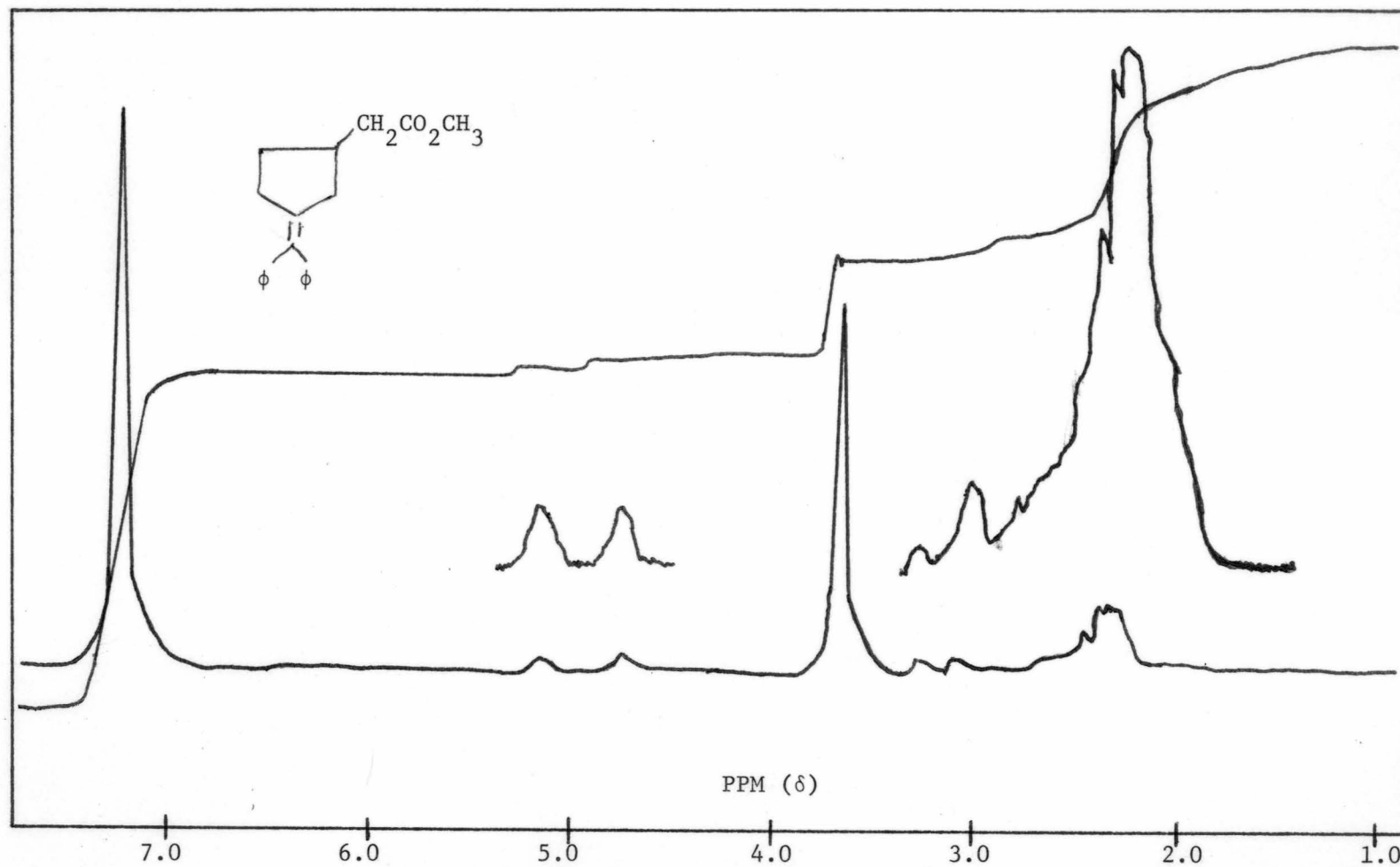


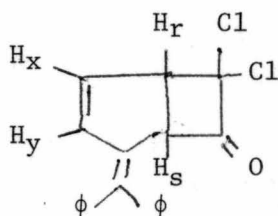
FIGURE 2. NMR SPECTRUM OF VII

## DISCUSSION

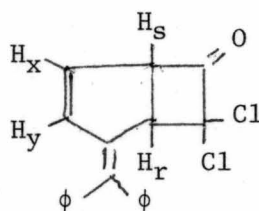
### Interpretation of NMR Spectra

#### Diphenylfulvene Adduct

The cycloaddition of dichloroketene to diphenylfulvene may form two isomers, IIa or IIb. The Diels-Alder adduct was rejected



IIa



IIb

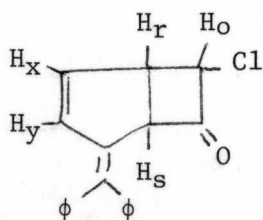
on the basis of the infrared spectrum. The carbonyl absorption at  $1804\text{ cm}^{-1}$  is reasonable for a cyclobutanone ring<sup>28</sup> but not representative of a cyclopentanone ring. A nmr spectrum was obtained and the chemical shifts and coupling constants are listed in Table 1. The values for  $J_{sx}$  and  $J_{rx}$  were measured as 0.9 and 2.9 Hz, respectively. The value for  $J_{rx}$  is too large for long range coupling as depicted in structure IIb. The value of 0.9 Hz for  $J_{sx}$  is acceptable for the system represented in IIa. A Dreiding model of IIa was constructed. The Barfield relationships<sup>29</sup> for allylic and saturated systems were used as approximations and gave as results, respectively,  $J_{ry}\text{ calcd} = -1.75\text{ Hz}$  ( $J_{ry} = -1.8$ )

and  $J_{sx}$  calcd = 0.6 Hz. Therefore, structure IIa was designated as the isomer formed.

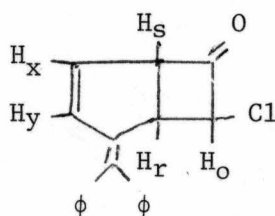
Table 1. NMR Spectral Data for Compound II

<u>Chemical Shift</u>	<u>Number of Protons</u>	<u>Coupling Constant (cps)</u>	<u>Proton Assignment</u>
7.28	10		<u>ArH</u>
6.52	1	$J_{yx}$ 5.7	<u>Hy</u>
		$J_{yr}$ 1.8	
6.02	1	$J_{xy}$ 5.7	<u>Hx</u>
		$J_{xr}$ 2.9	
		$J_{xs}$ 0.9	
4.73	1	$J_{sr}$ 6.6	<u>Hs</u>
		$J_{sx}$ 0.9	
4.22	1	$J_{rs}$ 6.6	<u>Hr</u>
		$J_{rx}$ 2.9	
		$J_{ry}$ 1.8	

Verification of this assignment was obtained by reducing one of the chlorine atoms and studying the nmr spectrum of the mono-chloro adduct. The adduct could be formed as structure XIa or XIb. The carbonyl absorption of the infrared spectrum was



XIa



XIb

consistent for a cyclobutanone ring. The chemical shifts and coupling constants are listed in Table 2. The values of  $J_{sx} = 1.0$  Hz and  $J_{rx} = 2.5$  Hz indicate that Hr and Hx are vicinal protons. In addition the value for  $J_{sx}$  is more reasonable for long range

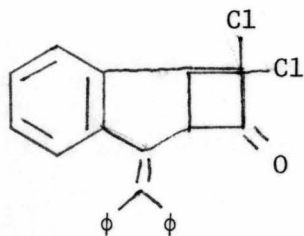
coupling than the value for  $J_{rx}$ . Similarly,  $J_{or} = 9.0$  Hz and  $J_{os} = 3.0$  Hz indicate that  $H_o$  and  $H_r$  are also vicinal protons. Only structure XIa meets these criteria.

Table 2. NMR Spectral Data for Compound XI

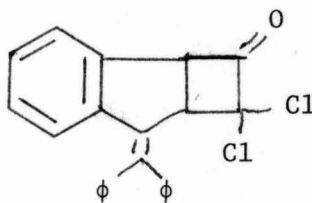
<u>Chemical Shift</u>	<u>Number of Protons</u>	<u>Coupling Constant (cps)</u>	<u>Proton Assignment</u>
7.30	10		<u>ArH</u>
6.48	1	$J_{yx} 6.0$	<u>Hy</u>
		$J_{yr} 1.5$	
		$J_{yx} 0.5$	
6.09	1	$J_{xy} 6.0$	<u>Hx</u>
		$J_{xr} 2.5$	
		$J_{xs} 1.0$	
5.07	1	$J_{or} 9.0$	<u>Ho</u>
		$J_{os} 3.0$	
4.36	1	$J_{sr} 7.0$	<u>Hs</u>
		$J_{so} 3.0$	
		$J_{sy} 1.0$	
		$J_{sx} 0.?$	
4.08	1	$J_{ro} 9.0$	<u>Hr</u>
		$J_{rs} 7.0$	
		$J_{rx} 2.5$	
		$J_{ry} 1.5$	

#### Benzodiphenylfulvene Adduct

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



IVa



IVb

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

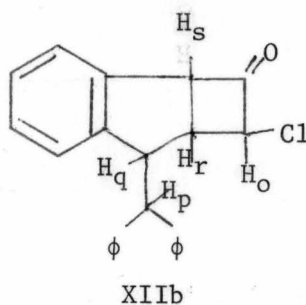
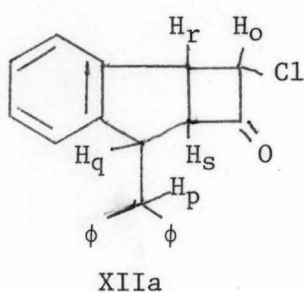


Table 3. NMR Spectral Data for Compound XII

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

XIIa was the correct structure. The coupling constants obtained from a Dreiding model gave reasonable results ( $J_{rq}$  calcd = -0.1 Hz,  $J_{rq}$  = -0.15 Hz). The PQ coupling constant was satisfactory when  $H_p$  was placed trans to  $H_q$ .

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.

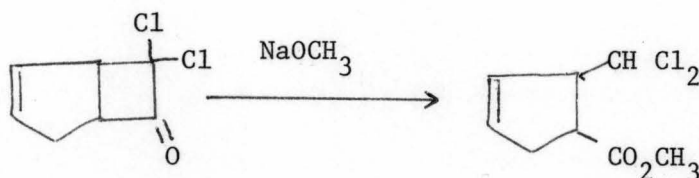
Table 4. Results from Computer Analysis of OPQRS

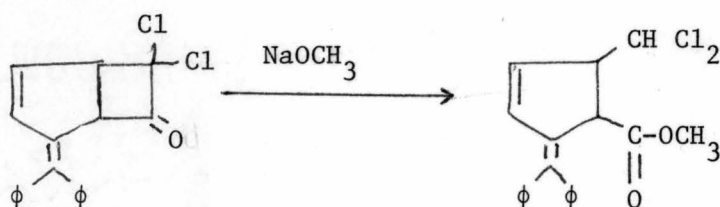
Proton Assignment	Chemical Shift	Coupling	Coupling Constant (cps)
<u>Ho</u>	4.96612	OP	0
<u>Hp</u>	4.56609	OQ	0
<u>Hq</u>	4.52081	OR	8.671
<u>Hr</u>	4.04953	OS	2.321
<u>Hs</u>	3.77501	PQ	12.272
		PR	0
		PS	-0.443
		QR	-0.149
		QS	7.647
		RS	7.414

RMS error of fit = 0.310

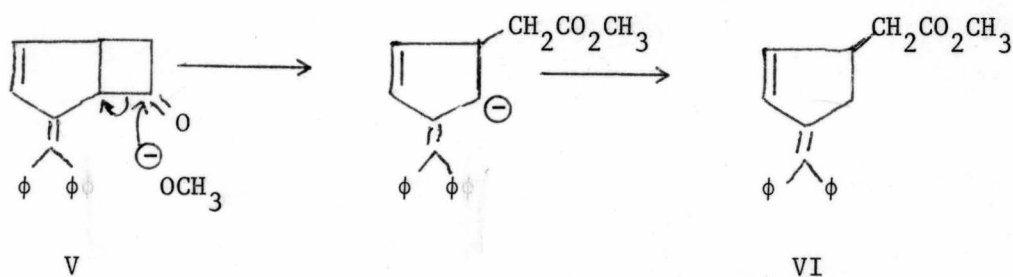
#### Degradation of II

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<sup>1</sup> 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 analogous 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.



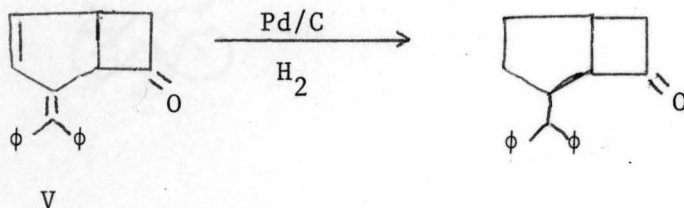
Complications ensued when VI was found to be unstable in air. Storage of freshly chromatographed VI under nitrogen, covered with foil, and placed in the refrigerator only succeeded in retarding



the decomposition. The conditions favorable to decomposition suggested an oxidation reaction might be occurring. The cyclic double bonds of 2,3,4,5-tetraphenylfulvene<sup>30</sup> and dimethylfulvene<sup>31</sup> 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<sup>32</sup> and palladium on silicon dioxide.<sup>33</sup> 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.<sup>34</sup> 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<sup>35</sup> 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.<sup>36</sup> These examples seemed analagous 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.

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## 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.