6,6-DIARYL FULVENES
6,6-DIARYL FULVENES.
REDUCTION TO BENZHYDRYL CYCLOPENTADIENE
BY AMIDE BASES

By

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SCOPE AND CONTENTS:

This work was started to investigate new methods of synthesizing certain fulvenes. It was hoped that nucleophilic aromatic substitution of chlorine on 6,6-bis-(p-chlorophenyl)fulvene would provide an alternate route for the preparation of para-substituted 6,6-diphenyl fulvenes which had previously been prepared through the appropriately para-substituted benzophenone and cyclopentadienide (1,2). Attempts to prepare these substituted 6,6-diphenylfulvenes were unsuccessful.

Secondly, a method of alkylating certain fulvenes in the cyclopentadiene ring was studied. With this in mind, 6,6-diphenylfulvene was treated with various nucleophiles which should give the relatively stable cyclopentadienide intermediate if the base adds to the exocyclic carbon atom. Alkylation of this anion, followed by expulsion of the nucleophilic group and a proton should then generate a new fulvene alkylated in
the cyclopentadiene ring. In no case was any alkylated fulvene isolated. The major reaction products were two isomers of benzhydryl cyclopentadiene, rather than the expected alkylated fulvenes. The benzhydryl cyclopentadiene (mixture of two isomers) appears to have resulted from a reduction reaction.

Since fulvenes of the type under study are generally unstable, an attempt was made to trap these alkylated fulvenes, if these were present, as their Diels-Alder adducts with tetracyanoethylene (TCNE). This attempt gave the adduct from one of the isomers of benzhydryl cyclopentadiene. The adducts from the other two possible isomers of benzhydryl cyclopentadiene were not detected. This result is an indication of the different reactivities of these isomers to TCNE.

From the absence of TCNE adducts of the expected alkylated fulvenes, it was concluded that these fulvenes had not materialized in the attempted alkylation.
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The author wishes to express his sincere appreciation to Dr. J. Warkentin for his continued advice and encouragement throughout the course of this investigation.

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I Attempted Nucleophilic Aromatic Substitution in 6,6-bis-\(\text{p-Chlorophenyl}\) fulvene.

The primary objective under this section was to find a new method of synthesizing para-substituted 6,6-diphenyfulvenes from 6,6-bis-\(\text{p-Chlorophenyl}\) fulvene. Secondly, it appeared interesting to determine the relative activating power of the 6-fulvenyl group and other common activating groups such as the nitro group, in nucleophilic aromatic substitution reactions.

According to the common mechanism of nucleophilic aromatic substitution, that reaction in the case of 6,6-bis-\(\text{p-Chlorophenyl}\) fulvene, would produce intermediate 1, which is stabilized by extensive delocalization.
By comparing the rates of nucleophilic aromatic substitution of 6,6-bis-(p-chlorophenyl)fulvene and p-halo-nitro-benzene, one might determine the relative activating power of the 6-fulvenyl group towards nucleophilic aromatic substitution. This would be a novel activating group, since all other activating groups contain hetero atoms. Synthetically, this scheme would be of some value, although para-substituted 6,6-diphenylfulvenes have been prepared in reasonable yield by G. Kreuze, et al.,(2) using the appropriately substituted benzophenones and cyclopentadienide. As it turned out the 6-fulvenyl substituent is not sufficiently activating to make the reaction go under relatively mild conditions.

II Alkylation of Fulvenes

From the unsuccessful attempts to effect nucleophilic aromatic substitution in 6,6-bis-(p-chlorophenyl)fulvene, it appeared that addition of the nucleophilic group at the exocyclic carbon atom of the fulvene was a more likely
process than substitution of chlorine on the phenyl carbon. This is not unlikely, considering the dipolar nature of the fulvenes and their reactivity towards organo lithium compounds (3,4).

Alkyl- and aryl-lithium compounds readily add to the exocyclic carbon atom of fulvenes giving a lithium-fulvenyl intermediate. From this evidence it seemed that lithium amide bases would also add to the 6-carbon atom in fulvenes to give fulvenyl intermediates such as 2.

Addition of a base at the exocyclic carbon atom, followed by alkylation of the intermediate cyclopentadienide 2 and elimination of the nucleophilic group and a proton would then generate a new fulvene with an alkyl group in the cyclopentadiene ring (equations 2,3). This would be a new and simple method of placing one or more alkyl groups in the cyclopentadiene ring of fulvenes.
In the above reaction sequence, $Y^-$ must be a strong nucleophile for addition to occur at the exocyclic carbon of the fulvene. The resonance stability of the cyclopentadienide 2 would be expected to drive the reaction towards the anion. The bimolecular substitution of the alkylating agent with the cyclopentadienide 2 should then yield the three possible isomers 3, 4, and 5. Elimination of the nucleophilic group could then occur through deamination yielding the new fulvenes 6 and 7.

That addition and elimination should occur in this system is supported by the work of E. Sturm and K. Hafner (5).
who have described a simple synthesis of fulvene and its 6-alkyl-derivatives. They found that the reaction of 6-dimethylamino-fulvene and methyl lithium gave the expected cyclopentadienide-lithium compound 8. On hydrolysis at 0° this salt was converted to the corresponding base, which rapidly lost dimethyl amine above 100° under high vacuum, or during chromatography to give 6-methylfulvene in 81% yield.

\[ \text{8} \]

The similarity between intermediates 2 and 8 is obvious, if \( Y = -N(CH_3)_2 \) and \( R_2 = -C_6H_5 \). The reactions leading to these intermediates differ in the order of introduction of the groups.
HISTORICAL INTRODUCTION

The nature of the bonding in fulvenes can be described qualitatively as a mesomeric superposition of the covalent structure A and the polar structure B.

\[
\begin{align*}
\text{A} & \quad \text{B} \\
\begin{array}{c}
\text{R}= R' = \text{H, Aryl, Alkyl} \\
\end{array}
\end{align*}
\]

The contribution of the dipolar structure B to the resonance in these fulvenes in the ground state amounts to only 5 - 10\% (6). This result may be assessed from the dipole moments of 6,6-dialkylfulvenes, and 6,6-diarylfulvenes. 6,6-Dialkylfulvenes have a dipole moment of about 1.4 D (7), whereas the corresponding 6,6-diarylfulvenes have moments close to 1.3 D (2). In either case, the dipole is directed towards the ring, leaving a partial negative charge on the ring and a partial positive charge on the exocyclic carbon. Quantum mechanical calculations (6) indicate the same general premise in more precise terms by showing the residual charge on the
various carbon atoms in the fulvene molecule. With increasing electron-donating character of substituents at carbon six, the polar structure B becomes more significant (1,8). This polarity can be explained in accordance with Hückel's rule (9) by stabilization through the cyclic conjugated system of six $\pi$ electrons, which is present in this structure, just as it is in cyclopentadienyl-metal compounds. In agreement with this concept, the bond character of the fulvenes can be shifted either towards the olefinic or towards the benzenoid side by variation of the substituents at carbon atom six (12).

Many of the reactions of fulvenes can be rationalized by consideration of their dipolar nature. The benzenoid character is useful in correlating the reactivity of fulvenes with nucleophilic and electrophilic reagents, while the olefinic character can account for such typical olefinic behaviour as the Diels-Alder additions of fulvenes to dienophiles.

Reactions of fulvenes with organo-metallic reagents can best be interpreted by considering the polarity of the exocyclic double bond. For example, reaction of 6,6-dimethylfulvene with phenyl-lithium (10) leads to 2 below, the expected product in view of the distribution of charge density of the fulvenes.
Hydrolysis of the intermediate complex gives substituted cyclopentadienes such as 10.

Similarly, 6,6-diphenylfulvene adds phenyl lithium to give an intermediate complex 2 where the methyl groups are replaced by phenyl groups.\(^{(10)}\).

One would expect that if carbonionic reagents such as phenyl lithium add to fulvenes in the above manner, then certain hetero atom anions would also add to give intermediates such as 11.

\[ R = -\text{H}, -\text{CH}_3, -\text{CH}_2\text{CH}_3 \]
As discussed in the General Introduction, attempts were made to alkylate this intermediate, if present. Deamination of the resultant Mannich base would then lead to an alkylated fulvene. Alkylation of the aryl-cyclopentadienyl anion appears likely, as evidenced by the work of McLean and Haynes (11). They have shown that the cyclopentadienide anion undergoes methylation quite readily to form methyl cyclopentadienes, and more highly methylated products.

The intermediate \( \text{I} \) differs from methyl cyclopentadiene mainly in the size of the substituent on the cyclopentadiene anion. If the steric factor in methylation is not too large, then this intermediate should also readily undergo methylation, as does methyl cyclopentadienide.

Electrophilic substitution in fulvene systems has not attracted much attention, since such experiments have so far been of doubtful success. The main application to date is the formylation reaction using Vilsmeier's complex (12). This reagent, formed from dimethyl formamide and phosphorous oxychloride, readily converts 6,6-diphenylfulvene into 1-formyl-6,6-diphenylfulvene. The theoretical electron density distribution can be used to rationalize the position of substitution (14).

Direct alkylation of fulvenes in the cyclopentadiene ring, using the appropriate electrophile leads to
polymeric products. Although 6,6-diphenylfulvene and 6,6-dimethylfulvene undergo alkylation (8) at -80°C, the σ-complex formed is stable only at -80°C.

\[ \text{R} \quad \text{C} \quad \text{R'} \quad \text{C} \quad \text{R} \quad \text{R'} \]

\[ \text{R} \quad \text{C} \quad \text{R'} \quad \text{C} \quad \text{R} \quad \text{R'} \]

(4)

The attempted conversion of the fulvenium salts into substituted fulvenes leads to polymeric products. Thiec and Wiemann (14) observed a similar polymerization with unsubstituted fulvenes.

One of the best known reactions where fulvenes exhibit their olefinic character is the Diels-Alder diene synthesis (15,16). Fulvenes react with many dienophiles to give the expected adducts. A typical example is the reaction of 6,6-dialkyl- and 6,6-diaryl-fulvenes with tetracyanoethylene (17). With alkyl fulvenes the reaction is quantitative.

Other typical olefinic reactions exhibited by certain fulvenes are autoxidation to form peroxides, and polymerization. 6,6-Dimethylfulvene yields a bis-peroxide to which the following structure has been assigned (18,19).
From 6,6-diphenylfulvene a polymer has been obtained at 140°, while at lower temperature a crystalline dimer has been formed (20). This type of dimer is formed by a Diels-Alder reaction in which the fulvene behaves as both diene and dienophile.

One type of reaction which has not received any attention is nucleophilic aromatic substitution in p-halo-substituted diphenylfulvenes of the following type.

\[
\begin{align*}
X &= \text{halogen} \\
R &= \text{aryl}
\end{align*}
\]

As already pointed out in the General Introduction, the substitution of halogen by bases would provide a simple means of synthesizing para-substituted diphenylfulvenes from a single p-halo-substituted diphenylfulvene.
(i) Analysis of Compounds

Column chromatography was done on neutral alumina (Fisher Scientific, 80-200 mesh), and on silica gel (Grace Chemical, 100-200 mesh). Thin layer chromatography (TLC) (Eastman Chromagram Kit) on silica gel and alumina was used in many cases to determine the number of components in the reaction mixture, and the purity of column chromatographed fractions. Reagent grade solvents (Fisher Scientific, Mallinckrodt) were fractionated through a three foot Vigreux column prior to use in chromatography, or in recrystallization. Solvents required for reactions were purified by published procedures.

Uncorrected melting points were determined using a Thomas "Unimelt" capillary melting point apparatus.

The major means of analysis was NMR spectroscopy. The NMR spectra were recorded on a Varian A-60 spectrometer and a HA-100 spectrometer, in carbon tetrachloride or acetone-d₆ solution (tetramethyldisilane as internal reference). The infra-red spectra of compounds were recorded on a Beckman I.R.5 instrument and a Perkin-Elmer 337 Grating Infrared Spectrophotometer, employing KBr wafer, or carbon tetrachloride solution. The ultra-violet spectra
were recorded on the Bausch and Lomb Spectronic 600 in n-hexane (Fisher Spectrograph) solutions. Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6A (80eV) mass spectrometer.

The expected absorptions in the NMR and UV spectra were observed for all the previously reported compounds that have been prepared. These spectral data are normally not reproduced in detail in this Thesis.

The spectra of some products is presented in tabular form in the section labelled Results and Discussion.

Microanalysis were performed by A. B. Gygli. All attempted alkylation reactions were conducted under an atmosphere of dry nitrogen.

(ii) Chemicals

Petroleum ether refers to the fraction boiling between 65-110°.

Ether used as solvent for reactions refers to anhydrous ether dried over sodium wire.

The amines needed to make the various lithium amide bases for the attempted alkylation reactions were distilled just before use and kept under anhydrous conditions. n-Butyl lithium was obtained as a solution in n-hexane from Foote Mineral Company.

Other reagents used were all reagent grade chemicals and were not purified to any degree.
**Preparation of Fulvenes**

(i) **Synthesis of 6,6-bis-(p-Chlorophenyl)fulvene**

The method used for synthesizing 6,6-bis-(p-chlorophenyl)fulvene was a variation of that described by G. Kresze (1) and K. Ziegler (21).

Cyclopentadiene monomer was distilled from dicyclopentadiene immediately before use. The fulvene synthesis was carried out in a three-necked flask equipped with a gas inlet tube, a dropping funnel, a magnetic stirrer, a dry-ice condenser, a thermometer, and a CaCl₂ drying tube. A slow stream of purified nitrogen was passed through the system during the course of the reaction.

Freshly cut sodium (3.10 g, 0.134 g atom) was added to 24.0 ml of tetrahydrofuran in small portions. A catalytic amount of t-butyl alcohol (1.0 ml) was added, followed by dropwise addition of cyclopentadiene (30.0 ml, 0.27 mol). The wine colored solution was cooled to maintain the temperature below 35°. After four hours all the sodium had reacted. p-p'-Dichlorobenzophenone (24.0 g, 0.096 mol) in 130 ml of tetrahydrofuran was added dropwise over a two hour period. After addition of the ketone, the mixture was stirred continuously at 25° for a further two hours. The product was poured into a mixture of ice water and ether. After extracting the aqueous phase several times with ether, the combined
ether extracts were dried and concentrated giving a dark red oil. The oil was chromatographed on a column of neutral alumina using benzene as eluant. Concentration and crystallization from pet ether under oxygen-free conditions, yielded 16.0g (55%) of dark red rhombic crystals: mp 108-110° (lit (2) mp 112-113°); nmr (CCl₄) 8 7.27 (m,8,phenyl), 6.52 (m,2,viny1), 6.13 (m,2, vinyl).

(ii) Synthesis of 6,6-Diphenylfulvene

This fulvene was synthesized using the above procedure for preparing 6,6-bis-(p-chlorophenyl)fulvene. The following reagents were used:

- sodium, (16.0g,0.70 g atom)
- t-butyl alcohol, (1.5 ml)
- benzophenone, (100g, 0.55 mol)
- cyclopentadiene, (65 ml, 0.75 mol)

Recovery after chromatography and crystallization gave 65g (52%) of 6,6-diphenylfulvene; mp 78-80° (lit (2) mp 81.5-82°); nmr (CCl₄) 8 7.29 (s,10,phenyl), 6.50 (m,2,vinyl), 6.20 (m, 2,vinyl).

If crystallization did not proceed immediately upon cooling of the fulvene solution, it was difficult to obtain the fulvene in pure crystalline form.

(iii) Synthesis of 6,6-Dimethylfulvene

The procedure described is that used by W. Freiesleben (22). The reaction was carried out at 25° under a slow stream of nitrogen. Freshly distilled
cyclopentadiene monomer (35g, 0.5mol) and a 25-30% v/v solution of methylamine in water (9ml, 0.075mol) were added in that order to acetone (30g, 0.5mol). After a period of stirring (1½ hr) the yellow organic layer was separated, and dried over sodium sulfate. Distillation gave 35g (67%) of yellow oil, bp 36° (5torr) (lit (22) bp 46° (11mm)); nmr (CCl₄) δ 6.34 (s,4, vinyl), 2.08 (s,6, methyl). Both the NMR and IR spectra confirmed the structure (22).

II Attempts at Nucleophilic Aromatic Substitution in

6,6-bis-(p-Chlorophenyl)fulvene

General

The usual procedure employed in the reaction of 6,6bis-(p-chlorophenyl)fulvene with various nucleophiles involved heating a solution of the fulvene and the base under oxygen-free, anhydrous conditions at constant temperature for several hours. Table I lists the various bases employed in the investigation, along with the reaction conditions and results. Typical reaction conditions with various bases are presently described.

Specific Nucleophiles

a) Sodium methoxide

Freshly cut sodium (0.111g, 0.0048g atom) was dissolved in 20 ml of methyl hydrate in a flask equipped with a condenser and a drying tube. Purified nitrogen was
slowly passed through the system. After adding 6,6-bis-(p-chlorophenyl)fulvene (0.304 g, 0.001 mol), the mixture was heated at reflux for 18 hours. The resultant dark brown solution was added to a mixture of 200 ml of water and 30 ml of carbon tetrachloride. The organic layer was separated, dried, and concentrated giving a dark brown oil. The NMR spectrum of the oil was essentially the same as the spectrum of the substrate.

When this reaction was carried out in a sealed tube, the tube was heated in an autoclave (1000ml cap, Parr Instrument Company) containing solvent so as to minimize the danger of bursting. The autoclave was heated at the specified temperature (100-160°, Table I) for several hours. NMR spectra of the crude reaction product indicated the presence of unreacted starting fulvene and other broad peaks which were not interpreted.

b) Piperidine

A thick walled glass tube was partially filled with 6,6-bis-(p-chlorophenyl)fulvene (1.00 g, 0.00325 mol) and piperidine (10 ml, 0.10 mol). After the contents were cooled, the tube was sealed under vacuum. The mixture was heated at 150° for 60 hours. Solvent was removed under vacuum and the product was analysed by thin-layer chromatography which indicated three components. A solution of the reaction product in benzene was chromatographed on a column of neutral alumina with benzene as
eluant. The NMR spectra of the three fractions collected did not indicate the presence of either 6,6-bis-(p-piperidinophenyl)fulvene or 6-p-chlorophenyl-6-(p-piperidinophenyl)-fulvene.

c) Sodium p-cresoxide

Sodium p-cresoxide was chosen as the nucleophile to facilitate identification of the expected substituted fulvene by NMR analysis.

The reagent p-cresoxide was prepared by adding one equivalent of freshly distilled p-cresol to one equivalent of sodium hydroxide in water. Solvent was removed under high vacuum. Excess p-cresol was removed by several ether extractions of the aqueous solution. Water was again removed under vacuum, and the white product placed in a desiccator under vacuum.

In a typical reaction, sodium p-cresoxide (3.38g, 0.0260mol) and 6,6-bis-(p-chlorophenyl)fulvene (1.10g, 0.0035mol) were dissolved in 25 ml of freshly distilled dimethyl sulfoxide in a heavy walled glass tube. The contents were cooled under nitrogen and the tube was sealed under vacuum. A reaction appeared to occur, as the initial red colored solution changed to dark green, and after heating for one-half hour, to dark blue. This color change was not observed when the procedure was repeated but without the fulvene. After heating the solution in a steam bath for 20 hours, the viscous dark
blue solution was added to a mixture of water and ether. The dark brown ether phase was separated and washed with water to remove dimethyl sulfoxide and excess base. Drying and concentration of the ether solution left a dark brown residue. The residue was chromatographed with benzene on a column of neutral alumina.

Three fractions were collected. The last fraction had a NMR spectrum identical to that of the last fraction from the piperidine reaction. This result suggests that the product is one of self reaction of the starting material. Recrystallization of the first fraction from a mixture of carbon tetrachloride and pet ether gave 50 mg of yellow crystals, mp 111-113°. The NMR spectrum consisted of a multiplet at 7.2δ, a broad singlet a 6.6δ and a multiplet at 3.5δ.

Since the NMR data was not consistent with the structure for the expected substituted fulvenes or the substrate fulvene, no attempt was made to identify this compound.

A test for halide ion in the aqueous phase of the reaction mixture, using silver nitrate solution, was negative.

d) Sodium iodide

A mixture of 6,6-bis-(p-chlorophenyl)fulvene (0.15 g, 0.0005 mol) and sodium iodide (0.300 g, 0.002 mol) in 3 ml of methyl ethyl ketone (MEK) was heated in a sealed glass tube
at 65° for three hours. Mass spectra and UV spectra of the reaction product did not show evidence of the expected substituted fulvenes.

III Attempted Alkylation of 6,6-bis-(p-Chlorophenyl) fulvene

Table II lists details of the reaction of 6,6-bis-(p-chlorophenyl) fulvene with sodium iodide and methyl iodide under various reaction conditions. During these attempts, 6,6-bis-(p-chlorophenyl) fulvene was used rather than 6,6-diphenyl fulvene, as the former was more readily available at that time. The usual procedure involved dissolving the sodium iodide in the appropriate solvent, adding the fulvene and methyl iodide, and heating the mixture for several hours. The resultant mixture consisted of either unreacted substrate alone or starting fulvene and the Diels-Alder dimer of 6,6-bis-(p-chlorophenyl) fulvene 12.

A typical reaction is described below. Sodium iodide (2.40g, 0.016mol) in 20ml of dimethyl sulfoxide was heated under a nitrogen atmosphere to dissolve the salt. Methyl iodide (2.0ml, 0.032mol) and 6,6-bis-(p-chlorophenyl) fulvene (0.500g, 0.0016mol) were added, and the mixture was heated at 60° on a steam bath for 15 hours. The reaction mixture was added to a water-ether mixture. Separation, drying, and concentration
of the organic layer gave an orange solid. This was recrystallized from abs ethanol-pet ether. Small yellow crystals formed, and were separated from the red solution. Recrystallization from acetone yielded 0.075g of colorless crystals. mp 153-4°; nmr (CCl₄) δ 6.99 (m,16, phenyl), 6.34 (d,1,H₆), 6.02 (s,2,H₄), 5.89 (d,1,H₅), 3.65 (m,1,H₇), 3.30 (m,2,H₆,H₇), 2.80 (m,1,H₈).
Crystallization of the red solution gave 70% recovery of starting fulvene.

![Chemical Structure](attachment:image.png)

IV Attempted Alkylation of 6,6-Diphenylfulvene

General

Table III list the reaction conditions for the attempted alkylation of 6,6-diphenylfulvene with four different amide bases. In all cases methyl iodide was
used as the alkylating agent. A typical reaction involved preparation of the lithium amide from n-butyl lithium and the appropriate anhydrous amine in some solvent at 0° under a steady stream of nitrogen. A solution of the fulvene was added dropwise, followed by methyl iodide. The mixture was stirred for several hours. In some cases products were chromatographed and the various fractions were analysed by NMR spectroscopy.

Specific Bases

a) Lithium diethylamide

The reaction vessel consisted of a three-necked round bottom flask equipped with a nitrogen inlet tube, a dropping funnel, a thermometer, a magnetic stirrer, a dry-ice acetone condenser, and a CaCl₂ drying tube. The entire reaction was carried out in an atmosphere of purified nitrogen. n-Butyl lithium (86ml, 0.13mol; 15.05% solution in n-hexane) was added to the reaction flask from a syringe. After evacuation to remove n-hexane, 30 ml of ether was added which dissolved the white organo-lithium salt. Anhydrous diethylamine (14ml, 0.138mol) in 25 ml of ether was added dropwise with continuous stirring at 0°. When all of the amine had been added, the Gilman test (23) was negative, which indicated that all the alkyl lithium had reacted. A solution of 6,6-diphenyl-fulvene (11.5g, 0.050mol) in 30 ml of ether was added
dropwise to the colorless solution at 0°. The red fulvene color disappeared almost immediately. Upon addition of methyl iodide a white precipitate formed which increased in mass in direct proportion to the amount of methyl iodide added. After addition of all the methyl iodide, the mixture was stirred at 0° for a further two hours. (For some reactions the mixture was heated to 35° for another three hours). The white solid was filtered under a nitrogen atmosphere in the dark, and washed with anhyd ether giving 36 g of white solid. The NMR spectrum of this solid in D$_2$O was identical to that of the quarternary ammonium salt, diethyl-dimethyl ammonium iodide. The orange ether solution was concentrated to 150 ml and a further portion of methyl iodide (13 ml, 0.2 mol) was added. The solution was stirred for five hours at 25° with no apparent change in color of the solution. Occasionally, the mixture was heated up to a maximum of 40° to promote deamination of the supposed intermediates 3 and 4, where R$_1$ = R$_2$ = -C$_6$H$_5$, R$_3$ = -CH$_3$, and Y = -NET$_2$. For some reactions sodium acetate-acetic acid buffer solution was added at 25° with constant stirring and gentle heating of the heterogeneous system. There was no apparent change in color of the ether layer. A change back to a deep red solution would indicate the formation of a new fulvene, hopefully 1- and 2-methyl-6,6-diphenylfulvene. The ether layer
was separated, dried, and concentrated giving 12.5g of a viscous red brown oil. A benzene solution of the oil was eluted on a column of neutral alumina using benzene and benzene-ethyl acetate mixtures as eluting solvents. The benzene fractions which gave identical NMR spectra were combined giving 8.8g of an orange oil. (As described later in the experimental section, 1.0g of this oil was treated with tetracyanoethylene to trap the expected 1- and 2-methyl-6,6-diphenylfulvenes.) According to thin-layer chromatography, this orange oil contained four components: a light sensitive colorless component, two yellow components, and a small amount of another colorless component. To separate these four components, the oil was chromatographed in the dark on a 5'x2½" column of silica gel, using various ratios of pet ether—benzene as well as benzene and mixtures of benzene—ethyl acetate. The four components were separated with some difficulty. The first and major fraction (6.0g) eluted with a 1:1 benzene—pet ether mixture was a colorless oil whose NMR spectrum was almost identical to that of the crude reaction product, the viscous red brown oil. This indicates that this colorless oil was the major reaction product in the reaction. Spectral data on the other minor components proved inconclusive. Attempts to crystallize the colorless oil were unsuccessful. The NMR spectrum of this oil was identical to that of
benzhydryl cyclopentadiene (mixture of isomers), which was prepared independently. Spectral and chemical data for the colorless oil are listed in Tables V and VI.

b) Lithium amide

The apparatus was the same as in part a) above. The dark blue amide solution was prepared by adding lithium metal (0.09g, 0.013g atom) to liquid ammonia (100ml). After the addition of fulvene (2.20g, 0.010mol) in 20ml THF, the reaction mixture turned a dark green color, indicating that the fulvene had reacted. The ammonia was removed under vacuum and replaced by THF. Under an atmosphere of nitrogen, methyl iodide (7.00ml, 0.112mol) was added, producing a clear light orange solution. The mixture was heated to 45° to encourage the substitution and deamination reactions. The usual take-down procedure using a mixture of carbon tetrachloride and water was followed. After drying and concentration of the organic layer, a red oil was obtained with NMR spectrum identical to that of 6,6-diphenylfulvene. Reaction conditions are tabulated in Table III.

c) Lithium dimethylamide

With dimethylamide as base the conditions were essentially the same as described for part a) above. Reaction conditions are listed in Table III.

Following the addition of methyl iodide the
reaction mixture was stirred for two hours at 0° and at 25° for three hours. The reaction was terminated at this stage. Assignment of the NMR spectrum of the crude reaction product, a red brown oil, is listed in Table VII. The product was a mixture of 6,6-diphenylfulvene and two isomers of benzhydryl cyclopentadiene.

d) Lithium cyclohexylamide

Attempted alkylation via lithium cyclohexylamide and methyl iodide was carried out at 25°, using conditions similar to those described in part a) above. The colorless amide solution turned red when the fulvene was added. After 1 hr the red fulvene color remained, indicating that the fulvene did not react with the base under these conditions. This was confirmed by recrystallizing 75% of the substrate fulvene from the reaction mixture.

V Hydrolysis of Intermediate from 6,6-Diphenylfulvene and Lithium Diethylamide

This reaction was carried out to determine the existence of the lithium cyclopentadienide 2, where $R_1=R_2=-C_6H_5$, and $Y=\text{NET}_2$. The apparatus and reaction conditions were the same as those described in Section IV, part a), up to the addition of methyl iodide. Instead of adding methyl iodide, water was added to the mixture at 5° with a resultant change in color from dark green to light yellow. The organic layer was washed with water until
the aqueous extract was at pH 7.5-8.0. Drying and concentration of the ether layer gave a dark red oil which consisted of at least seven components (by TLC).

The NMR spectrum of this oil was very complex. From the spectrum, the two major components of the reaction mixture were 6,6-diphenylfulvene and benzhydryl cyclopentadiene. It was not possible to determine the presence of mono-substituted cyclopentadiene from hydrolysis of intermediate 2.

VI Preparation of Benzhydryl Cyclopentadiene

This substitution reaction was carried out in a three-necked flask equipped with a gas inlet tube, a condenser, a dropping funnel, a drying tube, and a magnetic stirrer. The entire reaction was carried out under nitrogen at room temperature.

Freshly distilled cyclopentadiene monomer (2.31g, 0.035mol) in 10ml of tetrahydrofuran was added to the reaction flask. Sodium (0.410g, 0.018g atom) was added in small portions with continuous stirring. Chloro-diphenylmethane (2.03g, 0.010mol) in 10ml of tetrahydrofuran was added to the wine colored solution of sodium cyclopentadienide at 25°. After continuous stirring for six hours, water and ether were added to the reaction mixture, resulting in a light brown ether
layer. The ethereal layer was separated and extracted several times with water. Separation, drying, and concentration of the ether solution gave a light brown oil. After high vacuum evacuation to remove excess solvent and cyclopentadiene, a slightly brown oil was obtained (1.97g, 85%): nmr (CCl₄) δ 7.23 (s), 7.12 (s, 10, phenyl), (6.33 (d), 6.27 (m), 5.95 (m), 5.73 (q), 3, vinyl). 5.98 (s), 5.10 (m, 1, benzhydryl), 2.90 (m, 2, ring methylene). The NMR spectrum was identical to that of the colorless oil obtained from the attempted alkylation of 6,6-diphenylfulvene using lithium diethylanide and methyl iodide. A broad singlet at 7.23δ and a singlet at 5.98δ were from unreacted chlorodiphenylmethane.

VII Attempted Alkylation of 6,6-Dimethylfulvene

The attempted alkylation of 6,6-dimethylfulvene was carried out using lithium diethylanide as base and methyl iodide as alkylation agent. Vacuum distillation of the reaction product gave a mixture of at least three yellow oils, one of which was 6,6-dimethylfulvene. Attempts to trap the expected fulvenes with tetracyanoethylene were unsuccessful presumably due to highly alkylated fulvenes which react slowly for steric reasons. The reaction conditions used in the attempted alkylation of 6,6-dimethylfulvene are tabulated in Table IV. A typical reaction is described below.
The reaction vessel consisted of a three-necked flask equipped with a gas inlet tube, a dropping funnel, a thermometer, a dry ice-acetone condenser, and a drying tube. Nitrogen was passed through the system for the entire reaction. Diethylamine (4.1ml, 0.040mol) in 5ml of ether was added dropwise to n-butyl lithium (0.040mol) in 25 ml of ether at 0°, giving a colorless solution.

When the yellow ether solution of 6,6-dimethylfulvene (2.12g, 0.020mol) was added to the lithium diethylamide solution, the yellow fulvene color disappeared immediately forming a slightly cloudy solution. This change in color is evidence that a reaction had occurred. Methyl iodide (13ml, 0.20mol) was added rapidly at 0° giving a cloudy, slightly yellow solution. Stirring was continued at 25° for a further two and one-half hours. The white precipitate of diethyl-dimethyl ammonium iodide was filtered, and the ether solution was concentrated giving 2.0g of a yellow oil. The oil was dissolved in ether and extracted with water until the aqueous extract was only slightly basic. Drying and distillation of the ether gave a yellow oil. Distillation of the oil at 25° (2mm), yielded three fractions of yellow oils. These were labelled A-1, A-2, and A-3. A qualitative test for nitrogen on these fractions was negative.
VIII Reaction of Tetracyanoethylene with Fulvenes

The usual procedure involved dissolving equivalent amounts of the fulvene and tetracyanoethylene in a minimum amount of dry toluene, and mixing the two solutions at 25°. The resulting solution was kept at 0° to complete crystallization of the adduct. The colorless adducts were recrystallized from acetone-pet ether.

When this procedure was carried out using 6,6-diphenyldifulvene, colorless needles were obtained in 70% yield, mp 122-123° (lit (17) mp 112-113°). The NMR spectrum in acetone-\(d_6\) had a multiplet at 6.72\(\delta\), at 6.40\(\delta\) and at 4.12\(\delta\), area ratio 10:2:2 (theoretical ratio 10:2:2).

The Diels-Alder reaction on 1.0g of the 8.8g of orange oil described under Section IV, part a), gave colorless needles. These were twice recrystallized from acetone-pet ether to give 0.225g of colorless needles, mp 163-164°. This adduct is that of 1-benzhydryl-1,4-cyclopentadiene. The spectral and chemical data are given in Section (iii) of the Results and Discussion. The expected adduct of one of the alkylated fulvenes was not obtained.

The tetracyanoethylene reaction on the products of the attempted alkylation of 6,6-dimethylfulvene was unsuccessful. This result is discussed further in the section on Results and Discussion.
### Table I

**Attempted Nucleophilic Aromatic Substitution on 6,6-bis-(p-Chlorophenyl)fulvene**

<table>
<thead>
<tr>
<th>Experimental Reference Section</th>
<th>Reactants</th>
<th>Solvent</th>
<th>Reaction Type</th>
<th>Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>II(a)</td>
<td>6,6-bis-(p-chlorophenyl)fulvene (mol)</td>
<td>methyl hydrate</td>
<td>reflux</td>
<td>Time (hr)</td>
<td>Temp (°C)</td>
</tr>
<tr>
<td>(i)</td>
<td>0.001</td>
<td>0.55</td>
<td></td>
<td>18</td>
<td>70</td>
</tr>
<tr>
<td>(ii)</td>
<td>0.00016</td>
<td>0.57</td>
<td>methyl hydrate</td>
<td>43</td>
<td>70</td>
</tr>
<tr>
<td>(iii)</td>
<td>0.0005</td>
<td>1.9</td>
<td>methyl hydrate</td>
<td>3.5</td>
<td>108</td>
</tr>
<tr>
<td>(iv)</td>
<td>0.0033</td>
<td>14</td>
<td>methyl hydrate</td>
<td>20</td>
<td>160</td>
</tr>
<tr>
<td></td>
<td>piperidine (mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II(b)</td>
<td>piperidine</td>
<td>piperidine steam bath</td>
<td>10</td>
<td>100</td>
<td>Recovered substrate</td>
</tr>
<tr>
<td>(i)</td>
<td>0.0035</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ii)</td>
<td>0.0032</td>
<td>0.10</td>
<td>piperidine sealed tube</td>
<td>60</td>
<td>150</td>
</tr>
<tr>
<td>(iii)</td>
<td>0.0035</td>
<td>0.026</td>
<td>benzene sealed tube</td>
<td>20</td>
<td>160</td>
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<tr>
<th>Experimental Reference Section</th>
<th>Reactants</th>
<th>Solvent</th>
<th>Reaction Type</th>
<th>Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>II(c)</td>
<td>6,6-bis-(p-chlorophenyl)fulvene (mol) sodium p-cresoxide (mol)</td>
<td>DMSO</td>
<td>sealed tube</td>
<td>20 100</td>
<td>Inconclusive</td>
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<tr>
<td>(i)</td>
<td>0.0035</td>
<td>0.026</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ii)</td>
<td>0.0035</td>
<td>0.002</td>
<td>MEK</td>
<td>sealed tube 70</td>
<td>150</td>
</tr>
<tr>
<td>(ii)</td>
<td>0.0035</td>
<td>0.002</td>
<td>MEK</td>
<td>sealed tube 3</td>
<td>65</td>
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</table>

<table>
<thead>
<tr>
<th>II(d)</th>
<th>sodium iodide (mol)</th>
<th>MEK</th>
<th>sealed tube</th>
<th>3 65</th>
<th>Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i)</td>
<td>0.00035</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ii)</td>
<td>0.0035</td>
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### Table II

**Attempted Alkylation of 6,6-bis-(p-Chlorophenyl)fulvene**

<table>
<thead>
<tr>
<th>Experimental Reference Section</th>
<th>Reactants</th>
<th>Solvent</th>
<th>Reaction Type</th>
<th>Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>III(a)</td>
<td>6,6-bis-(p-chlorophenyl)fulvene (mol)</td>
<td>sodium methyl iodide (mol)</td>
<td>MEK</td>
<td>steam bath</td>
<td>Substrate</td>
</tr>
<tr>
<td>(i)</td>
<td>0.0010</td>
<td>0.0030</td>
<td>0.016</td>
<td>MEK</td>
<td>steam bath</td>
</tr>
<tr>
<td>(ii)</td>
<td>0.0016</td>
<td>0.016</td>
<td>0.0016</td>
<td>MEK</td>
<td>reflux</td>
</tr>
<tr>
<td>(iii)</td>
<td>0.0016</td>
<td>0.016</td>
<td>0.016</td>
<td>MEK</td>
<td>reflux</td>
</tr>
<tr>
<td>(iv)</td>
<td>0.0016</td>
<td>0.0016</td>
<td>0.030</td>
<td>DMSO</td>
<td>steam bath</td>
</tr>
<tr>
<td>(v)</td>
<td>0.0016</td>
<td>0.016</td>
<td>0.032</td>
<td>DMSO</td>
<td>steam bath</td>
</tr>
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</table>
Table III

Attempted Alkylation of 6,6-Diphenylfulvene

<table>
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<tr>
<th>Experimental Reference Section</th>
<th>Reactants and Concentration (mol)</th>
<th>Solvent</th>
<th>Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV(a)</td>
<td>6,6-diphenylfulvene</td>
<td>lithium diethylamide methyl iodide</td>
<td>Ether</td>
<td>Time (hr) Temp (°C)</td>
</tr>
<tr>
<td>(i)</td>
<td>0.010 0.017 0.040</td>
<td></td>
<td>16 25</td>
<td></td>
</tr>
<tr>
<td>(ii)</td>
<td>0.0075 0.015 0.012</td>
<td></td>
<td>7 25-60</td>
<td>was benzhydryl</td>
</tr>
<tr>
<td>(iii)</td>
<td>0.050 0.138 0.510</td>
<td></td>
<td>0-25</td>
<td>cyclopentadiene</td>
</tr>
<tr>
<td>IV(b)</td>
<td>lithium amide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.010 0.013 0.112</td>
<td>THF</td>
<td>3 -25,45</td>
<td>Substrate fulvene regenerated</td>
</tr>
<tr>
<td>IV(c)</td>
<td>lithium dimethylamide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.010 0.020 0.10</td>
<td>Ether</td>
<td>4 0-25</td>
<td>6,6-diphenylfulvene, benzhydryl cyclopentadiene</td>
</tr>
</tbody>
</table>

Continued ...
<table>
<thead>
<tr>
<th>Experimental Reference Section</th>
<th>Reactants and Concentration (mol)</th>
<th>Solvent</th>
<th>Conditions</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV(d)</td>
<td>6,6-diphenyl-cyclohexyl-methyl fulvene</td>
<td>lithium iodide</td>
<td>Time (hr)</td>
<td>Temp (°C)</td>
</tr>
<tr>
<td>Experimental Reference Section</td>
<td>Reactants and Concentration (mol)</td>
<td>Solvent</td>
<td>Conditions</td>
<td>Results</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>----------------------------------</td>
<td>---------</td>
<td>------------</td>
<td>---------</td>
</tr>
<tr>
<td>VI</td>
<td>6,6-dimethylfulvene, lithium diethylamide, methyl iodide</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i)</td>
<td>0.020 0.040 0.20</td>
<td>ether</td>
<td>3 25</td>
<td>3 yellow oils, A-1, A-2, A-3; A-1 was regenerated</td>
</tr>
<tr>
<td>(ii)</td>
<td>0.100 0.150 1.00</td>
<td>ether</td>
<td>5 25</td>
<td>6,6-dimethylfulvene</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

(i) Attempted Nucleophilic Aromatic Substitution

It is apparent from the results in Table I that the attempted substitution of a base for chlorine on 6,6-bis-(p-chlorophenyl)fulvene did not lead to the expected products, 6-p-chlorophenyl-6-p-Xphenylfulvene or 6,6-bis-(p-Xphenyl)fulvene, X=iodo, piperidino, p-cresoxy, methoxy.

In most attempts, substrate fulvene was recovered along with dark brown residue. Chromatography of the residue and NMR analysis of the various fractions did not indicate the presence of the above mentioned substituted fulvenes. When the reaction temperature was above 100°, only dark brown oils were obtained whose NMR spectra were uninterpretable.

As has already been discussed in the Historical Introduction, nucleophiles generally react at the exocyclic carbon atom of fulvenes, if they react at all. It appears that nucleophilic aromatic substitution does not occur readily in this fulvene system, presumably because the necessary intermediate 1 is not sufficiently stable, relative to the starting materials.
(ii) **Attempted Alkylation of 6,6-bis-(p-Chlorophenyl)fulvene**

Attempted alkylation of 6,6-bis-(p-chlorophenyl)-fulvene using iodide as nucleophile and methyl iodide as the alkylation agent (Table II), gave unreacted substrate fulvene and a small amount of 6,6-bis-(p-chlorophenyl)-fulvene dimer 12.

\[
\begin{align*}
&\text{p-Cl-C}_6\text{H}_4-C_6\text{H}_4-\text{p-Cl} \\
&\text{H}_a \quad \text{H}_f \\
&\text{H}_a \quad \text{H}_f \\
&\text{H}_a \quad \text{H}_f \\
&\text{H}_a \quad \text{H}_f \\
&\text{H}_a \quad \text{H}_f \\
&\text{p-Cl-C}_6\text{H}_4-C_6\text{H}_4-\text{p-Cl}
\end{align*}
\]

The assignments for \(H_a\), \(H_d\), \(H_e\), and \(H_f\) are based on the position of these protons in the NMR spectrum of dicyclopentadiene. From the NMR spectrum this compound is the Diels-Alder dimer of 6,6-bis-(p-chlorophenyl)-fulvene. Whether the Diels-Alder adduct of a fulvene is exo- or endo- depends on the dienophile used. In general, mixtures of exo- and endo- isomers are obtained (20). Dimerization and polymerization of fulvenes has been extensively surveyed by Day (15). From his review it appears that this dimer is not an unexpected product.
It appears that the addition of iodide ion at the exocyclic carbon atom of the fulvene does not compete with dimerization of 6,6-bis-(p-chlorophenyl)fulvene.

(iii). Attempted Alkylation of 6,6-Diphenylfulvene

The reaction conditions for the various alkylation attempts on 6,6-diphenylfulvene are listed in Table III. Spectral data on the reaction products with diethylamide and dimethylanide as base are given in Tables V, VI and VII. When lithium amide was used as base only starting fulvene was regenerated.

The alkylation reaction using lithium diethylamide as base was studied in detail. The major products were two isomers of benzhydryl cyclopentadiene, 14 and 15, and not the expected 1- and 2- methyl-6,6-diphenylfulvenes.

Since the mixtures of 14 and 15 could not be separated, the NMR assignments are of the mixture.
Table V

NMR spectrum for mixtures of 14 and 15

<table>
<thead>
<tr>
<th>Chemical Shift (ppm)</th>
<th>Proton(s)</th>
<th>Area Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.12 (s)</td>
<td>phenyl</td>
<td>10</td>
</tr>
<tr>
<td>6.33 (d), 6.27 (m)</td>
<td>vinyl</td>
<td>3</td>
</tr>
<tr>
<td>5.95 (m), 5.73 (q)</td>
<td>vinyl</td>
<td></td>
</tr>
<tr>
<td>5.10 (m)</td>
<td>benzhydryl</td>
<td>1</td>
</tr>
<tr>
<td>2.90 (m)</td>
<td>methylene</td>
<td>2</td>
</tr>
</tbody>
</table>

s = singlet, d = doublet, q = quartet, m = multiplet

For a more detailed interpretation, see page 43, and Appendix.

Table VI

IR spectrum of mixtures 14 and 15

Solvent: Carbon tetrachloride

Intensity: w = weak, m = medium, s = strong

<table>
<thead>
<tr>
<th>Wave length (μ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.30 s</td>
</tr>
<tr>
<td>3.50 m</td>
</tr>
<tr>
<td>5.18 w</td>
</tr>
<tr>
<td>5.32 w</td>
</tr>
<tr>
<td>5.56 w</td>
</tr>
</tbody>
</table>

| 6.28 s         | 7.50 w | 9.69 s |
| 6.70 s         | 8.03 w | 10.00 w |
| 6.90 s         | 8.48 w | 10.51 w |
| 7.28 m         | 8.67 w | 10.79 s |
| 7.35 m         | 9.29 s | 11.10 s |

There was no evidence of a methine proton at C-5 in the NMR spectrum, so that isomer 16 was not present in high concentration.
The UV max of the isomer mixture 14 and 15 was at 246 m\(\mu\) (EtOH) and 244 m\(\mu\) (hexane), \(\varepsilon_{\text{max}} = 3100\).

That the product from attempted alkylation of 6,6-diphenylfulvene was benzhydryl cyclopentadiene (two isomers) was further verified by synthesizing benzhydryl cyclopentadiene by a different route. The NMR spectrum of benzhydryl cyclopentadiene from the reaction of chlorodiphenylmethane and cyclopentadienide was identical to the spectrum of the mixture 14 and 15, from attempted alkylation. The identical spectra also indicates the same ratio of 14 and 15, 3:2 respectively, although these were obtained by two different methods. The ratio of 14 to 15 was obtained from the area of the ring methylenes in the NMR spectrum of the mixture of 14 and 15. On the HA-100 NMR spectrometer these protons appear as a triplet and a quartet separated by 7.4 Hz.

Rapid equilibration of alkyl cyclopentadienes has been demonstrated by McLean and Haynes (11). Using the NMR data obtained by these workers for 1-methyl cyclopentadiene and 2-methyl cyclopentadiene, isomer 14 was assigned the major isomer. The signals for the vinyl protons of 15 were identical to the signals for these protons in 2-methyl cyclopentadiene. However, the ring methylene signal for 14 was 7.4 Hz downfield from that in 1-methyl cyclopentadiene. This small difference may be attributed to deshielding by the phenyl groups of the substituent.
The reaction of the crude product from the attempted alkylation of 6,6-diphenylfulvene with tetracyanoethylene (TCNE) gave only the benzhydryl TCNE adduct of isomer 14. This result indicates that the expected methylated fulvenes were absent, and also that 15 reacts more slowly with TCNE than does does 14.

Spectral and chemical data for the adduct 13 are given below.

![Diagram of adduct 13]

**13**

**Anal.** Caled for C_{24}H_{16}N: C, 80.00; H, 4.45; N, 15.55.

<table>
<thead>
<tr>
<th></th>
<th>Found: C, 79.85; H, 4.62; N, 15.55.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMIR (acetone-d_6)</td>
<td>7.30 (m, 10, phenyl), 7.09 (d, 1, H_a), 6.60 (q, 1, J_{ab} = \text{6Hz}, H_b), 4.72 (s, 1, H_c), 3.83 (m, 1, J_{hc} = 3.2-3.4 Hz, H_c), 2.06 (s) and 2.04 (s), (2, H_e, H_f).</td>
</tr>
</tbody>
</table>

In the mass spectrum the most intense peak was that at m/e = 232, and there were no peaks at higher mass. The parent peak m/e = 232 in the mass spectrum indicates that the retro Diels-Alder reaction occurred under the conditions
NMR Spectrum of Benzhydryl Cyclopentadienes (two isomers), 14 and 15.

For further details on the NMR assignments, see the Appendix.
NMR spectrum for TONB adduct of l-Benzhydroxyl-1,4-cyclopentadiene.

phenyl

Hc, Hf

Hd

Ha, Hb

0.0 0.2 0.4
used to introduce the sample into the instrument. The assignments of the bridgehead, bridge, and olefinic hydrogens in the NMR spectrum of 13 were verified by comparison with the NMR spectrum of the cyclopentadiene-TCNE adduct and the 6,6-diphenylfulvene-TCNE adduct.

The values for the coupling constants from the NMR spectrum of this adduct agree fairly well with those of other norbornenes (24), except for the syn- and anti-7 hydrogens. The difference in chemical shift of 2 Hz in 13 is much smaller than the difference in chemical shift of these hydrogens in most norbornenes (24). This result is probably due to the cyano substituent.

The attempted alkylation of 6,6-diphenylfulvene using lithium amide as base gave back substrate fulvene. The fulvene reacted with the amide base as evidenced by a change in color of the reaction mixture. Regeneration of 6,6-diphenylfulvene must have occurred during work up of the reaction product.

From the NMR data in Table VII on the reaction product from the attempted alkylation of 6,6-diphenylfulvene with lithium dimethylamide as base, it appears that the product is a mixture of 6,6-diphenylfulvene and benzhydryl cyclopentadienes 14 and 15.
Table VII

NMR spectrum of reaction product from attempted alkylation of 6,6-diphenylfulvene using lithium dimethylamide as base.

<table>
<thead>
<tr>
<th>Chemical Shift (ppm) Proton(s)</th>
<th>Chemical Shift (ppm) Proton(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.24* (s) phenyl</td>
<td>6.29 (m) vinyl</td>
</tr>
<tr>
<td>7.12 (s) phenyl</td>
<td>5.95 (m) vinyl</td>
</tr>
<tr>
<td>6.48* (m) vinyl</td>
<td>5.72 (q) vinyl</td>
</tr>
<tr>
<td>6.33 (d) vinyl</td>
<td>5.10 (m) benzhydryl ring</td>
</tr>
<tr>
<td>6.21* (m) vinyl</td>
<td>2.90 (m) methylene</td>
</tr>
</tbody>
</table>

*6,6-diphenylfulvene

The other peaks correspond to benzhydryl cyclopentadiene (two isomers).

The hydrolysis of the product from the reaction of 6,6-diphenylfulvene and lithium diethylamide was carried out to determine the existence of the intermediate cyclopentadienide salt 2 where $Y = -\text{NET}_2$, $R_1 = R_2 = -\text{C}_6\text{H}_5$. The reaction mixture turned a dark green color when the red fulvene solution was added, and a further change in color occurred when water was added. This observation was evidence of a reaction. Most of the peaks in the NMR spectrum of the reaction product corresponded to 6,6-diphenylfulvene and benzhydryl cyclopentadiene. The remaining peaks in the spectrum could not be accounted for with any certainty.
The question now arises why 6,6-diphenylfulvene is reduced to benzhydryl cyclopentadiene during the alkylation attempts, and does not proceed by the scheme outlined in the General Introduction to the methylated 6,6-diphenylfulvenes.

One possible mechanism to account for benzhydryl cyclopentadiene formation is the following anion-radical scheme:

(i) [Chemical structure diagram]

(ii) [Chemical structure diagram]
and

and

and

and

R = -CH₃, -CH₂CH₃
The anion-radical from equation (i) is probably a more stable species than the cyclopentadienide 2.

\[ \text{Anion-radical from } \text{equation (i)} \]

The anion-radical would also be colored. The source of the H donor in step (ii) is uncertain. During work-up of the reaction product (iv) water will protonate the carbanion.

If the lithium cyclopentadienide 2 were the intermediate, there is no way of rationalizing the formation of cyclopentadienes 14 and 15.

When lithium amide was used as base, benzhydryl cyclopentadiene (two isomers) was not obtained. Instead substrate fulvene was regenerated. This result is reasonable since the alkyl groups in equation (i) would stabilize the amine radical to a greater extent than two hydrogen atoms. With lithium amide, the amide probably adds to the exocyclic carbon atom of the fulvene forming a cyclopentadienide such as 2 where \( Y = -\text{NH}_2 \), which then adds a proton from water during
the work-up. Deamination must then occur to regenerate
6,6-diphenylfulvene. In any case, methyl iodide does
not appear to react on 6,6-diphenylfulvene in any of
the alkylation attempts.

(iv) Attempted Alkylation of 6,6-Dimethylfulvene
Attempts to alkylate 6,6-dimethylfulvene did
not produce the expected 1,6,6-trimethylfulvene or
2,6,6-trimethylfulvene. This fulvene was chosen since
there would be less steric hindrance for the attacking
amide base at the exocyclic carbon atom than in 6,6-
diphenylfulvene. Of course, the disadvantage of using
this alkyl fulvene is that the acidic methyl hydrogens
also react with base, leading to an anion which does
not lead to the expected methylated fulvenes, upon
further reaction with methyl iodide. The products
obtained from attempted alkylation of 6,6-dimethylfulvene
were yellow oils. Although TLC indicated only three
components, the NMR spectrum of the mixture of yellow
oils was very complex, making it impossible to predict
the presence of any particular fulvene. Attempts to
separate the oils proved unsuccessful. The reaction
conditions are given in Table IV.

The physical appearance, boiling point, and
smell of the mixture of oils were similar to those of
the substrate fulvene. This fact suggested that the
yellow oils were fulvenes. L. Skaltebøl (25) has prepared 2,6-dimethylfulvene and 1,2-dimethylfulvene. The ring methyl in the former fulvene gives rise to a singlet at 1.98 ppm, while the two methyl groups in the latter fulvene give rise to a singlet at 1.86 ppm. Since the NMR spectrum of the mixture of oils was much more complex than one would expect from the methylated-6,6-dimethylfulvenes alone, it was concluded that the attempted methylation of 6,6-dimethylfulvene leads to other fulvenes, but the expected fulvenes, 1,6,6-trimethyl- and 2,6,6-trimethyl-fulvene, were not detected. If these oils were fulvenes similar to 6,6-dimethylfulvene, then they should certainly react with TCNE as does 6,6-dimethylfulvene. The mixture gave no evidence of a reaction at all. The position of two high field singlets at 1.17 ppm and 1.05 ppm may indicate the presence of t-butyl groups. The absence of a methylene quartet further indicates that the 6-methyl group of the fulvene is probably highly substituted. Steric hindrance would probably prevent TCNE from adding to these new highly substituted fulvenes. The competitive reaction where a hydrogen atom is abstracted from one of the acidic methyl groups in 6,6-dimethylfulvene by the amide base, is probably more likely to occur than the addition of the base to the exocyclic carbon atom of the fulvene. If this occurs, then with the addition of methyl iodide and excess base in the system many fulvenes are possible.
APPENDIX

A detailed assignment of the NMR spectrum of the benzhydryl cyclopentadiene isomers 14 and 15 is discussed in this section. The HA-100 NMR spectrum of the mixture of these isomers on page 53 shows improved resolution over this same spectrum taken on the A-60 NMR spectrometer (see page 143).

The results of an NMR decoupling experiment on the mixture of the isomers verifies the previous conclusion that isomer 14 is the major isomer. Assignments of all the hydrogens for the major isomer was also possible from the decoupled spectrum, but not for the minor isomer 15.
Partial NMR Spectrum of Benzhydryl Cyclopentadiene (two isomers), $^{14}$ and $^{15}$. 
Decoupled NMR Spectrum of Benzhydryl Cyclopentadiene (mixture of two isomers).

The change in signals on decoupling hydrogens from the major isomer are shown below.
There are three possible ways of assigning the vinyl hydrogens to isomer $1^4$. From the decoupled spectrum the two hydrogens, $H_a$, are coupled only to $H_b$ resulting in a doublet. When the coupling from $H_b$ is removed the $H_a$ doublet degenerates to a singlet. Also, $H_b$ is simplified when the coupling from $H_a$ is removed. Since $H_d$ appears to be a triplet, these hydrogens must be coupled to $H_b$ and to $H_c$. When $H_b$ is decoupled, $H_d$ degenerates to a doublet. A doublet for $H_d$ is also observed when $H_c$ is decoupled. Thus, the two hydrogens, $H_a$, are not coupled to the methylene hydrogens, $H_d$.

The results from the decoupled spectrum eliminates the other two possible ways of assigning the vinyl hydrogens. Assigning the vinyl hydrogens for isomer $1^5$ was not possible, since the signals for these hydrogens were too close together.
REFERENCES