6,6-DIARYL FULVENES

6,6-DIARYL FULVENES.

REDUCTION TO BENZHYDRYL CYCLOPENTADIENE

BY AMIDE BASES

By

HELMUTH HEINRICH LORENZ, B.Sc.

A Thesis

Submitted to the Faculty of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree

Master of Science

McMaster University

February 1969

MASTER OF SCIENCE (1969)　　　　　　　McMASTER UNIVERSITY
　　　　　　　　　　　　　　　　　　　　Hamilton, Ontario.

TITLE:　　　6,6-Diaryl Fulvenes.　Reduction to Benzhydryl
　　　　　　Cyclopentadiene by Amide Bases

AUTHOR:　　Helmuth Heinrich Lorenz,　B.Sc. (McMaster
　　　　　　　　　　　　　　　　　　　　　　University)

SUPERVISOR: Dr. J. Warkentin

NUMBER OF PAGES: 57, ix

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 cyclo-
pentadienide (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

ii

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 cyclopenta-
diene (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.

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Dr. J. Warkentin for his continued advice and encouragement throughout the course of this investigation.

The gratitude of the author is also expressed to Mr. B. Sayer, who ran many of the NMR spectra, and to Mr. P. Rasmussen, a fellow graduate student, who gave his own time to obtain mass-spectral data.

The author wishes also to thank Mrs. B. Hamilton-Wright for her typing skill.

INDEX

LIST OF SPECTRA

LIST OF TABLES

GENERAL INTRODUCTION

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

The primary objective under this section was to find a new method of synthesizing para-substituted 6,6-diphenylfulvenes from 6,6-bis-(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-(p-chlorophenyl)fulvene, would produce intermediate 1, which is stabilized by extensive delocalization.

1

1

(1) $Y^- = I^-$, [piperidine structure] , [p-methylphenolate O^- ... CH_3] , $^-OCH_3$
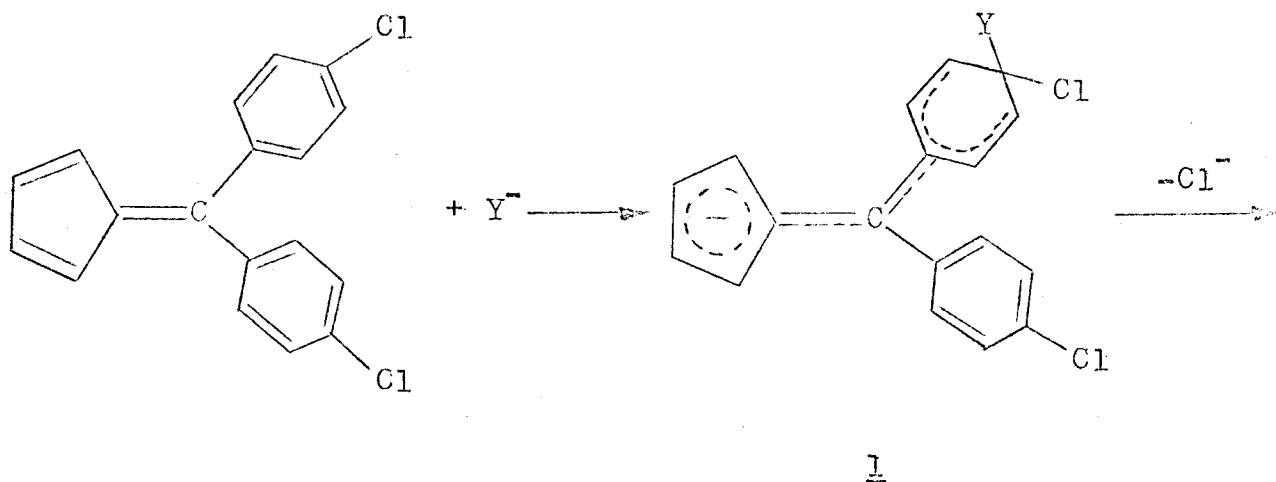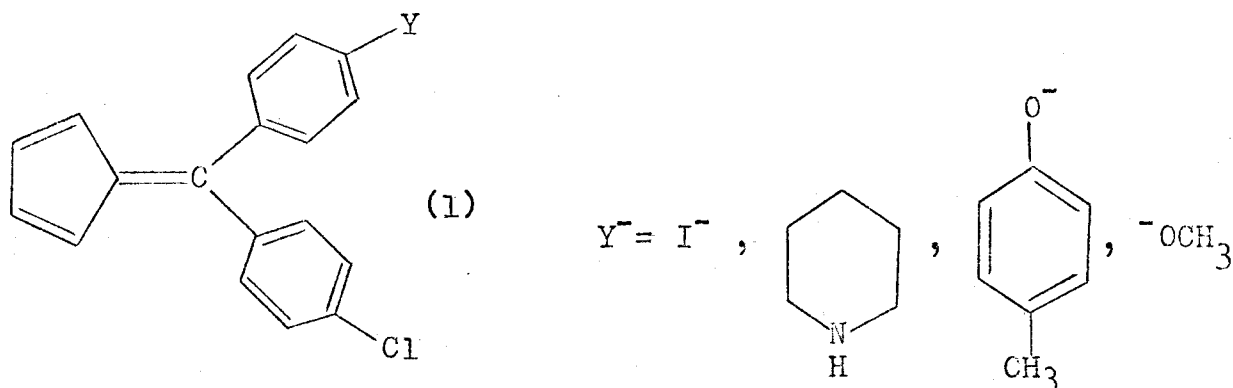
By comparing the rates of nucleophilic aromatic
substitution of 6,6-bis-(p-chlorophenyl)fulvene and p-halo-
nitro-benzene, one might determine the relative activating
power of the 6-fulvenyl group towards nucleophilic aromatic
substitution. This would be a novel activating group,
since all other activating 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. Kresze, et al,(2) using the appropri-
ately 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 cyclopenta-dienide 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.

2   3

$$3 \quad + \quad 4 \xrightarrow{-HY} \quad 6 \quad + \quad 7 \qquad (3)$$

$$R_1 = R_2 = -C_6H_5, \ -CH_3, \ R_3 = -CH_3$$
$$Y^- = \ ^-NH_2, \ ^-NEt_2, \ ^-NMe_2, \ ^-NHC_6H_{11}$$
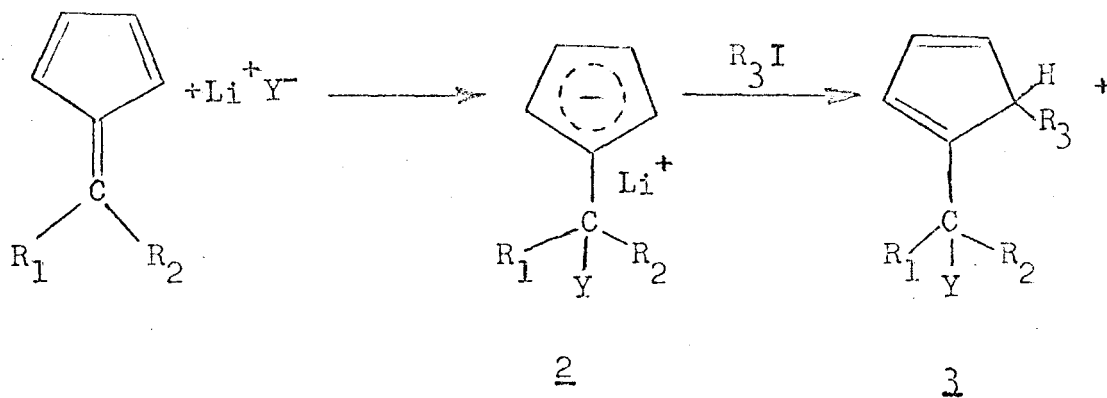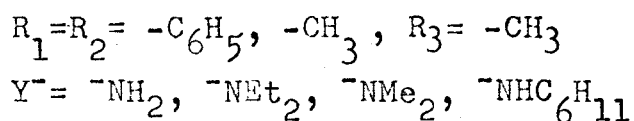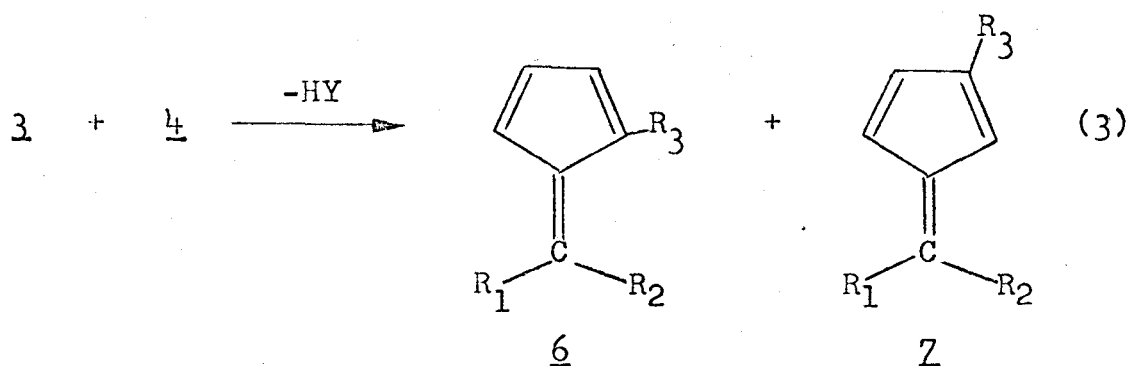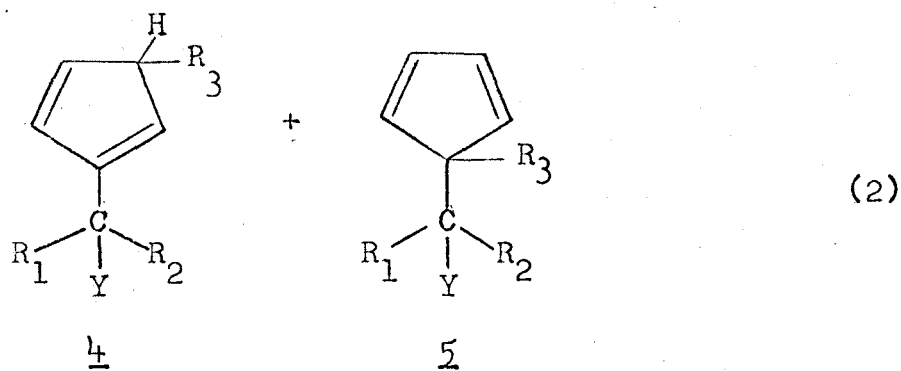
In the above reaction sequence, Y^- must be a strong nucleophile for addition to occur at the exocyclic carbon of the fulvene. The resonance stability of the cyclopentadienide 2 would be expected to drive the reaction towards the anion. The bimolecular substitution of the alkylating agent with the cyclopentadienide 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 elimation 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 $\underline{8}$. 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.

$$R_1 = H$$

$$R_2 = \text{alkyl, aryl}$$

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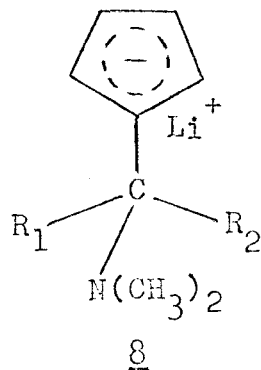
The similarity between intermediates $\underline{2}$ and $\underline{8}$ is
obvious, if $Y = -N(CH_3)_2$ and $R_2 = -C_6H_5$. The reactions
leading to these intermediates differ in the order of
introduction of the groups.

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.
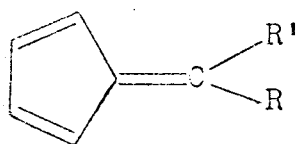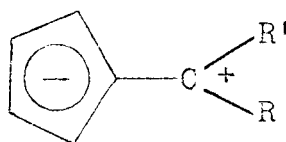
A   B

R= R'= H, Aryl, Alkyl

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-diaryl-fulvenes. 6,6-Dialkylfulvenes have a dipole moment of about 1.4 D (7), whereas the corresponding 6,6-diaryl-fulvenes 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 π 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 rational-
ized by consideration of their dipolar nature. The benzen-
oid 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 9 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.
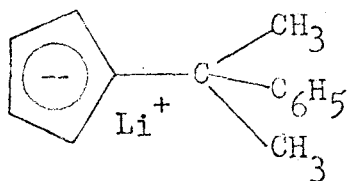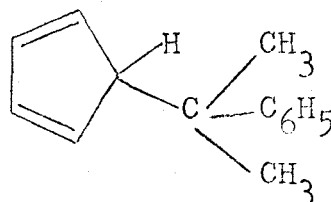
2   10

Similarly, 6,6-diphenylfulvene adds phenyl lithium to give an intermediate complex 9 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.
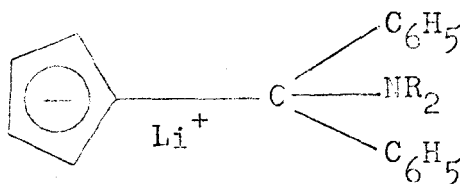
11

R= --H, --CH_3, --CH_2CH_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 11 differs from methyl cyclo-
pentadiene 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 cyclopen-
tadiene ring, using the appropriate electrophile leads to

polymeric products. Although 6,6-diphenylfulvene and
6,6-dimethylfulvene undergo alkylation (8) at -80°,
the σ-complex formed is stable only at -80°.

(4)
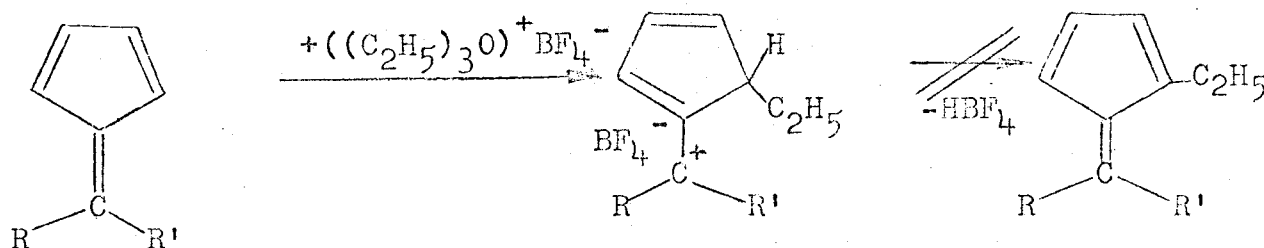
The attempted conversion of the fulvenium salts
into substituted fulvenes leads to polymeric products.
Thiec and Wiemann (14) observed a similar polymerization
with unsubstituted fulvenes.

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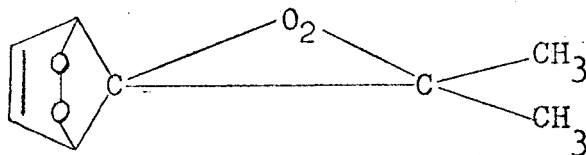
From 6,6-diphenylfulvene a polymer has been
obtained at 140°, while at lower temperature a crystalline
dimer has been formed (20). This type of dimer is formed
by a Diels-Alder reaction in which the fulvene behaves
as both diene and dienophile.

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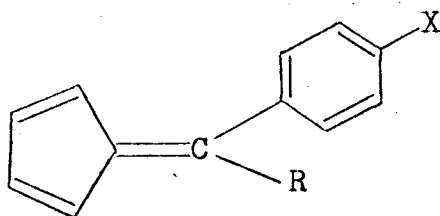
X= halogen
R= aryl

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.

EXPERIMENTAL

(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 chromato-
graphed fractions. Reagent grade solvents (Fisher Scienti-
fic, 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-d_6 solution (tetramethylsilane 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.

I 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 $CaCl_2$ drying tube. A slow stream of purified
nitrogen was passed through the system during the course
of the reaction.

Freshly cut sodium (3.10g, 0.134 g atom) was added
to 24.0 ml of tetrahydrofuran in small portions. A
catalytic amount of t-butyl alcohol (1.0ml) was added,
followed by dropwise addition of cyclopentadiene (30.0ml,
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
(24.0g, 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 (CCl$_4$) δ 7.27 (m,8,phenyl), 6.52 (m,2,vinyl), 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, 0.75mol)

Recovery after chromatography and crystallization gave 65g (52%) of 6,6-diphenylfulvene; mp 78-80° (lit (2) mp 81.5-82°); nmr (CCl$_4$) δ 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% w/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° (5mm) (lit (22)

bp 46° (11mm)); nmr (CCl$_4$) 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 (o.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 (0.304g, 0.001mol), 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 (1.00g, 0.00325mol) and piperidine (10ml, 0.10mol). 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 (0.154g,
0.0005mol) and sodium iodide (0.300g, 0.002mol) in 3ml of
methyl ethyl ketone (MEK)was heated in a sealed glass tube

at 65° for three hours. Mass spectra and UVspectra 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-diphenylfulvene, 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-chloro-
phenyl)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 (CCl$_4$) δ 6.99 (m,16,
phenyl), 6.34 (d,1,H$_b$), 6.02 (s,2,H$_a$), 5.89 (d,1,H$_c$),
3.65 (m,1,H$_g$), 3.30 (m,2,H$_e$,H$_d$), 2.80 (m,1,H$_f$).
Crystallization of the red solution gave 70% recovery
of starting fulvene.
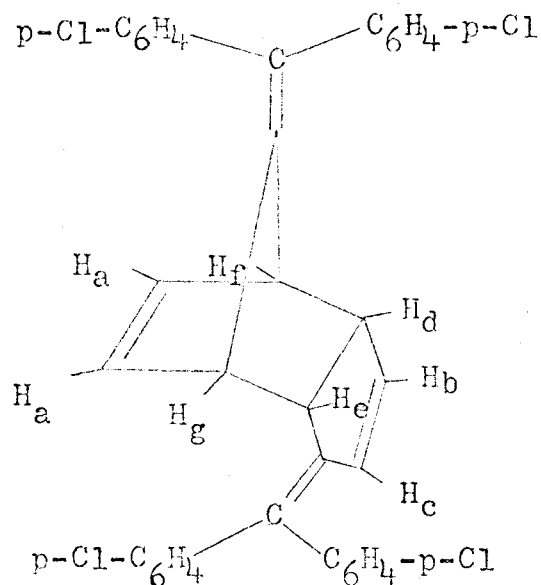
12

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 $CaCl_2$ 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 36g of white solid. The
NMR spectrum of this solid in D_2O was identical to that
of the quarternary ammonium salt, diethyl-dimethyl
ammonium iodide. The orange ether solution was concen-
trated to 150 ml and a further portion of methyl iodide
(13 ml, 0.2mol) 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 $\underline{3}$ and $\underline{4}$, where $R_1 = R_2 = -C_6H_5$,
$R_3 = -CH_3$, 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 hetero-
geneous 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 $5'x2\frac{1}{4}"$
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 NMRspectrum 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 tetra-
chloride 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 $\underline{2}$, where $R_1=R_2= -C_6H_5$, and $Y^- = \ ^-NEt_2$. 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 concen-
tration 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 cyclo-
pentadiene. 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 (o.410g, 0.018g atom) was added
in small portions with continuous stirring. Chloro-
diphenylmethane (2.03g, 0.010mol) in 10ml of tetra-
hydrofuran 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 etheral 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 (CCl$_4$) 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 diethylamide 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 diethylamide as base and
methyl iodide as alkylating 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 tetracyano-
ethylene 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-dimethyl-
fulvene 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-diphenylfulvene, 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 6.72δ , at 6.40δ and at 4.12δ , 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

Experimental Reference Section	Reactants		Solvent	Reaction Type	Conditions		Results
II(a)	6,6-bis-(p-chloro-phenyl)fulvene (mol)	sodium methoxide (% solution)			Time (hr)	Temp (°C)	
(i)	0.001	0.55	methyl hydrate	reflux	18	70	Recovered substrate
(ii)	0.00016	0.57	methyl hydrate	reflux	43	70	Above 100°
(iii)	0.0005	1.9	methyl hydrate	sealed tube	3.5	108	increasing amount of
(iv)	0.0033	14	methyl hydrate benzene	sealed tube	20	160	dark residue
II(b)		piperidine (mol)					
(i)	0.0035	0.10	piperidine	steam bath	10	100	Recovered
(ii)	0.0032	0.10	piperidine	sealed tube	60	150	substrate and dark
(iii)	0.0035	0.026	benzene	sealed tube	20	160	residue

Table I Continued

Experimental Reference Section	Reactants		Solvent	Reaction Type	Conditions		Results
II(c)	6,6-bis-(p-chloro-phenyl)fulvene (mol)	sodium p-cresoxide (mol)			Time (hr)	Temp (°C)	
(i)	0.0035	0.026	DMSO	sealed tube	20	100	Inconclusive
II(d)		sodium iodide (mol)					
(i)	0.00035	0.002	MEK	sealed tube	3	65	Recovered
(ii)	0.00035	0.002	MEK	sealed tube	70	150	substrate

Table II

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

Experimental Reference Section	Reactants			Solvent	Reaction Type	Conditions		Results
III(a)	6,6-bis-(p-chloro-phenyl)fulvene (mol)	sodium iodide (mol)	methyl iodide (mol)			Time (hr)	Temp (°C)	
(i)	0.0010	0.0030	0.016	MEK	steam bath	18	100	Substrate
(ii)	0.0016	0.016	0.0016	MEK	reflux	7	65	fulvene and
(iii)	0.0016	0.016	0.016	MEK	reflux	16	65	dimer of
(iv)	0.0016	0.0016	0.030	DMSO	steam bath	4	80	6,6-bis-(p-
(v)	0.0016	0.016	0.032	DMSO	steam bath	15	60	chlorophenyl)
								fulvene

Table III

Attempted Alkylation of 6,6-Diphenylfulvene

Experimental Reference Section	Reactants and Concentration (mol)			Solvent	Conditions		Results
IV(a)	6,6-diphenyl-fulvene	lithium diethyl-amide	methyl iodide		Time (hr)	Temp (°C)	
(i)	0.010	0.017	0.040	ether	16	25	Major product
(ii)	0.0075	0.015	0.012	ether	7	25-60	was benzhydryl
(iii)	0.050	0.138	0.510	ether		0-25	cyclopentadiene
IV(b)		lithium amide					
	0.010	0.013	0.112	THF	3	-25,45	Substrate fulvene regenerated
IV(c)		lithium dimethyl-amide					
	0.010	0.020	0.10	ether	4	0-25	6,6-diphenylfulvene, benzhydryl cyclopentadiene

Table III Continued

Experimental Reference Section	Reactants and Concentration (mol)			Solvent	Conditions		Results
IV(d)	6,6-diphenyl-fulvene	lithium cyclohexyl-amide	methyl iodide		Time (hr)	Temp (°C)	
	0.010	0.010	0.024	DME	7	25-60	No reaction under these conditions

Table IV

Attempted Alkylation of 6,6-Dimethylfulvene

Experimental Reference Section	Reactants and Concentration (mol)			Solvent	Conditions		Results
VI	6,6-dimethyl-fulvene	lithium diethyl-amide	methyl iodide		Time (hr)	Temp (°C)	
(i)	0.020	0.040	0.20	ether	3	25	3 yellow oils, A-1, A-2, A-3; A-1 was regenerated
(ii)	0.100	0.150	1.00	ether	5	25	6,6-dimethylfulvene

RESULTS AND DISCUSSION

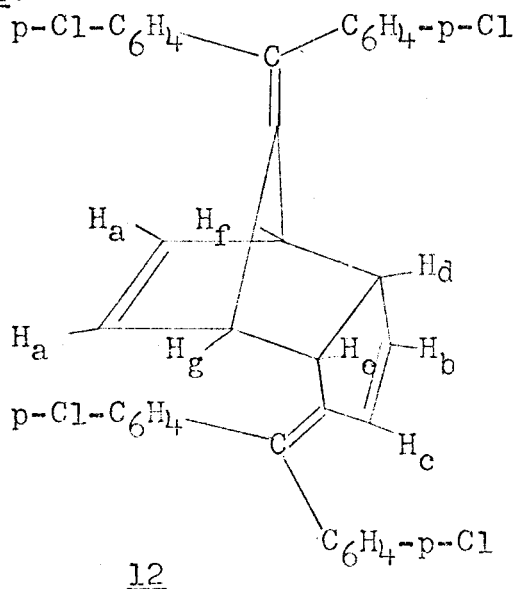(i) <u>Attempted Nucleophilic Aromatic Substitution</u>

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 recov-
ered 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 exocy-
clic 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 <u>1</u> is not sufficiently
stable, relative to the starting materials.

(ii) <u>Attempted Alkylation of 6,6-bis-(p-Chlorophenyl)fulvene</u>

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

p-Cl-C$_6$H$_4$— C —C$_6$H$_4$-p-Cl

H$_a$ H$_f$ H$_d$

H$_a$ H$_g$ H$_e$ H$_b$

p-Cl-C$_6$H$_4$— C H$_c$

C$_6$H$_4$-p-Cl

<u>12</u>

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 dimethylamide 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.

14   15   16
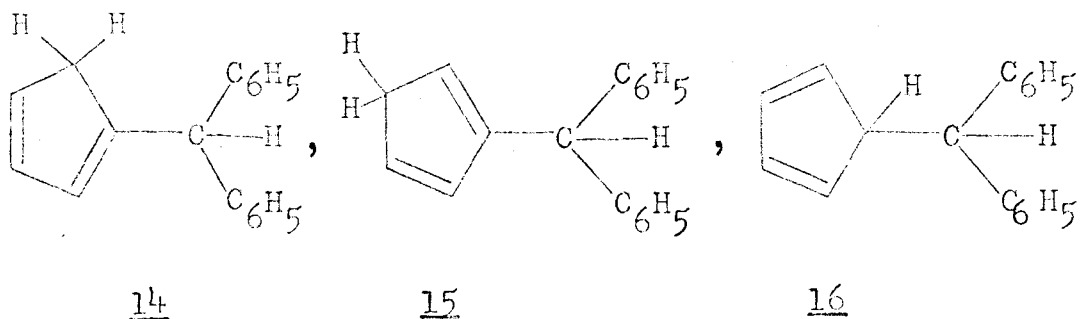
Since the mixtures of 14 and 15 could not be separated, the NMR assignments are of the mixture.

40

Table V

NMR spectrum for mixtures of 14 and 15

Chemical Shift (ppm)	Proton(s)	Area Ratio
7.12 (s)	phenyl	10
6.33 (d), 6.27 (m)	vinyl	3
5.95 (m), 5.73 (q)	vinyl	
5.10 (m)	benzhydryl	1
2.90 (m)	methylene	2

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

Wave length (μ)

3.30 s	6.28 s	7.50 w	9.69 s
3.50 m	6.70 s	8.03 w	10.00 w
5.18 w	6.90 s	8.48 w	10.51 w
5.32 w	7.28 m	8.67 w	10.79 s
5.56 w	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 mμ (EtOH) and 244 mμ (hexane), ϵ_{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 chloro-diphenylmethane 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 cyclopenta-diene 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.
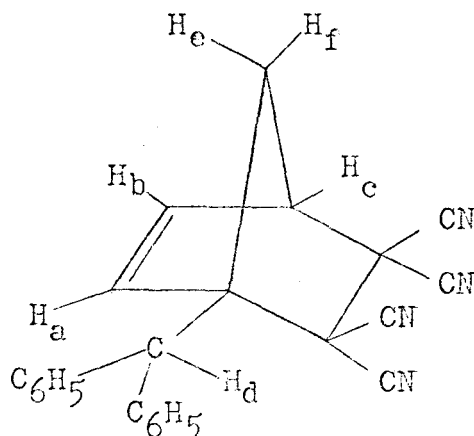
13

Anal. Calcd for $C_{24}H_{16}N_4$: C, 80.00; H, 4.45; N, 15.55.
Found: C, 79.85; H, 4.62; N, 15.55.

NMR (acetone-d_6) δ 7.30 (m,10,phenyl), 7.09 (d,1,H_a), 6.60 (q,1, J_{ab} = 6Hz, H_b), 4.72 (s,1,H_d), 3.83 (m,1, J_{bc} = 3.2-3.4 Hz, H_c), 2.06 (s) and 2.04 (s), (2, H_e,H_f).

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.
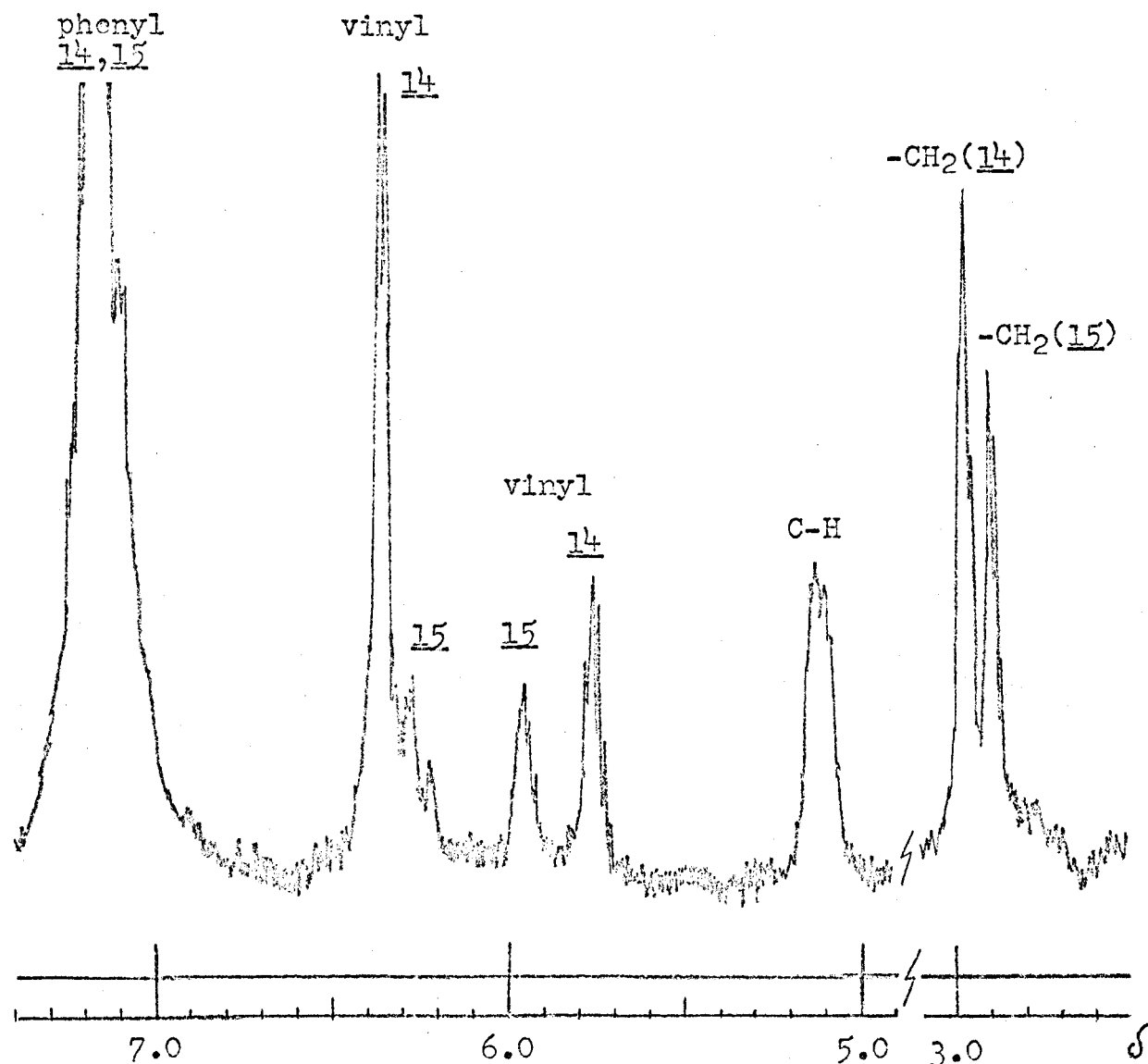
For further details on the NMR assignments, see the Appendix.

NMR spectrum for TCNE adduct of 1-Benzhydryl-1,4-cyclopentadiene.

phenyl

Ha

Hb

Hd

Hc

He, Hf

7.0

4.0

2.0

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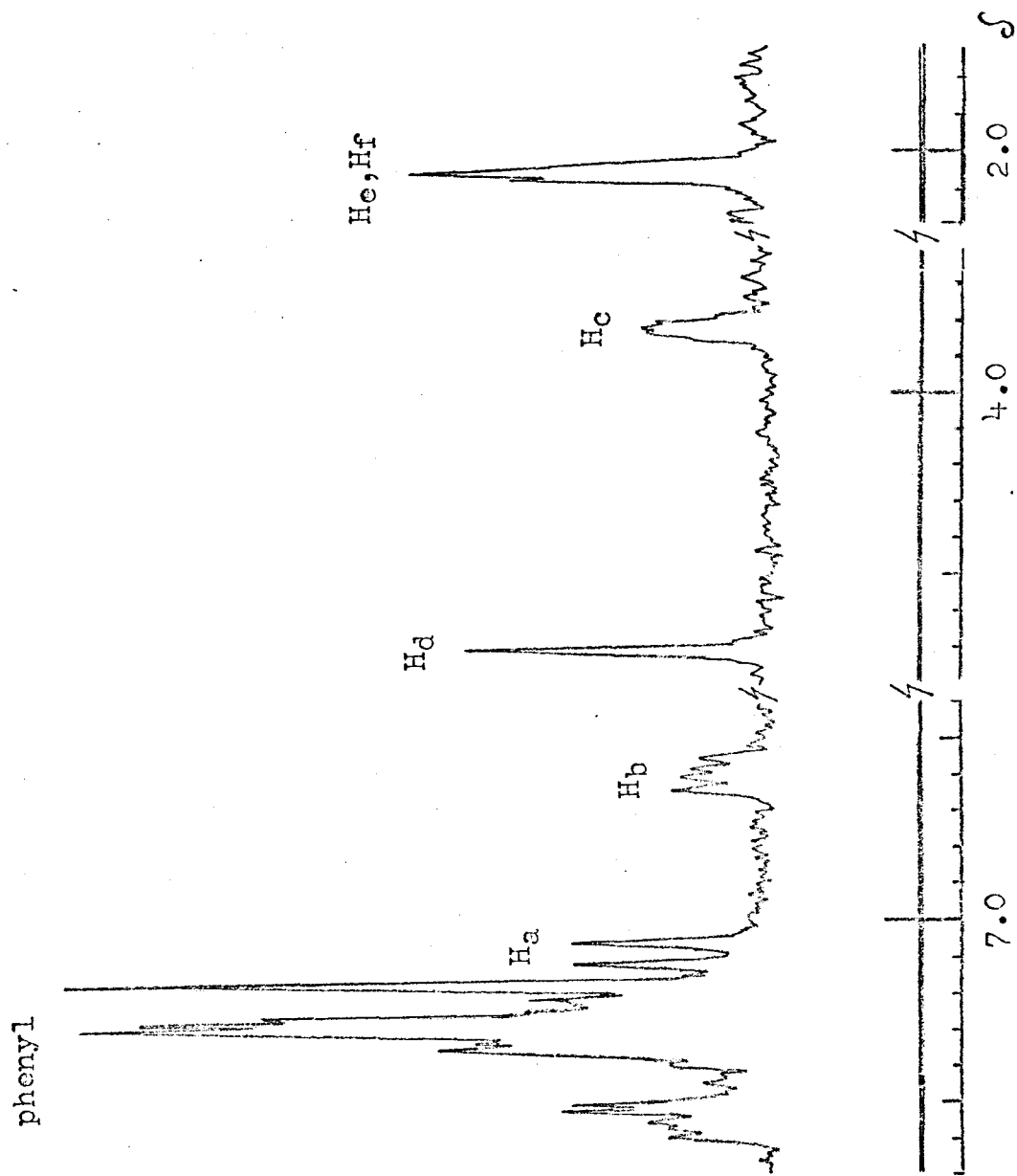
used to introduce the sample into the instrument. The
assignments of the bridgehead, bridge, and olefinic hydrogens
in the NMR spectrum of 13 were verified by comparison with
the NMR spectrum of the cyclopentadiene-TCNE adduct and the
6,6-diphenylfulvene-TCNE adduct.

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-diphenyl-
fulvene 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.

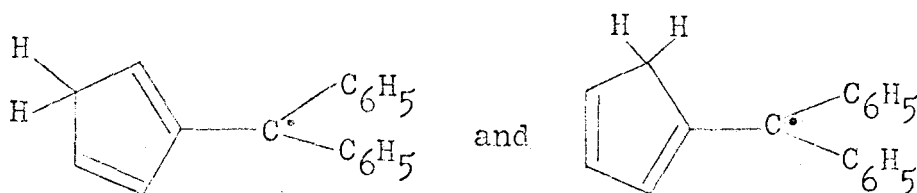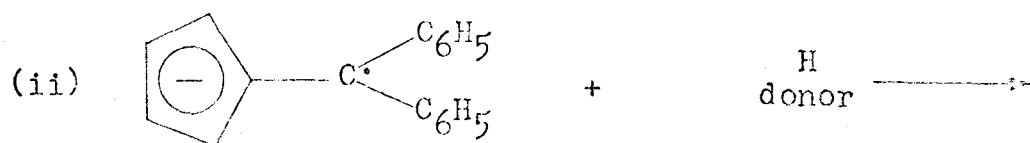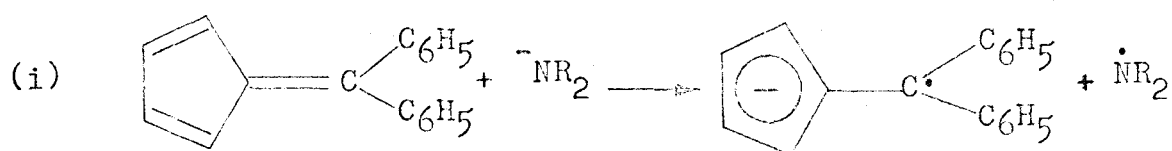| Chemical Shift(ppm)	Proton(s)	Chemical Shift(ppm)	Proton(s)
7.24*(s)	phenyl	6.29 (m)	vinyl
7.12 (s)	phenyl	5.95 (m)	vinyl
6.48*(m)	vinyl	5.72 (q)	vinyl
6.33 (d)	vinyl	5.10 (m)	benzhydryl
6.21*(m)	vinyl	2.90 (m)	ring methylene

*6,6-diphenylfulvene

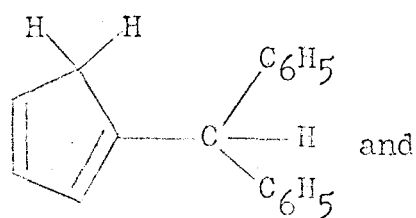The other peaks correspond to benzhydryl cyclopentadiene (two isomers).
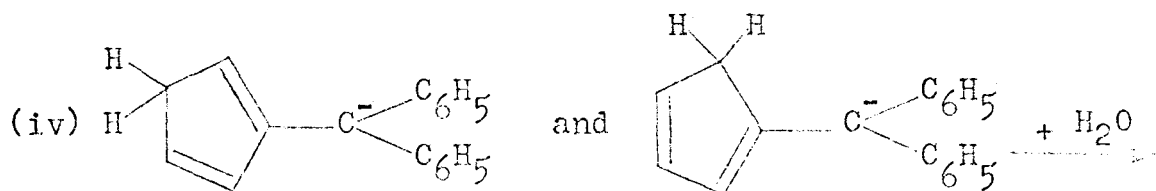
The hydrolysis of the product from the reaction of 6,6-diphenylfulvene and lithium diethylamide was carried out to determine the existence of the intermediate cyclopentadienide salt $\underline{2}$ where $Y = -NEt_2$, $R_1 = R_2 = -C_6H_5$. The reaction mixture turned a dark green color when the red 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)

$$\text{(cyclopentadiene)}=C\underset{C_6H_5}{\overset{C_6H_5}{<}} + {}^-NR_2 \longrightarrow \text{(cyclopentadienyl} \ominus)-C\underset{C_6H_5}{\overset{C_6H_5}{\cdot}} + \dot{N}R_2$$

(ii)

$$\text{(cyclopentadienyl} \ominus)-C\underset{C_6H_5}{\overset{C_6H_5}{\cdot}} + \underset{\text{donor}}{\overset{H}{}} \longrightarrow$$

$$\underset{H}{\overset{H}{}}\text{(cyclopentadiene)}-C\underset{C_6H_5}{\overset{C_6H_5}{\cdot}} \quad \text{and} \quad \underset{H \; H}{}\text{(cyclopentadiene)}-C\underset{C_6H_5}{\overset{C_6H_5}{\cdot}}$$

(iii) [structure: cyclopentadienyl–$C^{\cdot}$ with two C_6H_5 groups] and [structure: cyclopentadienyl–$C^{\cdot}$ with two C_6H_5 groups] $+ \; ^{-}NR_2 \longrightarrow$

[structure: cyclopentadienyl–C^{-} with two C_6H_5 groups] and [structure: cyclopentadienyl–C^{-} with two C_6H_5 groups] $+ \; \overset{\cdot}{N}R_2$

(iv) [structure: cyclopentadienyl–C^{-} with two C_6H_5 groups] and [structure: cyclopentadienyl–C^{-} with two C_6H_5 groups] $+ \; H_2O$

[structure: cyclopentadienyl–C with C_6H_5, H, C_6H_5] and [structure: cyclopentadienyl–C with C_6H_5, H, C_6H_5]

<u>14</u>   <u>15</u>

$$R = -CH_3, \; -CH_2CH_3$$

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

2
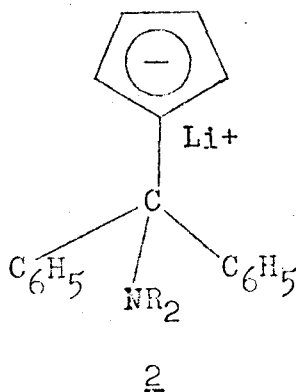
The anion-radical would also be colored. The source of the H donor in step (ii) is uncertain. During work-up of the reaction product (iv) water will protonate the carbanion.

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 = -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) <u>Attempted Alkylation of 6,6-Dimethylfulvene</u>

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 2,5-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 43).
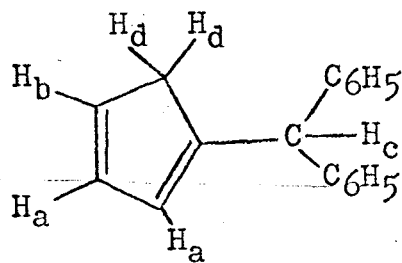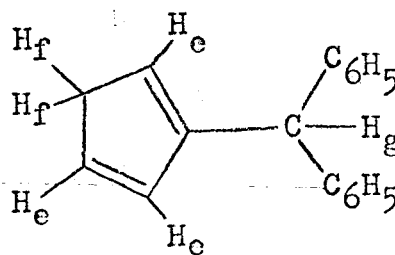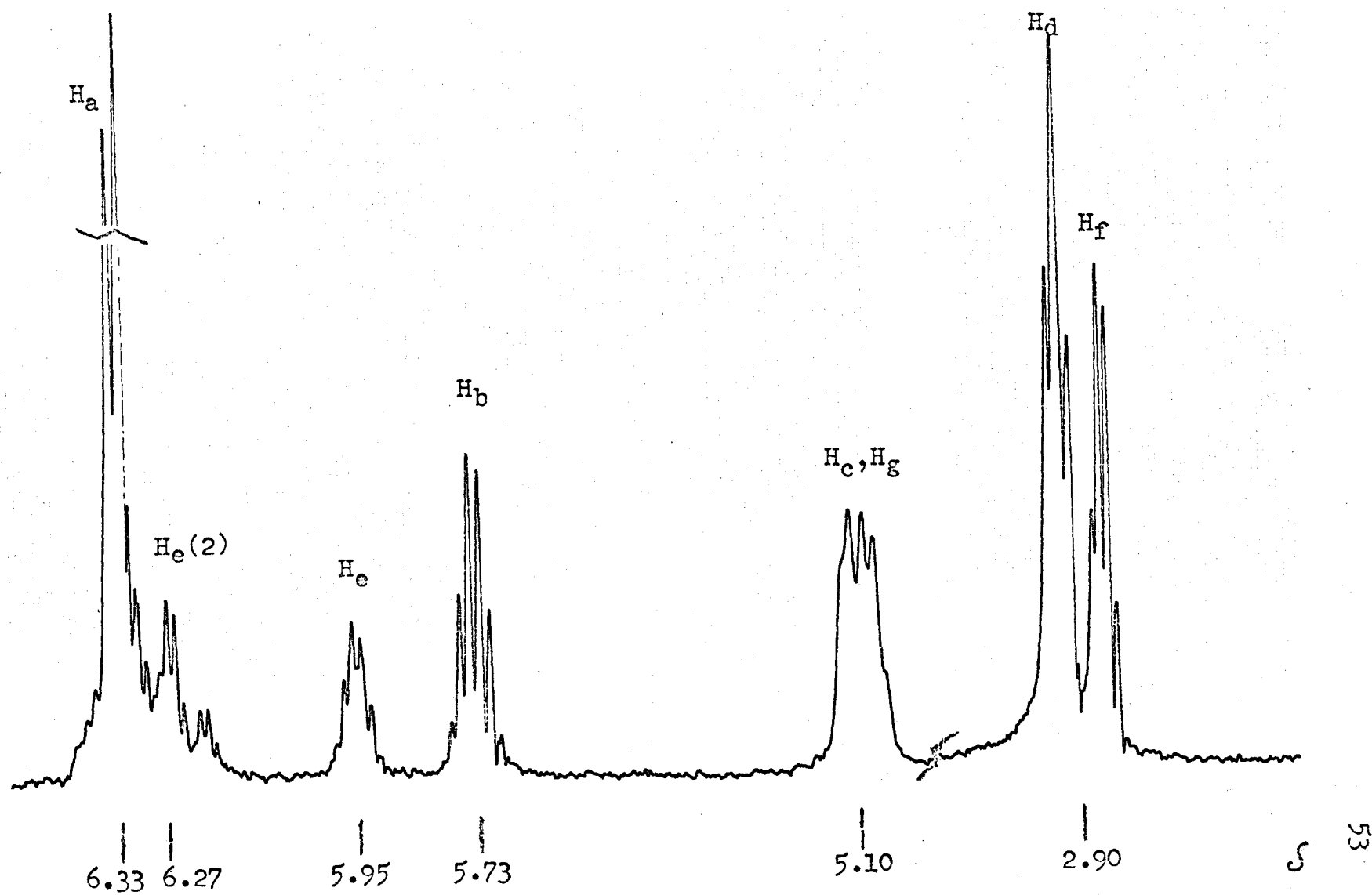

14   15

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.

H_a H_b H_c H_d

H_b H_c H_d

H_a H_b H_d
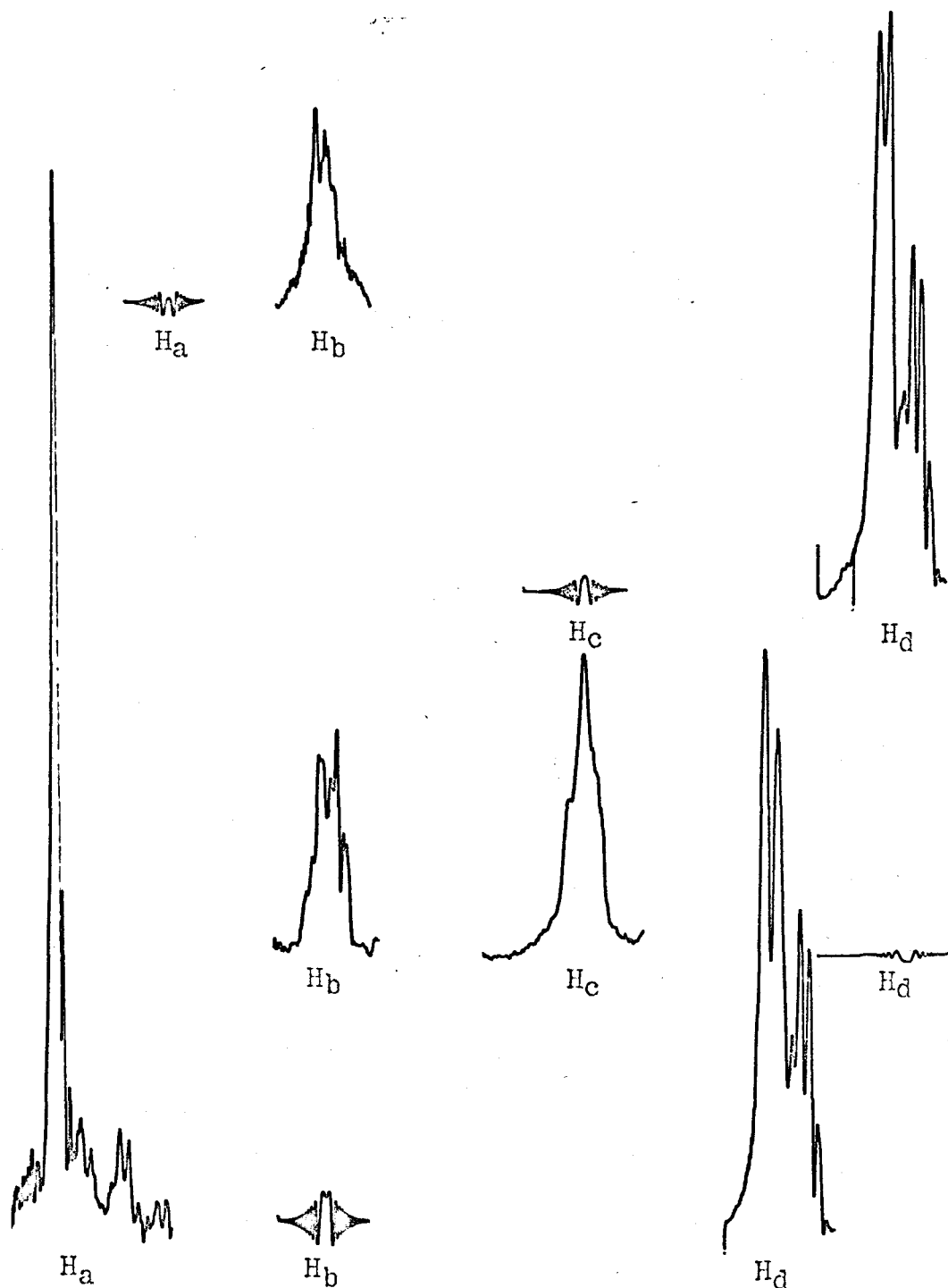
There are three possible ways of assigning the vinyl hydrogens to isomer 14. From the decoupled spectrum the two hydrogens, H_a , are coupled only to H_b resulting in a doublet. When the coupling from H_b is removed the H_a doublet degenerates to a singlet. Also, H_b is simplified when the coupling from 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 15 was not possible, since the signals for these hydrogens were too close together.

REFERENCES

1. G. Kresze and H. Goetz, Chem. Ber., 90, 2161 (1957).

2. G. Kresze, S. Rau, G. Sabelus and H. Goetz, Ann., 648, 51 (1961).

3. E. D. Bergmann, Chem. Rev., 68, 41 (1968).

4. K. Ziegler, et al., Ann., 473, 1 (1929).

5. K. Hafner and E. Sturm, Angew. Chem., 3 (Int'l), 749 (1964).

6. G. W. Wheland and D. E. Mann, J. Chem. Phys., 17, 264 (1949).

7. E. D. Bergmann and E. Fischer, Bull. Soc. Chim. Fr., 17, 1084 (1950).

8. K. Hafner, Angew. Chem., 74, 499 (1962).

9. E. Hückel, Z. Physik 70, 204 (1931).

10. K. Zeigler and W. Schäfer, Ann., 511, 101 (1934).

11. S. McLean and P. Haynes, Tetrahedron, 21, 2313 (1965).

12. K. Hafner, K. H. Häfner, et al., Angew. Chem., 2 (Int'l), 123 (1963).

13. G. Berthier and B. Pullmann, Bull. Soc. Chim. Fr., 16, D461 (1961).

14. J. Thiec and J. Wiemann, Bull. Soc. Chim. Fr., 177 (1956), 366 (1957), 1066 (1960).

15. J. H. Day, Chem. Rev., 53, 167 (1953).

16. K. Alder and R. Rührmann, Ann., 566, 1 (1950).

17. G. Kresze, S. Rau, G. Sabelus and H. Goetz, Ann., 648, 57 (1961).

18. C. Engler, Z. Elektrochem., 18, 945 (1912).

19. W. Frankenstein, Chem. Ber., 34, 2933 (1901).

20. K. Alder, F. W. Chambers and W. Trimborn, Ann., 566, 27 (1950).

21. K. Ziegler, H. Froitzheim-Kühlhorn and K. Hafner, Ber., 89, 434 (1956).

22. W. Freiesleben, Angew. Chem., 2 (Int'l), 396 (1963).

23. H. Gilman and F. Schulze, J. Am. Chem. Soc., 47, 2002 (1925).

24. A. P. Marchand and J. E. Rose, J. Am. Chem. Soc., 90, 3724 (1968).

25. L. Skatteb\u00f8l, Tetrahedron, 23, 1107 (1967).