PART I

THE SYNTHESIS OF ETHYL 3,3-DI-(4-HYDROXY-3,5-DI-TERT-BUTYL)-PHENYL-2-AMINOPROPIONATE

PART II

NOVEL REACTION PRODUCTS OF 4-HYDROXY-2,3,4-TRIPHENYL-2-CYCLOPENTEN-1-ONE

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
MARY ELIZABETH CONNER
1969

This is to certify that the

thesis entitled

PART I
THE SYNTHESIS OF ETHYL 3,3-DI-(4-HYDROXY-3,5-DI-TERT-BUTYL)-PHENYL-2-AMINOPROPIONATE
PART II
NOVEL REACTION PRODUCTS OF 4-HYDROXY-2,3,4-TRIPHENYL-2- presented by CYCLOPENTEN-1-ONE

Mary Elizabeth Conner

has been accepted towards fulfillment
of the requirements for

PhD degree in Chemistry

Eugene L. Stogryn
Major professor

Date 8 December 1969

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PART I

THE SYNTHESIS OF ETHYL 3,3-DI-(4-HYDROXY-3,5-DI-TERT-BUTYL)PHENYL-2-AMINOPROPIONATE (20)

PART II

NOVEL REACTION PRODUCTS OF 4-HYDROXY-2,3,4-TRIPHENYL-2-CYCLOPENTEN-1-ONE

BY

Mary Elizabeth Conner

For the purpose of studying conductivity properties the synthesis of a stable free radical substituted amino acid was attempted. The precursor for this amino acid was ethyl 3,3-di-(4-hydroxy-3,5-di-tert-butyl)phenyl-2-amino-propionate (20). Amino ester 20 was synthesized by the Raney nickel catalyzed reduction of ethyl 3,3-di-(4-hydroxy-3,5-di-tert-butyl)phenyl-2-nitropropionate (18). The nitro ester (18) was obtained by the addition of ethyl nitroacetate to 2,6,3',5'-tetra-tert-butyl-4'-hydroxyphenyl-4-methylene-2,5-cyclohexadien-1-one (17) (1) or to 4,4'-dihydroxy-3,3',5,5'-tetra-tert-butyldiphenylethoxymethane (19).

When oxidation of the side chain of amino ester 20 was attempted the amino ester moiety was cleaved giving only unsubstituted free radical. The desired free radical substituted amino acid could not be obtained.

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When either cyclohexadienone 17 or ethoxy compound 19 in acetic acid solution was treated with several drops of sulfuric acid, 4,4'-dihydroxy-3,3',5,5'-tetra-tert-butylbenzophenone (28) was obtained. Standard methods for the preparation of benzophenone 28 were unsuccessful.

PART II

Highly colored reaction products were found to result from novel rearrangements of 4-hydroxy-2,3,4-triphenyl-2-cyclopenten-1-one (29) (2). A green crystalline compound, 1,2,3-triphenyl-4-azazulene (30), resulted from reaction of hydroxy ketone 29 with pyrrolidine and p-toluenesulfonic acid in toluene. The spectral and chemical properties necessary for its identification are discussed.

Dehydration of hydroxy-ketone 29 also results in colorful products. In p-toluenesulfonic acid catalyzed reactions the red 3,3',4,4',5,5'-hexaphenyl-3,4-dihydro-2,2'-biscyclopentadienone (48) was formed. In 10% sulfuric acid-acetic acid the yellow (E)-3,3',4,4',5,5'-hexaphenyl[bi-3-cyclopenten-1-ylidene]-2,2'-dione (31) is a minor product. The formation of both cyclone 48 and bicyclopentenylidene 31 can be rationalized via rearrangement of a dimer of 2,3,4-triphenylcyclopentadienone (34). In the 10% acid solution a blue compound (32) is the major product. On the basis of available evidence it was suggested to be 6-hydroxy-5,5 ,8, 9,10-pentaphenylbenzo[cd]cyclopent[f]azulen-4-(5H)-one.

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A new cyclopentadienone, 2,3,4-triphenyl-5-bromocyclopentadienone (50) was obtained from the bromination of 2,3,4-triphenyl-2-cyclopenten-1-one (40). Cyclone 50 appears to exist as a monomer. Bicyclopentenylidene 31 served as a precursor for the preparation of 3,3',4,4',5,5'-hexaphenyl-2,2'-biscyclopentadienone (47), which is the simplest biscyclone known.

The chemical and spectral data as well as further reactions of these compounds are discussed.

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2. C. F. Koelsch and T. A. Geissman, J. Org. Chem., 3, 480 (1938).

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PART I

THE SYNTHESIS OF ETHYL 3,3-DI-(4-HYDROXY-3,5-DI-TERT-BUTYL)-PHENYL-2-AMINOPROPIONATE

PART II

NOVEL REACTION PRODUCTS OF 4-HYDROXY-2,3,4-TRIPHENYL-2-CYCLOPENTEN-1-ONE

By

Mary Elizabeth King Conner

A THESIS

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

1969

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ACKNOWLEDGMENTS

I wish to express sincere appreciation to Dr. E. LeGoff for his patience and helpful suggestions in the course of this research and for the financial assistance provided me through his PRF, NSF, and NIH research grants. I would also like to thank NSF for financial assistance in the form of a summer fellowship in 1966.

In addition, I would like to express appreciation to Mr. Eric Roach of Michigan State University for running 100 MHz nmr spectra, and to Mrs. Lorraine Guile of Michigan State University and Rodger L. Foltz of Battelle Memorial Institute for providing mass spectral data. Sincere thanks also to Dr. A. A. Bothner-By of Carnegie-Mellon University for sending us the LAOCOON III program description and FORTRAN deck, and to Kurt L. Loening of Chemical Abstracts Service for his assistance in naming several compounds.

INTRODUCTION

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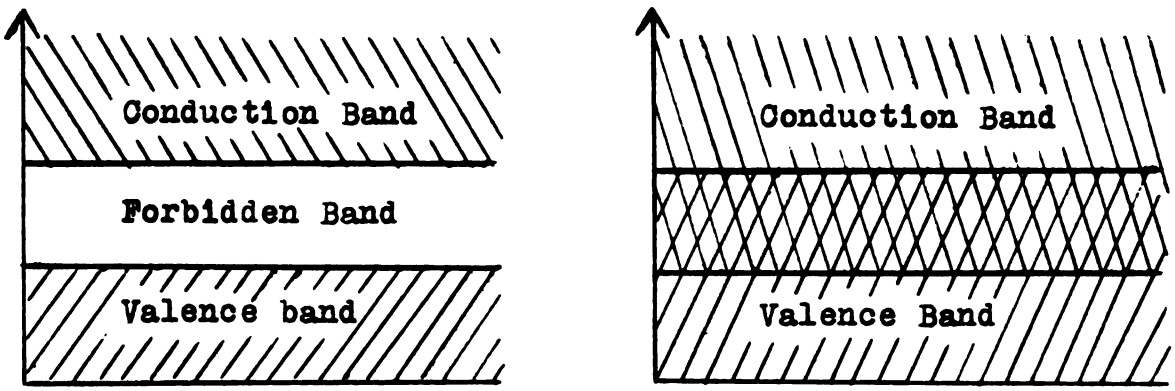
INTRODUCTION

The preparation of an organic molecule having conductivity properties comparable to those of metallic conductors presents a challenge to the synthetic chemist. Various models have been proposed but no working model has yet been synthesized.

In contrast to metallic conductors, semiconductors have a finite energy gap or forbidden band between the valence band or ground state and the conduction band (Figure 1).



Semiconductor Metal

Figure 1. Diagram of semiconductor and metal. (1)

Thermal excitation will occasionally raise an electron from the ground state to the excited conducting state. As more electrons obtain sufficient energy to cross over the forbidden band the conductivity increases.

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In organic crystals the overlap of molecular orbitals is generally very small, even to the extent that orbitals of one molecule may be isolated from those of other molecules. The relative weakness of the intermolecular attractions results in low electron mobility. Since electron transfer between molecules must occur by tunneling, any free electrons formed may be very localized (2). In order to observe enhanced conductivity, intermolecular mixing of molecular orbitals is required.

In spite of the difficulties encountered in synthesizing organic semiconductors, W. A. Little has presented a model of a molecule which he predicts will possess superconductivity properties (3,4,5). Whereas metallic superconductors function as such only at temperatures near absolute zero, Little suggests the possibility that certain types of organic compounds may be superconducting near or even above room temperature. In simplified terms, when a metal enters a superconducting state it gives up electrons which are free to travel through the ionic lattice. An electron passing an ionic center, and that ionic center are attracted to each other. Due to the greater velocity of the electron, it is beyond the ionic center when the ionic center has reached maximum displacement. However, before the ionic center has returned to its initial position, a second electron passing this center is also attracted to it. The ionic center has, in effect, caused a binding or pairing of the two electrons. This pairing is the basis for quantum mechanical considerations

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of superconductivity. Pairing occurs at low temperatures where the increase in energy resulting from pairing more than offsets the disadvantages involved in the loss of freedom of the individual electrons. If the temperature becomes too high, thermal agitation will eventually break up the pairing and disrupt the superconducting state.

Little's model of an organic system consists of two main features: a spine in which electrons fill the various states and a series of side chains which provide interaction of electrons in the spine. Even if the spine is an insulator, the addition of side chains can conceivably increase electron-electron interaction to a point where it becomes energetically favorable to enter a superconducting state. The backbone of Little's model is a polyene and the side chains are molecules of the dye, diethylcyanine iodide (Figure 2). In the side chain the positive charge is delocalized and can resonate from one end of the side chain to the other (Figure 3). This ionic site should have the same pairing effect on electrons as the ionic center in a metallic superconductor. The difference, however, is that in contrast to the metallic case where a metal ion is being displaced, it is the motion of an electron which causes the ionic movement in the side chain. The temperature below which superconductivity can occur is dependent upon the mass displaced. Since the mass of an electron is very small compared to that of a metal ion, Little's calculations predict superconductivity for this polymer to occur below $2000^{0}K$ (5).

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Figure 2.

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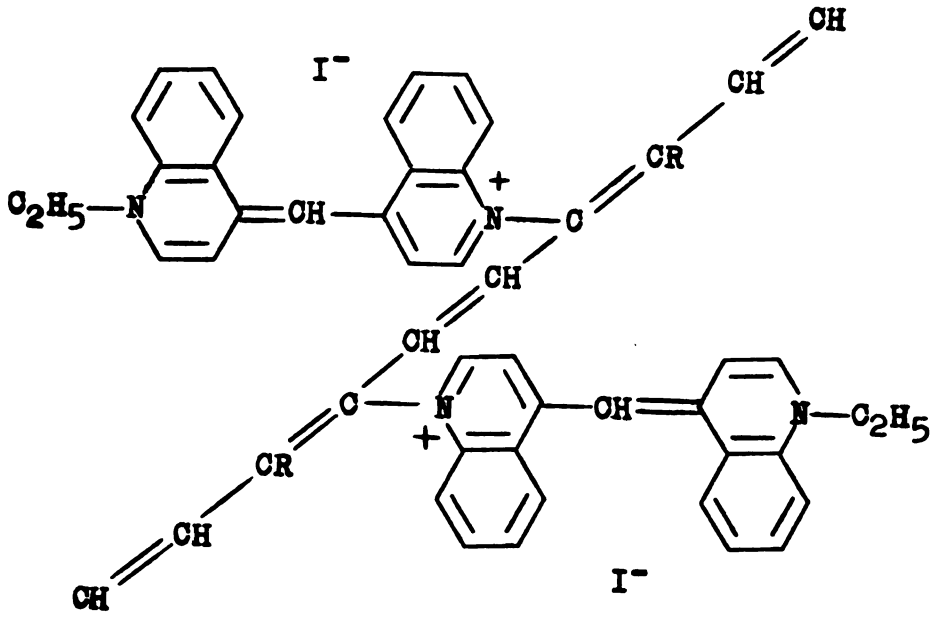


Figure 2. Little's model of an organic superconductor. (3)

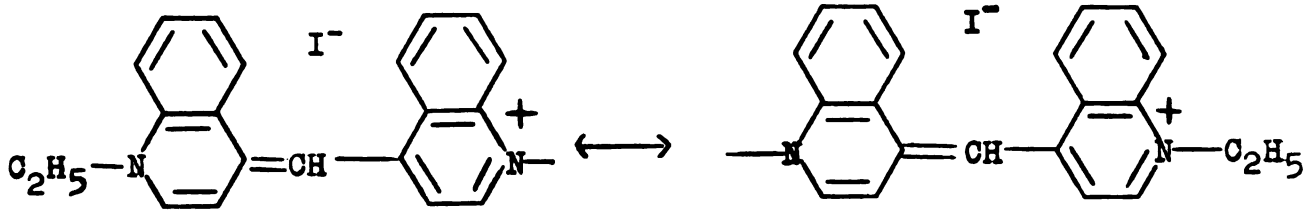
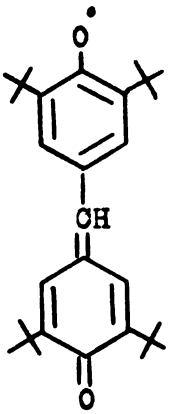


Figure 3. Extreme resonance forms of side chain. (3)

The accuracy of his calculations and the value of his model are at best only of theoretical interest. The synthesis of this particular molecule with its rigid specifications is at present too demanding. However, it may be possible to determine the validity of Little's model by incorporating electron deficient side chains on a known spine and determine the effect of the side chains on its conductivity relative to the unsubstituted compound. Greatly enhanced properties would warrant further attempts at synthesizing organic conductors having such features.

Experimental evidence suggests that a polypeptide might be a useful backbone. As early as 1941 Szent-Györgyi suggested that proteins have energy levels associated with the whole protein rather than with any particular unit within the protein (6). In his laboratory the conductivity of protein films was found to increase considerably by irradiation (7). The conductivity of proteins could also be increased by the addition of small amounts of chloranil (2). In terms of acceptance of electrons by the chloranil, transitory cations were left in the valence band. The incorporation of an electron deficient side chain on a polypeptide spine should show the same effect as chloranil in accepting electrons from the spine. One useful side chain might be the galvinoxyl free radical (1). Galvinoxyl is an electron deficient free radical having an intense blue color (8,9). If this radical could be attached as a side chain on an amino acid the energy gap may be decreased. In addition, the



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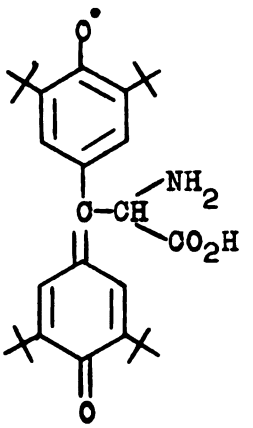

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polypeptide which could then be formed would be an interesting polymer for conductivity studies. The electron deficient side chain may accept electrons from the spine, thus increasing the conductivity of the polypeptide. This interaction may occur between the radical site and the amide bond (Figure 4). The actual effect of the side chain could then be determined by comparison with the unsubstituted polypeptide.

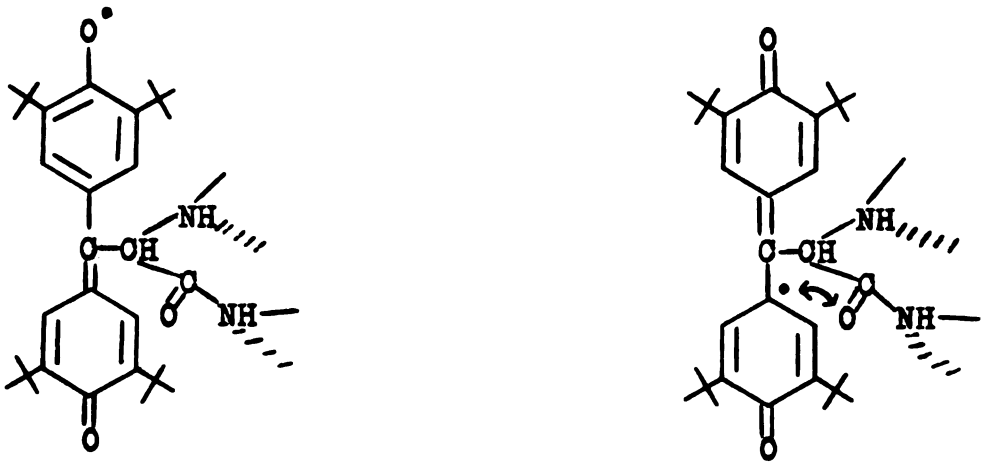
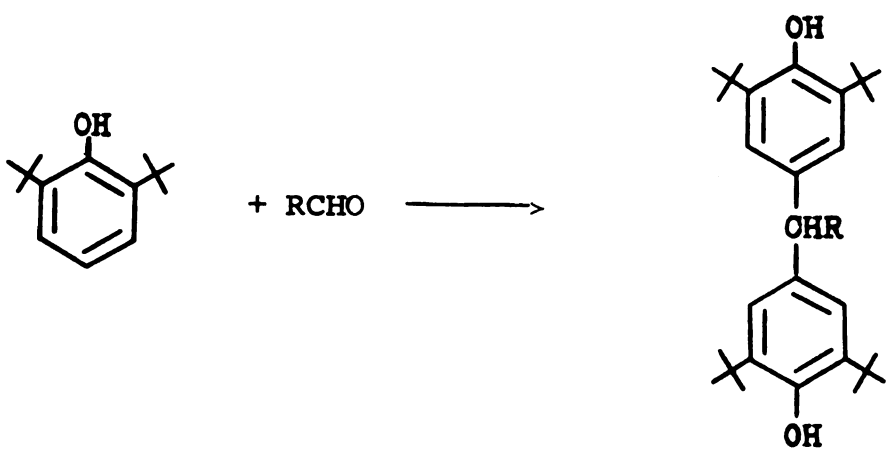


Figure 4. Interaction of side chain and spine.

RESULTS AND DISCUSSION

The synthesis of 4,4'-dihydroxy-3,3',5,5'-tetra-tert-butyldiphenyl methane (3), the precursor to galvinoxyl, involves the condensation of 2,6-di-tert-butylphenol with formaldehyde (8).



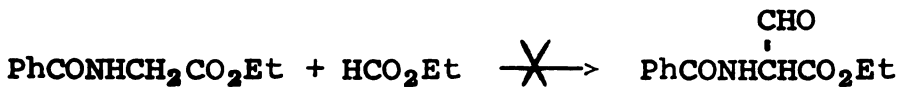
3 R = H

4 R = CH(NHCOPh)(CO_2Et)

5 R = C(NHCOCH$_3$)(CO_2Et)$_2$

By choosing the appropriate aldehyde in this condensation compounds 4 and 5 might be obtained. However, the desired aldehydes could not be obtained. Several

attempts at synthesizing ethyl α-formylhippurate (6) by condensation of ethyl hippurate and ethyl formate failed.



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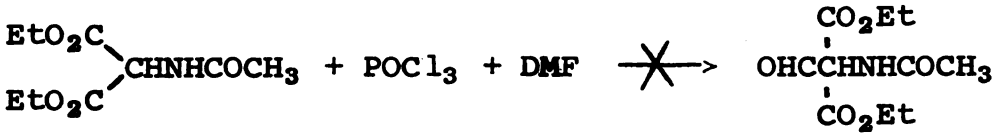
Likewise, formylation of ethyl acetamidomalonate under Vilsmeier conditions failed to give ethyl α-formylacetamidomalonate (7). In this case N-formylation rather than C-formylation apparently occurred.



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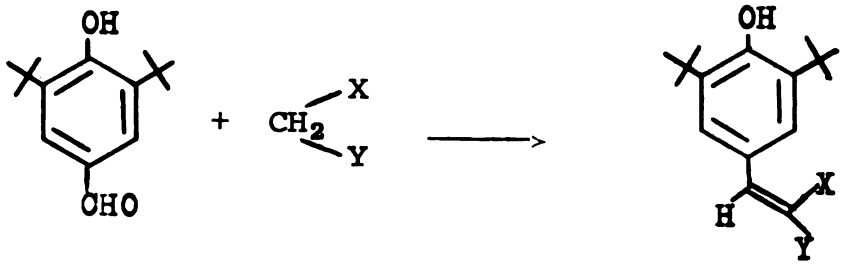
Another compound which appeared useful was 3,5-di-tert-butyl-4-hydroxybenzaldehyde (10). Benzaldehyde 8 has been condensed with various active methylene compounds to give benzylidenes 9, 10, and 11 (10). Michael addition of 2,6-di-tert-butylphenol to the benzylidene would give a galvanoxyl precursor 13. Thus a benzylidene having substituents readily convertible to an amino acid was desired.



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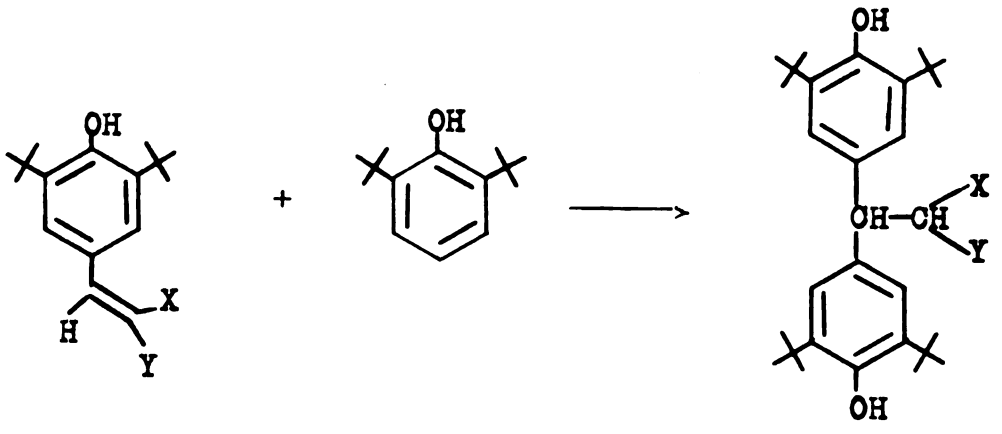
9 X = CN, Y = CO_2Et

10 X = Y = CO_2Et

11 X = Y = CN

12 X = CO_2Et, Y = NO_2



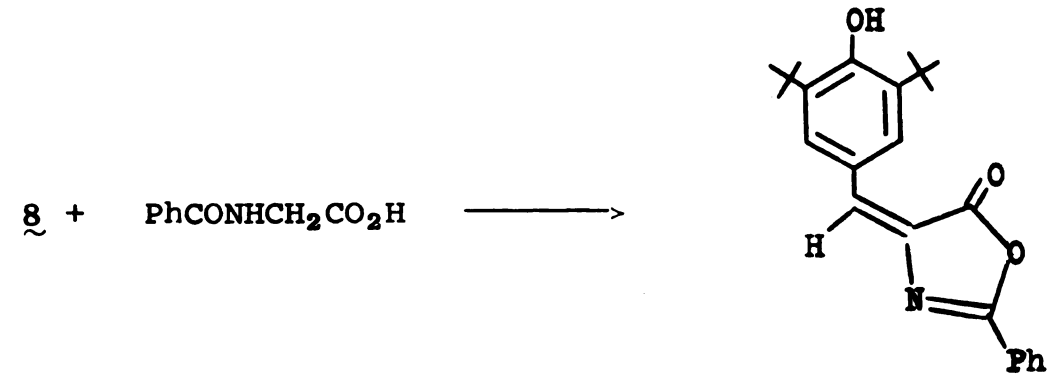
13

Reaction Scheme 1. Proposed reaction of 2,6-di-tert-butylphenol with 4-hydroxy-3,5-di-tert-butylbenzylidenes.

Condensation of ethyl nitroacetate with benzaldehyde 8 should give nitro ester 12. Although condensation was

attempted using piperidine in benzene, potassium fluoride in dimethylsulfoxide, and potassium fluoride in refluxing benzene suitable conditions could not be found for this condensation. It is possible that condensation occurs, but due to the strong electron attracting nitro and ester groups, retroreaction to starting materials becomes favorable.

Another potential precursor, 4-(3,5-di-tert-butyl-4-hydroxybenzylidene)-2-phenyl-3-oxazolin-5-one (14), resulting from the condensation of benzaldehyde 8 with hippuric acid in acetic anhydride has been reported (11).



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Michael addition of 2,6-di-tert-butylphenol to 14 would give a convenient precursor 15 to an amino acid. When such Michael condensations were attempted using benzylidenes 9, 10, and 11 as model compounds, addition did not occur. Likewise, Michael addition to 14 did not occur. Since these condensations were attempted under basic conditions the failure to add is probably due to the enhanced acidity of

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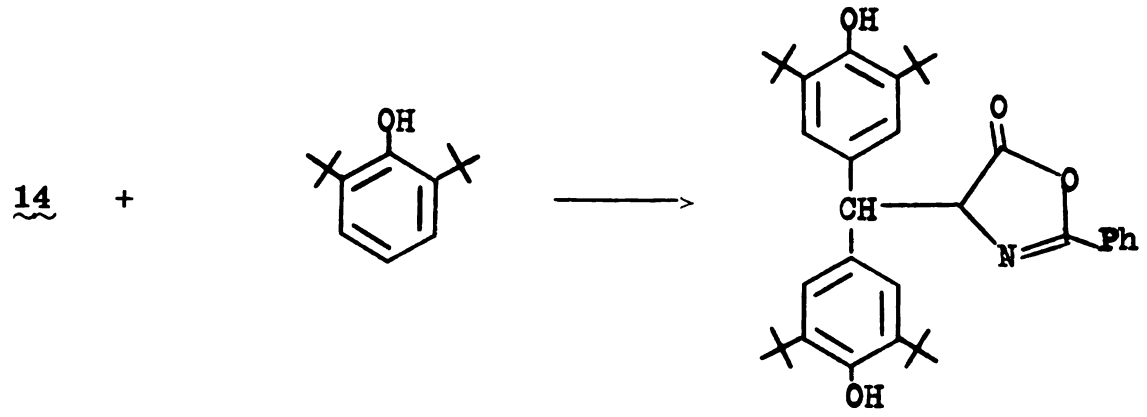

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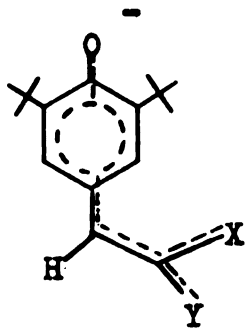
Reaction Scheme 2. Proposed reaction of 2,6-di-tert-butylphenol with 4-(3,5-di-tert-butyl-4-hydroxybenzylidene)-2-phenyl-3-oxazolin-5-one (14)

the benzylidenes relative to 2,6-di-tert-butylphenol. Thus formation of anions from the benzylidene compounds is favored due to delocalization of the charge into the substituents.



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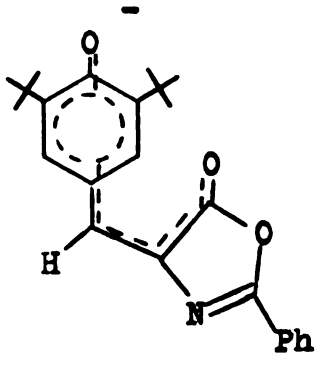

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Figure 5. Stabilization of benzylidene anions.

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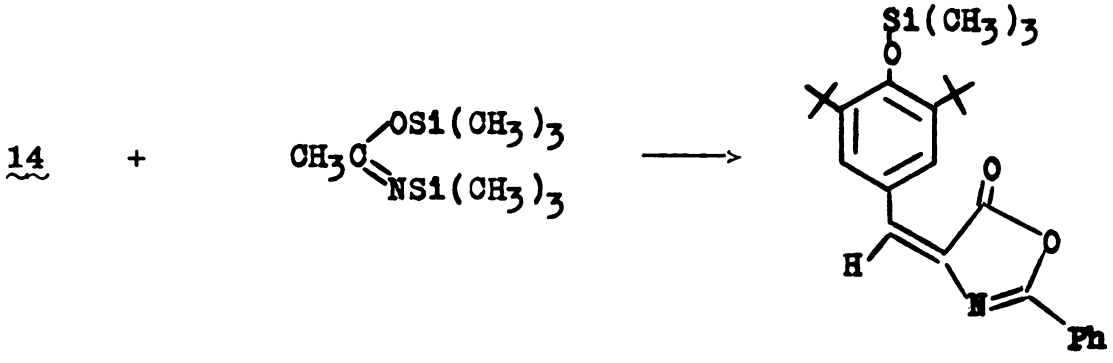
In an attempt to prevent anion 14 from forming the use of a protecting group was investigated. Trimethylsilylation of 2,6-di-tert-butylphenol with N,O-bis(trimethylsilyl)acetamide (BSA) occurs in excellent yield (12). Likewise, BSA gave excellent results with 14. Subsequent condensation of 2,6-di-tert-butylphenol with 16 by using either



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an alkoxide or 1,5-diazbicyclo[4.3.0]non-5-ene (13) as base, gave a deep red solution from which the unsilylated compound 14 was isolated. Apparently exchange or displacement of the trimethylsilyl group with the base occurred, producing the red anion of 14. The use of milder bases was ineffective.

Another approach to galvinoxyl precursor 13 which appeared promising was a 1,6-addition across 2,3',5',6-tetra-tert-butyl-4'-hydroxyphenyl-4-methylene-2,5-cyclohexadiene-1-one (17) (8). Condensation in basic solutions could not be achieved due to formation of the purple anion of 17. Even when the hydroxyl group was protected with a

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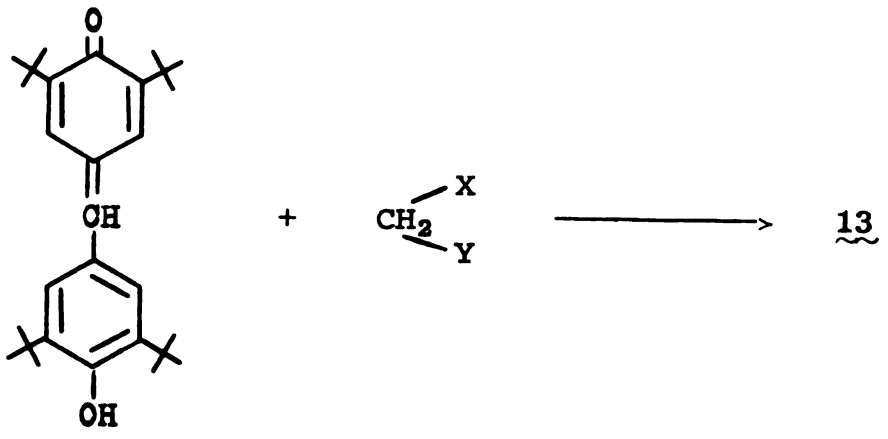

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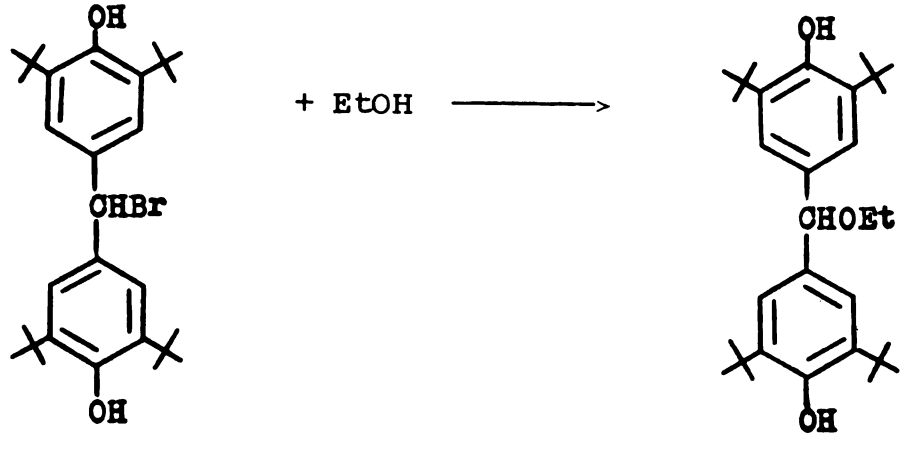
trimethylsilyl group, the protecting group was cleaved in base. Purple solutions characteristic of the anion of 17 resulted.

Some addition did occur when cyclohexadienone 17 and ethyl nitroacetate were allowed to react in benzene. However, a better precursor for the condensation product, ethyl-3,3-di-(4-hydroxy-3,5-di-tert-butylphenyl)-2-nitro-propionate (18), was found to be 4,4'-dihydroxy-3,3',5,5'-tetra-tert-butyldiphenylethoxymethane (19). Ethoxy compound 19 was



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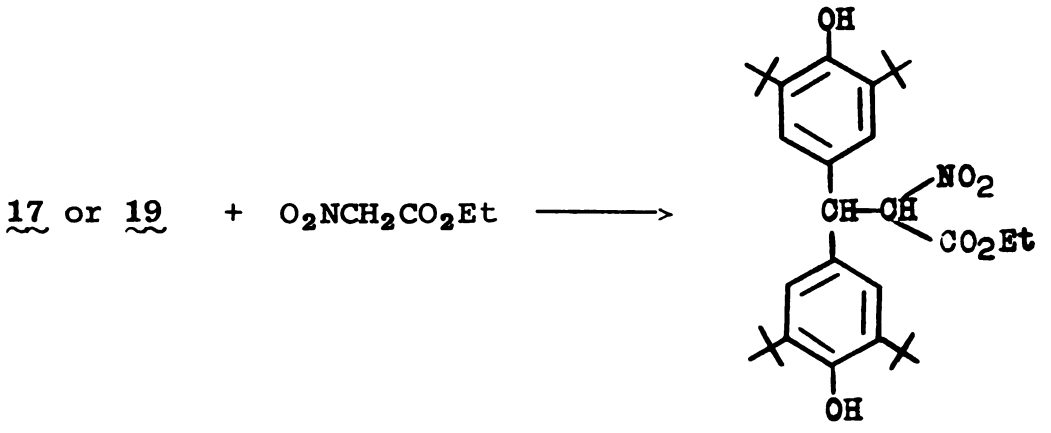
obtained when 4,4'-dihydroxy-3,3',5,5'-tetra-tert-butyl-diphenylbromomethane (8) was heated in ethanol. The structure of the ethoxy compound (19) was supported by C, H analysis, and the presence of an ether absorption in the infrared at 1075 cm^{-1}. When ethoxy compound 19 was reacted with ethyl nitroacetate in ethanol excellent yields of nitro ester 18 resulted.



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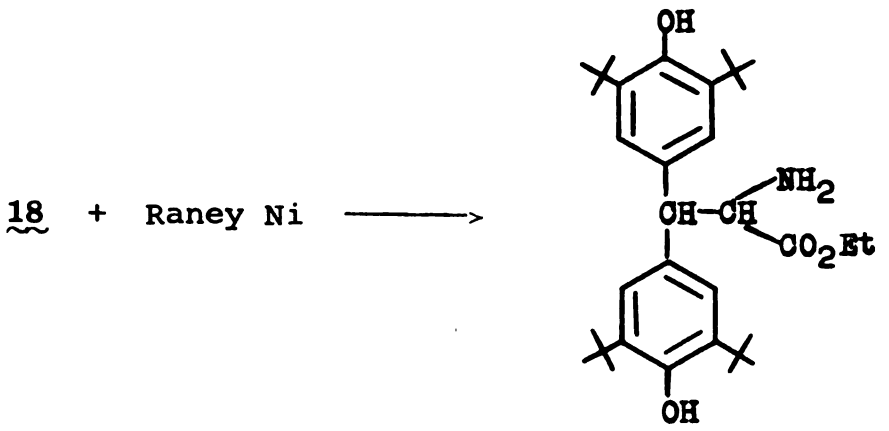
Reaction Scheme 3. Reaction of cyclohexadienone 17 with ethyl nitroacetate.

The structure of 18 was substantiated by C, H analysis and spectral data. In the infrared a sharp peak is present at 3630 cm^{-1}, indicative of a hindered phenol. In addition, absorptions appear at 1750 and 1560 cm^{-1} corresponding to an ester carbonyl and a nitro group, respectively. The ether absorption at 1075 cm^{-1} is no longer present. In the nmr there are overlapping singlets present at δ 7.15 and 7.11 (phenyl hydrogens) as well as at δ 5.15 and 5.11 (hydroxyl hydrogens). The nonequivalence of the phenyl hydrogens as well as the

nonequivalence of the hydroxyl hydrogens may be attributed to the presence of an asymmetric center in the molecule. Two doublets are centered at δ 5.80 and 4.79 (J = 12 Hz) corresponding to the methine hydrogens. The ester quartet is centered at δ 3.92 (J = 7.5 Hz) and the triplet at δ 0.89 (J = 7.5 Hz), whereas the tert-butyl hydrogens all appear as a singlet at δ 1.41.

The next step in the synthesis was the reduction of the nitro ester to an amino ester. Some problems were encountered in this reduction. Adams catalyst failed to effect reduction after 12 hours at atmospheric pressure or after 5 hours in a Paar apparatus at initial pressure of 50 psi. Reduction with iron in hydrochloric acid or with aluminum amalgam in ethanol gave complex mixtures of reduction products. Finally, it was found that the use of a Raney nickel catalyst in a Paar apparatus at initial pressure of 50 psi, gave after 6 days nearly quantitative reduction of the nitro group.



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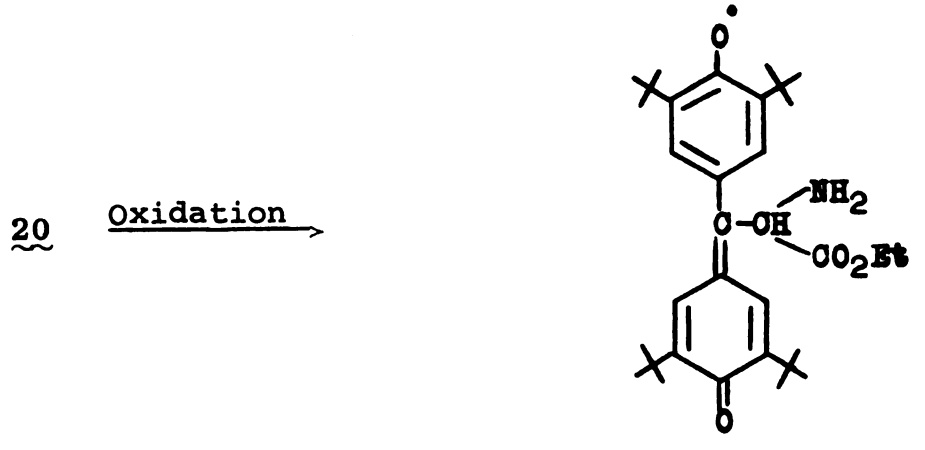
The structure of ethyl-3,3-di-(4-hydroxy-3,5-di-tert-butylphenyl)-2-aminopropionate (20) is consistent with the C, H analysis as well as with spectral data. In the infrared a carbonyl absorption is present at 1730 cm^{-1} and a hindered phenol at 3640 cm^{-1}. Instead of the nitro absorption at 1560 cm^{-1} there is an amine absorption at 3310 and 3375 cm^{-1}. In the nmr overlapping singlets are present at δ 7.15 and 7.11 (phenyl hydrogens). The tert-butyl hydrogens give rise to a singlet at δ 1.42. The ester consists of a quartet centered at δ 3.87 (J = 7.5 Hz) and a triplet at δ 0.87 (J = 7.5 Hz). The methine protons are buried under the ester quartet. The only other absorption present is a very broad one at δ 5.13. This is probably due to chemical exchange occurring between the nonequivalent hydroxyl and amino hydrogens (13).

It was anticipated that oxidation of amino ester 20 would give the desired galvinoxyl amino acid (21).



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Unfortunately, when this oxidation was attempted by using potassium ferricyanide or lead dioxide, the amino ester moiety was cleaved giving only the unsubstituted galvanoxyl radical (1). This result is reasonable considering a free radical oxidation mechanism. Initial hydrogen abstraction gives a phenoxy radical. The radical site at the para position can undergo cleavage of the most stable α-substituent. The final oxidation product is thus galvinoxyl.

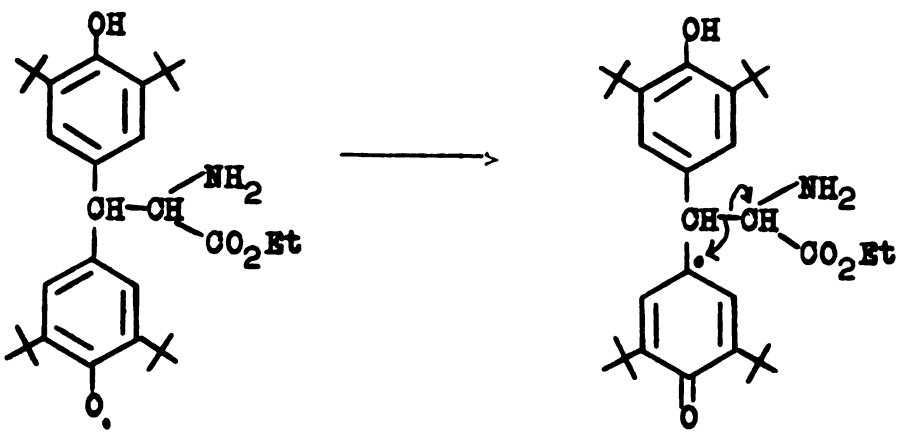

Figure 6. Cleavage of the amino ester moiety.

This problem might be circumvented if two amino ester groups could be substituted at the benzilic positions. The proposed scheme for accomplishing this consisted of a) NBS bromination of nitro ester 18, b) elimination of hydrogen bromide, c) addition of ethyl nitroacetate, d) reduction of the nitro groups, and e) oxidation to the galvinoxyl amino ester.

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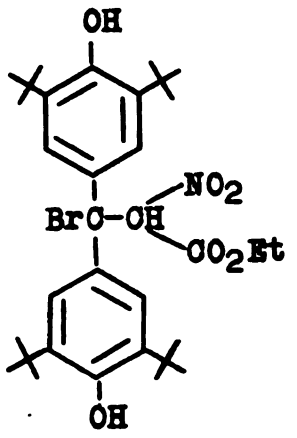

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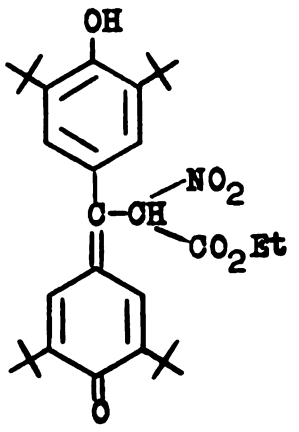
b) 22 $\xrightarrow{-HBr}$



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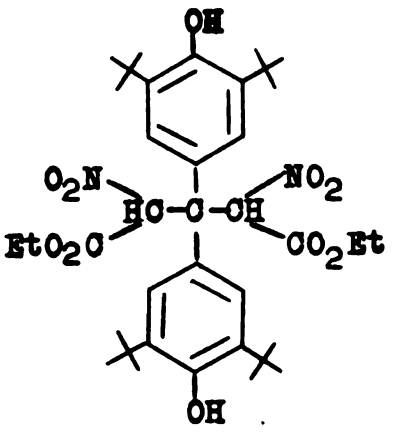
c) 23 + $O_2NCH_2CO_2Et$ ⟶



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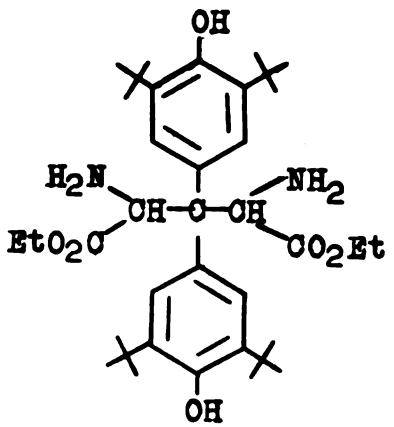
d) 24 —Reduction→ 

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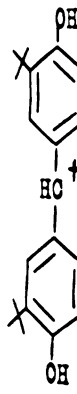
e) 25 —Oxidation→ 21

Reaction Scheme 4. Proposed incorporation of two amino acid groups on galvanoxyl precursor.

The initial NBS step again resulted in cleavage of the amino ester group giving cyclohexadienone 17. Apparently the same type of free radical side chain cleavage occurred.

Since no further ways of avoiding this cleavage could be envisioned this synthesis was abandoned.

In the course of the preceding synthesis an interesting reaction was discovered. Protonation of cyclohexadienone 17 in acetic acid -- sulfuric acid should give carbonium ion 26. It was anticipated that phenyl alanine would undergo alkylation with this carbonium ion giving the substituted phenyl alanine (27). However, phenyl alanine did not participate in the reaction. Instead, a colorless compound which analyzed for $C_{29}H_{42}O_3$ was obtained. The hindered phenol absorbs at 3610 cm^{-1} in the infrared and the carbonyl absorbs at 1660 cm^{-1}. The infrared absorption as well as the fact



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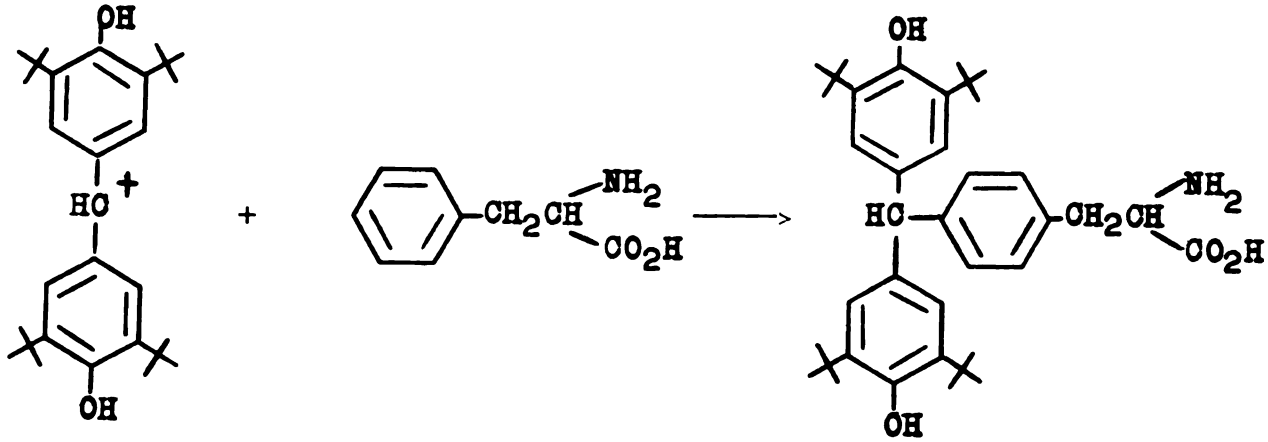
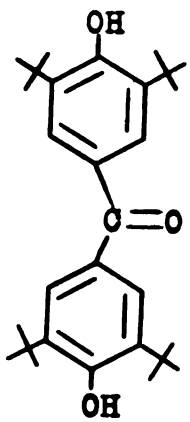


26 27

that the compound formed a red 2,4-DNP indicates the presence of a benzophenone-like carbonyl. The nmr consists of three singlets at δ 7.75 (2H), 5.70 (1H), and 1.48 (18H). These data are consistent with 4,4'-dihydroxy-3,3',5,5'-tetra-tert-butylbenzophenone (28).



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The bistrimethylsilyl derivative of 28 was readily formed by using BSA. The analysis indicated that two trimethylsilyl groups are present. In addition, the hydroxyl absorptions are no longer present in the infrared. The nmr, as expected, consists of three singlets at δ 7.75 (2H), 1.44 (18H), and 0.43 (9H).

Benzophenone 18 was obtained in about 80% yield when a solution of either cyclohexadienone 17 or ethoxy compound 19 was stirred in acetic acid - sulfuric acid solution in an open flask. The reaction apparently proceeds *via* oxidation of carbonium ion 26.

An alternate synthesis involving Friedel-Crafts reactions of 2,6-di-*tert*-butylphenol with carbon tetrachloride or phosgene using catalysts such as aluminum chloride, or stannic chloride, resulted in cleavage of the *tert*-butyl moiety. In view of the failure of conventional synthetic methods, this carbonium ion oxidation represents a valuable synthetic preparation of benzophenone 28.

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EXPERIMENTAL

1. General Procedures

The infrared spectra were recorded on a Perkin-Elmer Model 237B spectrometer. The nmr were obtained on a Varian A-60, 56-60D, or HA-100 spectrometer. Computer calculations of nmr spectra were done on a CDC 3600 computer. Ultraviolet spectra were recorded on a Unicam Model SP-800 instrument using 1 cm quartz cells.

Low resolution mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6 mass spectrometer. The high resolution mass spectra were run at Battelle Memorial Institute on an A.E.I. MS-9 double-focusing mass spectrometer.

Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan, or by Galbraith Laboratories in Knoxville, Tennessee.

2. 4,4'-Dihydroxy-3,3',5,5'-tetra-tert-butyldiphenylethoxymethane (19)

A solution of 3 g of 4,4'-dihydroxy-3,3',5,5'-tert-butyldiphenylbromomethane (8) in 20 ml of absolute ethanol

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and 1 ml of hydrochloric acid was refluxed for 2 hrs. Upon cooling, 1.5 g (54%) of yellow product was obtained. Two recrystallizations from ethanol and one from pentane gave a colorless product: mp 162-163°; ir ($CHCl_3$) 3640 (hindered phenol) and 1075 cm^{-1} (ether); nmr ($CDCl_3$) δ 7.11 (s, 4H), 5.21 (s, 1H), 5.07 (s, 2H), 3.51 (q, 2H, J = 7 Hz), 1.41 (s, 36H) and 1.25 (t, 3H, J = 7 Hz).

Anal. Calcd. for $C_{31}H_{48}O_3$: C, 79.49; H, 10.25.
Found: C, 79.38; H, 10.23.

3. Ethyl 3,3-di-(4-hydroxy-3,5-di-tert-butyl)phenyl-2-nitro propionate (18)

a) From cyclohexadienone 17: To 3 g (0.0071 mole) of cyclohexadienone in 20 ml of benzene was added 3 g of ethyl nitroacetate (0.0213 mole) and the mixture heated to reflux for 24 hours. The benzene was removed on a rotary evaporator and the residue dissolved in ethanol. The first crop was starting material (1.0 g). The second crop contained 0.2 g of product: mp 153-154°; ir ($CHCl_3$) 3620 (hindered phenol), 1745 (ester C=O) and 1560 cm^{-1} (nitro); nmr ($CDCl_3$) δ 7.15, 7.11 (overlapping s, 4H), 5.80 (d, 1H, J = 13 Hz), 5.15, 5.11 (overlapping S, 2H), 4.79 (d, 1H, J = 12 Hz), 3.92 (q, 2H, J = 7.5), 1.41 (s, 36H), and 0.89 (t, 3H, J = 7.5).

Anal. Calcd. for $C_{33}H_{49}NO_6$: C, 71.23; H, 8.89.
Found: C, 71.32; H, 8.77.

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b) From 4,4'-dihydroxy-3,3',5,5'-tetra-tert-butyl-diphenylethoxymethane (19): To 37 g of ethoxy compound 19 in 200 ml of absolute ethanol was added 15 g of ethyl nitroacetate. The solution was heated to reflux for 2 hrs and the ethanol solution then allowed to evaporate to dryness in an evaporating dish. The residue was recrystallized from ethanol to give 40.7 g (93.5%) of product identical to nitroester prepared in procedure a.

4. Ethyl 3,3-di-(4-hydroxy-3,5-di-tert-butyl)phenyl-2-amino-propionate (20)

A mixture of 10.7 g of nitroester 18 and 2 g of freshly prepared Raney nickel catalyst in 200 ml of isopropanol was hydrogenated in a Paar apparatus at initial pressure of 49 psi. After 6 days the pressure was 37 psi, and no further uptake was evident. The mixture was filtered to remove the catalyst and the filtrate evaporated to dryness (reduced pressure). The residue was crystallized from ethanol to give 9.94 g (98%) of reduction product: mp 141-142°; ir ($CHCl_3$) 3610 (OH), 3370, 3290 (NH_2), and 1725 cm^{-1} (ester C=O); nmr ($CDCl_3$) δ 7.15, 7.11 (overlapping s, 4H), 3.87 (q, 2H, J = 7.5 Hz), 3.87 (2H buried under quartet), 1.42 (s, 36H), 0.87 (t, 3H, J = 7.5 Hz) and 5.3-4.9 (very broad absorption).

Anal. Calcd. for $C_{33}H_{51}NO_4$: C, 75.38; H, 9.78.

Found: C, 75.45; H, 9.80.

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5. Oxidation of Amino Ester 20

a) Potassium ferricyanide: To a stirred mixture of 3.94 g (0.012 mole) of potassium ferricyanide, 0.6 g of sodium hydroxide, 15 ml of water and 80 ml of benzene was added 1.73 g of amino ester 20 in 15 ml of benzene over a period of 30 minutes. The mixture was stirred under nitrogen for 30 minutes. The layers were separated and the benzene washed with water and dried ($MgSO_4$). Upon removal of the solvent 0.9 g of purple crystals remained. The ir was identical with that of galvinoxyl.

b) Lead dioxide: A mixture of 0.3 g of amino ester 20 and 1.5 g of lead dioxide in 20 ml of benzene was stirred overnight. The mixture was filtered through filter cel and the solvent removed from the filtrate. The residue was dissolved in chloroform and filtered. Removal of the chloroform gave a purple residue with an ir identical with that of galvinoxyl.

6. 4,4'-Dihydroxy-3,3'-5,5'-tetra-tert-butylbenzophenone (28)

a) From ethoxy compound 19: A solution of 0.5 g of ethoxy compound 19 in 5 ml of acetic acid containing 3 drops of concentrated sulfuric acid was stirred in an open flask for 24 hrs. The solid which separated was isolated by filtration. Water was slowly added to the filtrate to give additional product. The combined solids were dried and

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recrystallized from carbon tetrachloride to give 0.38 g (81%) of benzophenone 28: mp 221-222°; 2,4-DNP mp 180-182°; ir ($CHCl_3$) 3620 (hindered phenol), and 1635 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.75 (s, 2H), 5.70 (s, 1H) and 1.48 (s, 18H).

Anal. Calcd. for $C_{29}H_{42}O_3$: C, 79.50; H, 9.59.
Found: C, 79.45; H, 9.65.

b) From cyclohexadienone 17: Following the same procedure as in a, 2 g of cyclohexadienone in 25 ml of acetic acid containing 10 drops of concentrated sulfuric acid gave 1.6 g (78%) of benzophenone 28.

7. 4,4'-Di-(trimethylsilyl)-3,3',5,5'-tetra-tert-butyl-benzophenone

To 1.09 g (0.0025 mole) of benzophenone 28 in 8 ml of acetonitrile (freshly distilled from P_2O_5) was added 1.5 g (0.0075 mole) of BSA. The mixture was heated to reflux for 12 1/2 hrs. The solution was allowed to cool to room temperature during which time colorless crystals separated. After filtration and washing with solvent 1.0 g (80%) of product was obtained: mp 183-184°; ir ($CHCl_3$) 1648 (C=O), 1260, 1225, 835 and 750 cm^{-1} (trimethylsilyl); nmr ($CDCl_3$) δ 7.75 (s, 2H), 1.44 (s, 18H), and 0.43 (s, 9H).

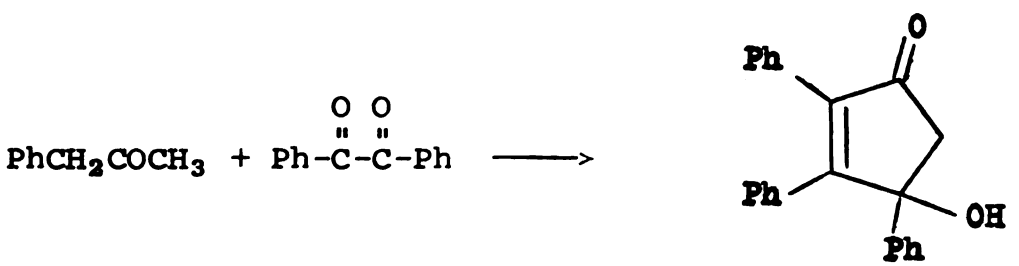
Anal. Calcd. for $C_{35}H_{58}Si_2O_3$: C, 72.10; H, 10.03.
Found: C, 72.10; H, 10.06.

PART II

NOVEL REACTION PRODUCTS OF 4-HYDROXY-2,3,4-TRIPHENYL-2-CYCLOPENTEN-1-ONE

INTRODUCTION

The synthesis of 4-hydroxy-2,3,4-triphenyl-2-cyclopenten-1-one (29) via condensation of phenylacetone with benzil was first reported in 1934 by Dilthey and Hurtig (15).



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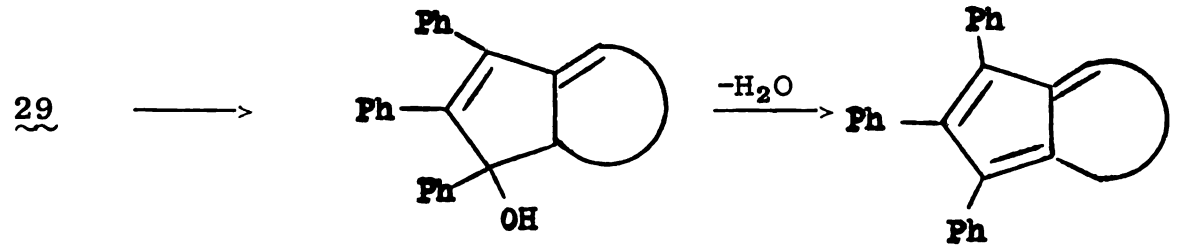
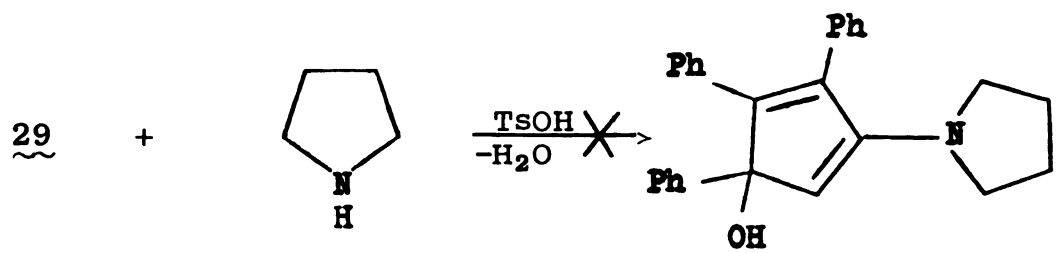
Such structural features as the carbonyl, active methylene, and hydroxyl groups make this compound a valuable starting material for the synthesis of theoretically interesting molecules. Fused ring systems might be obtained by condensation across the carbonyl and active methylene of hydroxyketone 29. The hydroxyl group would then provide a means for introducing another double bond into the system.

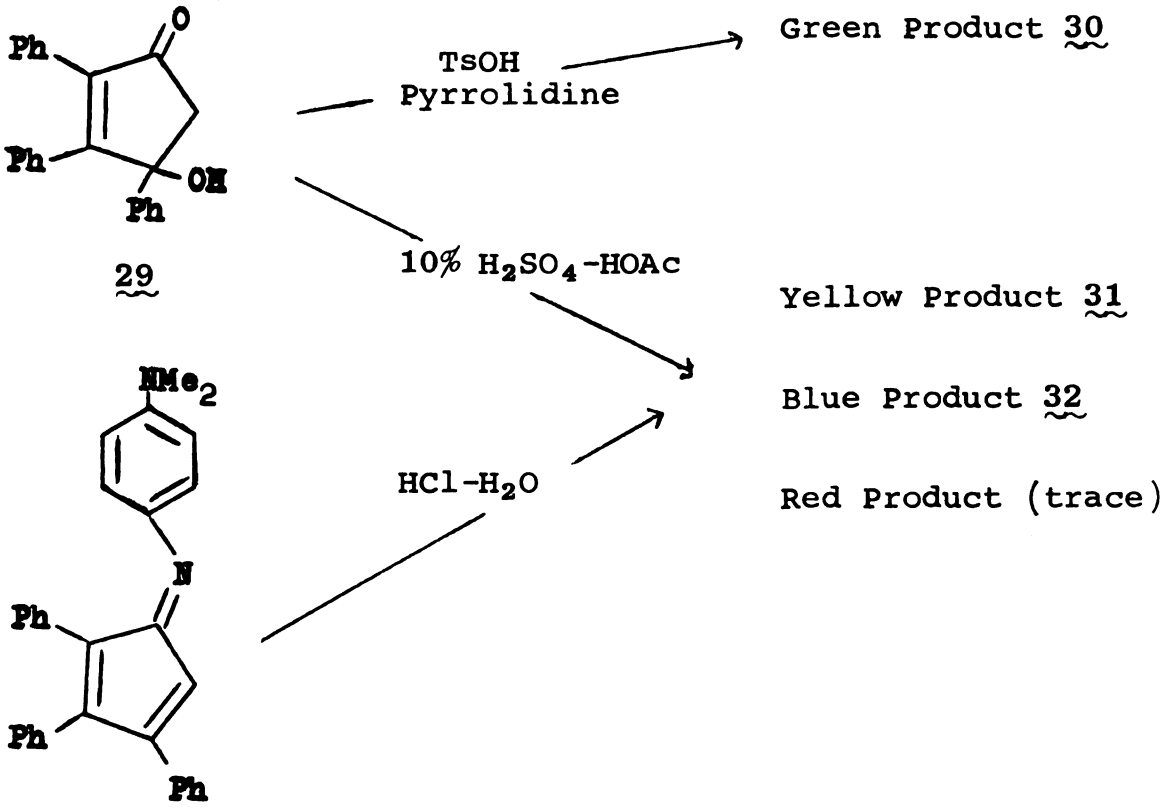


One precursor for accomplishing such cyclizations would be the pyrrolidine enamine of hydroxy-ketone 29. With such cyclizations as the objective the synthesis of the enamine was attempted. An attempt to prepare this enamine from pyrrolidine and 29 resulted instead in the formation of a dark green crystalline compound (30).



One reaction which might have occurred is a simple dehydration by p-toluenesulfonic acid, which is used as a catalyst in the reaction. However, the acid dehydration of hydroxy-ketone 29 has been reported (16) and none of the products are identical with green compound 30. These dehydration products are interesting since they are also highly colored. The minor product (31) is yellow and the

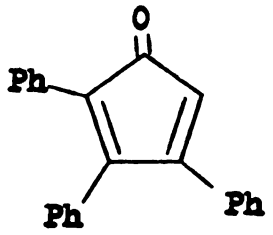
major product (32) is blue. A trace of red product was also reported. These same products also resulted from the hydrolysis of 5-p-dimethylaminoanilino-1,2,3-triphenyl-cyclopentadienone (33) (16).



An obvious common reaction product which could result from either the dehydration or hydrolysis reaction is 2,3,4-triphenylcyclopentadienone (34). In fact, cyclone 34 was the structure assigned to the blue product. The yellow product was reported to be a dimer but not the usual cyclopentadienone dimer.

An investigation of the properties of cyclopentadienones (I) (or cyclones) casts doubt on the assignment of

a cyclone structure to either blue compound 32 or green compound 30.



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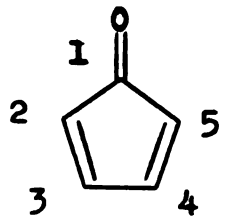

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Cyclones are in general very reactive compounds. Molecular orbital calculations predict a very reactive 2,3 double bond as well as strong dienic ability (17). In the absence of other reactants, cyclones may dimerize via a Diels-Alder reaction. This dimerization is sterically dependent upon the bulk of the substituents on the cyclone ring.

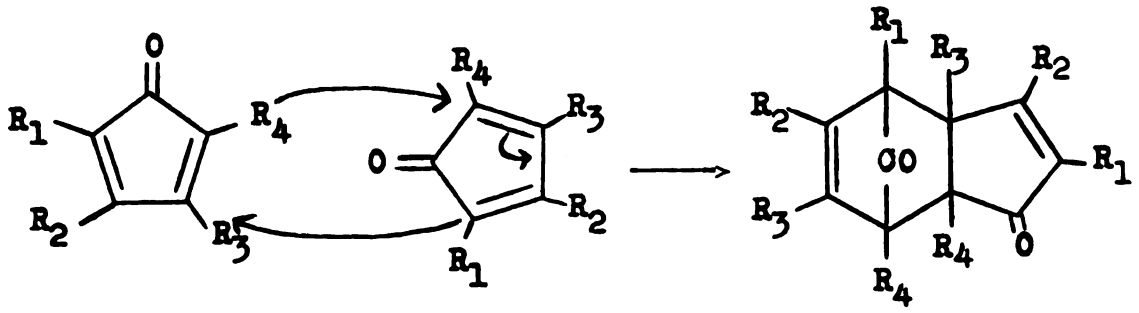
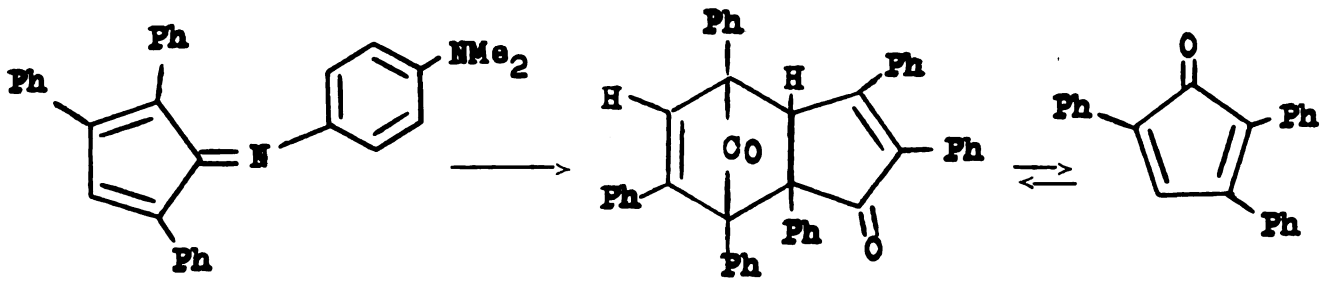


Figure 7. Dimerization of cyclopentadienones.

The parent cyclopentadienone exists exclusively in the dimeric form and has eluded all attempts at isolation (18).

On the other hand, dimerization is completely inhibited in the case of tetraarylcyclones, although they still function as reactive dienes (19). Steric factors also inhibit the dimerization of 2,3,5-tri(tert-butyl)cyclone, 2-methyl-3,4,5-triphenylcyclone, and tetra(trifluoromethyl)cyclone (20).

Certain other cyclones such as 2,5-dimethyl-3,4-diphenylcyclone, 2-methyl-3,4-diphenyl-5-ethylcyclone, and 2,3,5-triphenylcyclone exist as temperature dependent dissociating dimers (20). For example, the hydrolysis of 5-p-dimethylaminoanilino-1,2,4-triphenylcyclopentadiene (35) is reported to give 2,3,5-triphenylcyclone dimer (36a), which is in thermal equilibrium with its monomer (36) in solution (21). The colorless dimer can be isolated but when solutions of the dimer are heated the characteristic red color of cyclone monomers results.



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In view of the steric factors influencing dimerization, intuitively it might be predicted that 2,3,4-triphenylcyclone (34) should dimerize more readily than

2,3,5-triphenylcyclone (36). Addition of the diene portion of one molecule is sterically more favorable across the less substituted double bond of a second molecule. In the case of 2,3,4-triphenylcyclone the addition should be more favorable because the termini of the diene portion are substituted with one hydrogen and only one phenyl group. The diene portion of 2,3,5-triphenylcyclone, however, has two phenyl substituents at its termini. In each case the steric effects of the dienophilic double bonds are comparable.

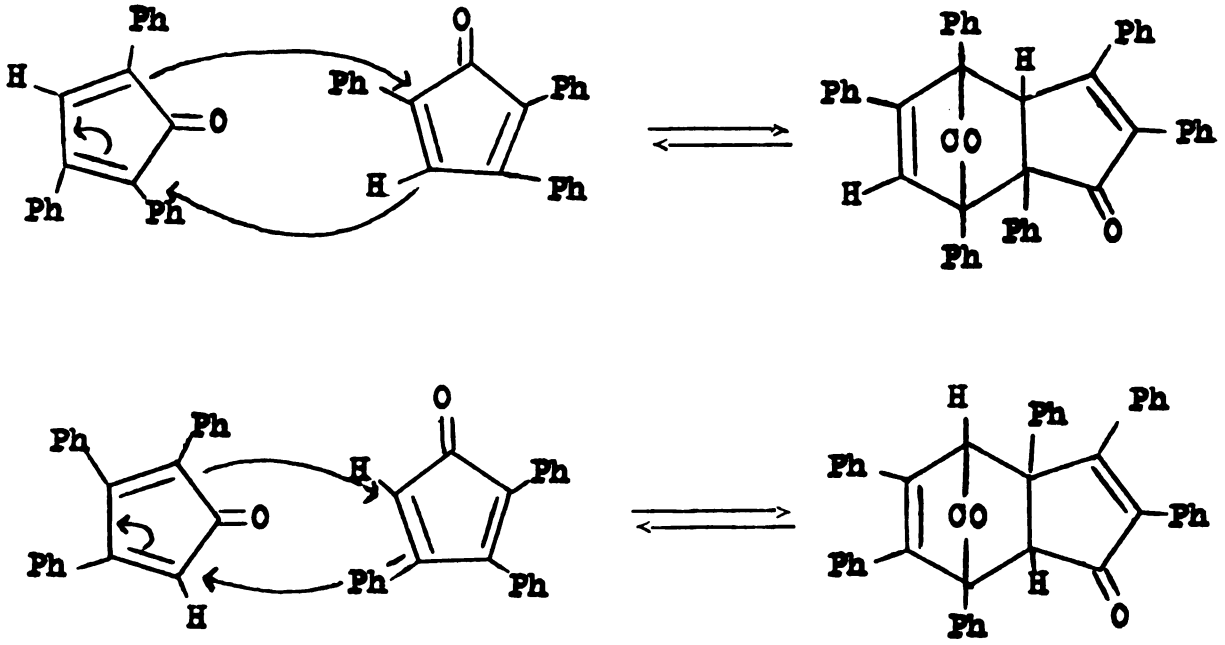


Figure 8. Comparison of steric effects on dimerizations of triphenylcyclones.

It appears that the existence of 2,3,4-triphenylcyclone in exclusively the monomeric form is unlikely. If, however, the monomer could exist it would be expected to be the characteristic red color of cyclone monomers. If a cyclone

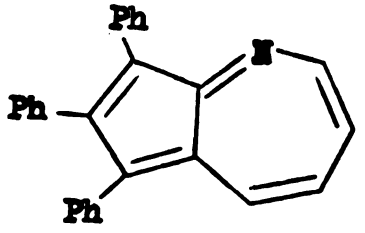
structure were to be suggested for either blue compound 32 or green compound 30, a satisfactory explanation for the large bathochromic shift would have to be made. There is no pecularity in the structure of 2,3,4-triphenylcyclone which could account for this shift. Thus, a cyclone structure for either green compound 30 or blue compound 32 is discredited because of color and because of steric effects which influence dimerization.

Whereas one of the standard methods for the preparation of cyclopentadienones involves the dehydration of 4-hydroxy-2-cyclopenten-1-ones it is apparent that dehydration of hydroxy-ketone 29 occurs in a completely different manner. The reaction products are unusual not only because they are not normal products, but also because they are so intensely colored. This suggests that the most favorable reaction paths available are ones which lead to highly stable conjugated products. In order to determine why these reactions occur as they do it was necessary to attempt to identify these novel reaction products. It was anticipated that once the structures of the products were known a reasonable explanation of the reaction paths could be made. The discussion which follows concerns the identification of these products based on spectral and chemical evidence.

RESULTS AND DISCUSSION

Identification of 2,3,4-Triphenyl-4-azazulene (30)

The green product resulting from the reaction of hydroxy-ketone 29 with pyrrolidine was found to be 1,2,3-triphenyl-4-azazulene (30). This novel 4-azazulene structure is well substantiated by spectral data. Its intense



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color and absorptions in the visible region at 610, 654 and 710 mμ (acetonitrile) are immediately suggestive of an azulene type structure. The molecular formula $C_{27}H_{19}N$, derived from the elemental analysis and mass spectrum, is also consistent with the proposed structure.

A computer analysis of the high resolution mass spectrum (22) shows initially only fragmentation of hydrogens from the parent molecular ion at mass 357. The most favorable fragmentation is the loss of a phenyl group. In

addition, there is an abundance of peaks attributed to doubly ionized fragments. In general such an abundance of doubly ionized fragments is found only in highly stabilized molecules such as fused ring aromatics (23). Furthermore, the absence of functional groups in this molecule is evident from the infrared spectrum.

The nmr spectrum (Figure 25) is also consistent with an aromatic compound. The nmr consists of two low field multiplets at δ 8.33-8.08 and 8.07-7.82, each due to one hydrogen, and a higher field multiplet at δ 7.32-6.82 due to 17 hydrogens. These chemical shifts are similar to the chemical shifts of the hydrogens on azulene (Table I) (24).

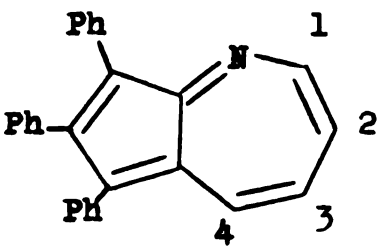
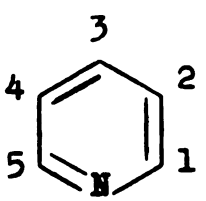
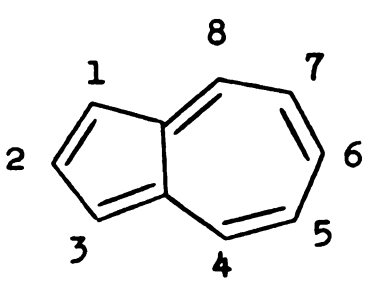
Of the 17 hydrogens in the highest field multiplet of azazulene 30, 15 are due to the phenyl hydrogens. The remaining two hydrogens in this region are due to two hydrogens on the azazulene ring. Since no significant spin interaction could occur between the phenyl hydrogens and the hydrogens on the azazulene ring, the nmr can be analyzed as a four spin case. This was accomplished by use of the LAOCOON III computer program (25). In order to determine the relative chemical shifts and coupling constants to be used as input in LAOCOON III, the two low field hydrogens were decoupled from each other. When each of the two low field hydrogens was decoupled from the other, the patterns of these two hydrogens coalesced to four lines each. Thus, they appeared to be weakly coupled to each other and each, in turn, coupled more strongly to the two higher field

hydrogens. Because the weakest coupling occurred between the two low field hydrogens they were assumed to be H_1 and H_4 (Table I). The relative positions of H_1 and H_4 were based on comparison with pyridine and azulene (Table I). The adjacent nitrogen should cause H_1 to be shifted downfield relative to the corresponding hydrogen on azulene (Table I). In addition, H_4 is in the shielding region of the nearby phenyl group and should appear at higher field than the corresponding hydrogen on azulene. Thus, H_1 was assumed to be at lowest field.

The two higher field absorptions, which are obscured by the phenyl multiplet, are due to H_2 and H_3. Of these two, H_2 was assumed to be at lower field by comparison with the corresponding hydrogens on azulene. Using these relative assignments, the estimated chemical shifts and coupling constants were refined until a good match of the calculated and experimental spectra of the low field region (460-510 Hz) was obtained (Figure 26). The refined values of the chemical shifts and coupling constants are listed in Table I. The values for pyridine and azulene are also given for comparison.

By comparison of the calculated values of the chemical shifts of the azazulene hydrogens with the corresponding hydrogens on pyridine and azulene, the relative positions of the azazulene hydrogens appear reasonable. For example, the relative positions of H_2 and H_3 might be obtained by comparing the difference in chemical shifts of H_2 and

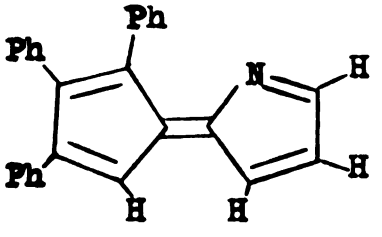
Table I. Calculated nmr spectra of 1,2,3-triphenylazazulene (30), pyridine (25), and azulene (24)

	Hydrogen	Chem Shift (Hz)	(ppm)	$J_{m,n}$	(Hz)
	1	495.8	8.26	1,2	6.52
	2	425.9	7.10	1,3	1.11
	3	420.3	7.05	1,4	0.267
	4	478.4	7.97	2,3	9.46
				2,4	1.30
				3,4	8.96
30					
	1	516.5	8.6	1,2	4.88
				4,5	4.88
	2	427.4	7.12	1,3	1.84
				3,5	1.84
	3	450.1	7.5	1,4	0.995
				2,5	0.995
	4	427.4	7.12	1,5	-0.132
	5	516.5	8.6	2,3	7.67
				3,4	7.67
				2,4	1.37
	1		7.27	1,2	4.0
	2		7.80	2,3	4.0
	3		7.27	4,5	9.5
	4		8.22	7,8	9.5
	5		7.04	5,6	10.3
	6		7.47	6,7	10.3
	7		7.04	4,6	1.5
	8		8.22	6,8	1.5

H_3, with the difference in chemical shifts of the corresponding hydrogens on pyridine and azulene. An estimate of the difference in the chemical shifts of H_2 and H_3 might be:

$$\Delta H_2,H_3(\text{azazulene}) = \Delta H_2,H_3(\text{pyridine}) + \Delta H_5,H_6(\text{azulene})$$

By substituting the values from Table I for pyridine and azulene in the lefthand side, a value of 0.05 ppm is obtained. This same value is obtained by subtracting H_2-H_3 for the azazulene hydrogens. This result lends some support to the relative assignments assumed when making the calculations. In any case, a plot of the calculated downfield portion of the nmr (i.e., H_1 and H_4) of azazulene using the parameters in Table I results in an excellent match with the observed spectrum. However, since the lines for H_2 and H_3 are buried under the phenyl region it is not known whether they coincide exactly with the calculated lines in that region. Thus, the calculated parameters may not be exact. The important result is that the observed spectrum must arise from four interacting adjacent hydrogens. This eliminates from consideration any structures such as the isomeric heterofulvalene below. In this compound all of the

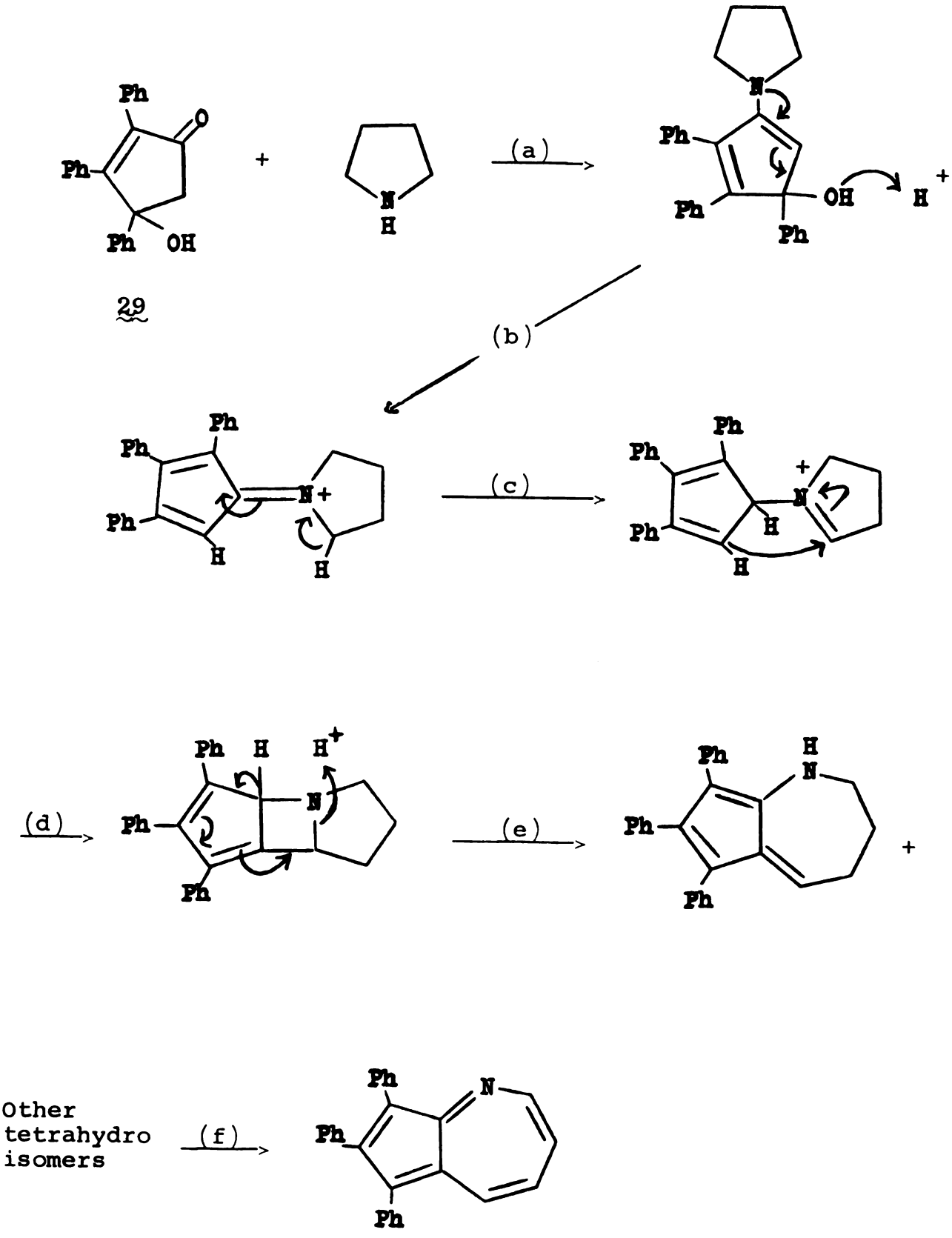


hydrogens do not interact with each other. Overall, the establishment of a four spin system of the type ABCD, in conjunction with the starting materials, supports the assignment of 1,2,3-triphenyl-4-azazulene (30).

The formation of azazulene 30 can be rationalized by a logical mechanistic scheme (I): (a) initial formation of the pyrrolidine enamine of hydroxy-ketone 29, (b) acid catalyzed loss of the hydroxyl group, (c) isomerization to a more favorable intermediate, (d) Vilsmeier type addition to the cyclopentadiene ring, (e) ring expansion to tetrahydroazazulene isomers, and (f) air oxidation during chromatography.

Evidence in support of the oxidation during chromatography is that an initial yellow band began to separate on an alumina column. Before it could be completely eluted the band turned green. No yellow product was subsequently eluted. If a nylon column (26) was used it could be cut apart when sufficient separation had occurred. The yellow compound could then be extracted from the alumina before oxidation occurred. Due to the many different tetrahydro isomers possible, the nmr was useful only in establishing the number of aliphatic hydrogens relative to phenyl hydrogens in this compound. This ratio, 8:15, as well as the elemental analysis, is in accord with a tetrahydroazazulene. The ease of oxidation reflects the stability of the heteroaromatic system which is formed.

When alkylation of azazulene 30 with methyl



(30)

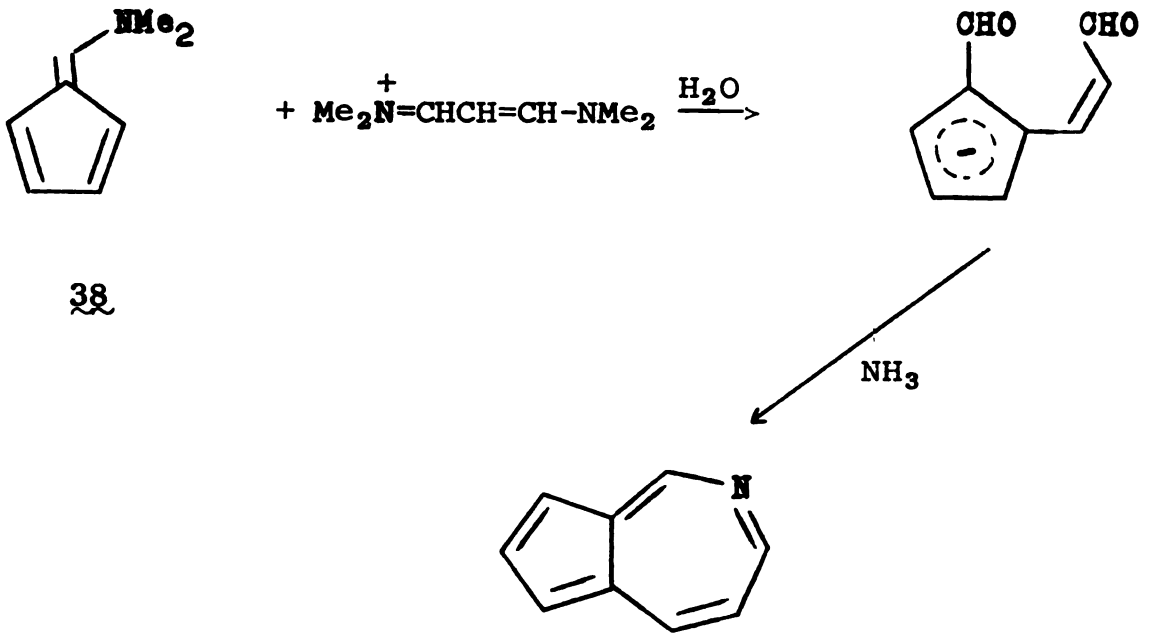
Mechanistic Scheme I. The formation of 1,2,3-triphenyl-4-azazulene (30).

lithium in ether at room temperature was attempted, no addition occurred. However, when benzene was used as the solvent and the temperature increased to 60°, the green solution turned yellow and a mixture of products resulted. Although these attempts failed to give useful alkylation products, it should be possible to find proper conditions under which controlled alkylation can occur.

Likewise, an attempt to prepare the N-oxide of azazulene 30 by using hydrogen peroxide in acetonitrile was unsuccessful. Only unreacted starting material was isolated. However, when m-chloroperbenzoic acid was used as the oxidizing agent the reaction mixture faded to light yellow within 15 minutes. The failure of the N-oxide to form is probably due to the steric effects of the nearby phenyl group on the nitrogen. The stronger reagent apparently reacts with a double bond in the aromatic system. The destroyed conjugation results in loss of the green color.

This particular system is one of only a few azazulenes known in which the heteroatom is present in the seven membered ring. The parent 5-azazulene has been prepared by Hafner (27). The reaction scheme involves a Vilsmeier addition to 6-N,N-dimethylaminofuvene (38) followed by hydrolysis and condensation with ammonia. The parent 5-azazulene is reported to have its long wavelength absorption in the visible region at 652 mμ.

The only other example of a 4-azazulene known is 1-cyano-2,6-dibenz-4-azazulene (39) (28). Azazulene 39



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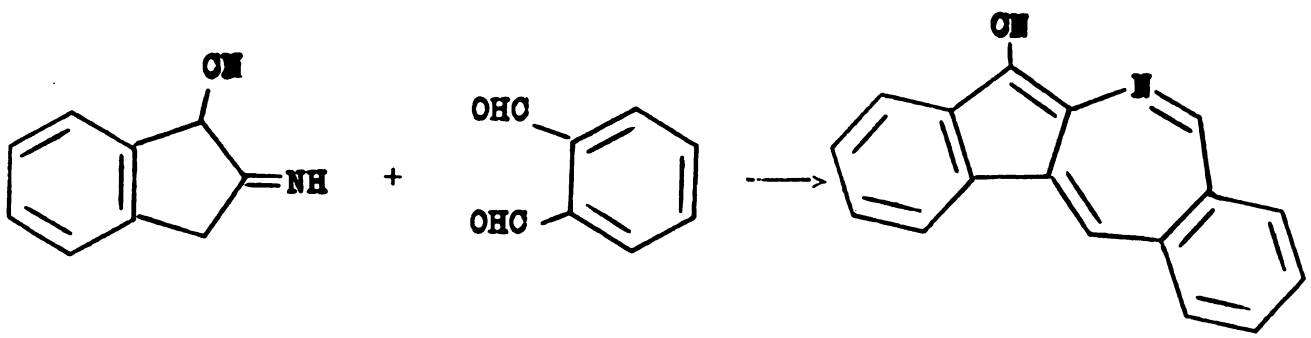
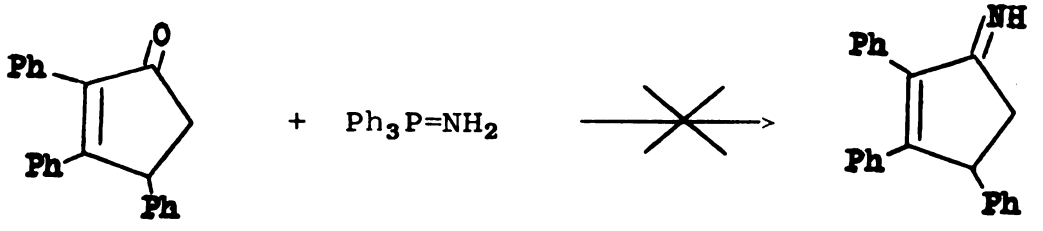
37

resulted from the condensation of 1-cyano-2-indanonimine with phthaldehyde. This product was a red crystalline solid which absorbs in the visible region at 438 mμ. The hypsochromic shift of azazulene 39 relative to azazulene 30 is due to the presence of the benzo groups which remove some of the electron density from the azazulene system.



39

Several attempts were made to synthesize 1,2,3-triphenyl-4-azazulene (30) by an alternate route. A procedure analogous to the scheme used in the preparation of 4-azazulene 39 was attempted. Triphenylphosphinimine (29) has been reacted with benzophenone to give benzophenonimine (30). It was anticipated that the reaction of triphenylphosphinimine with 2,3,4-triphenyl-2-cyclopenten-1-one (40) (31) would give the corresponding imine. Condensation of the resulting imine with diacetoxydihydrofuran (32) might give the desired azazulene. However, reaction of ketone 40 with triphenylphosphinimine failed to give the imine of ketone 40. This may be due to enolization occurring rather than addition of the imine to the carbonyl.



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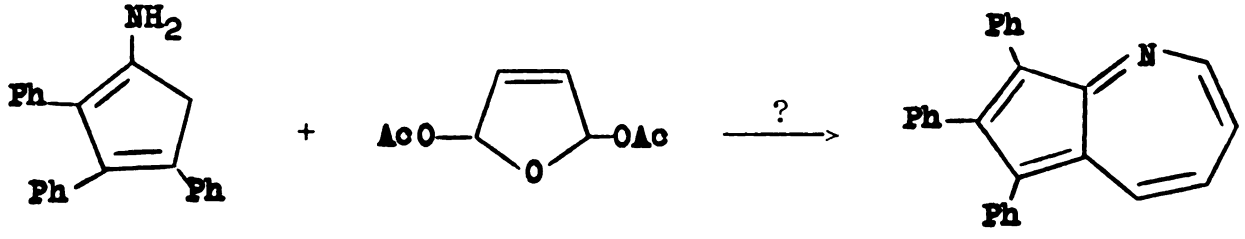

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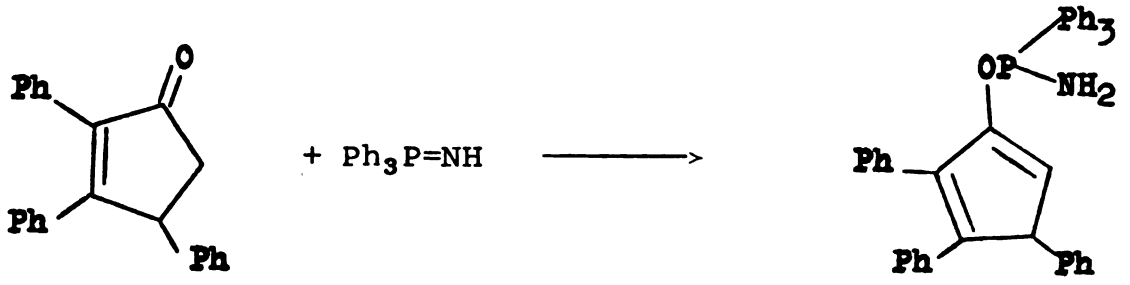

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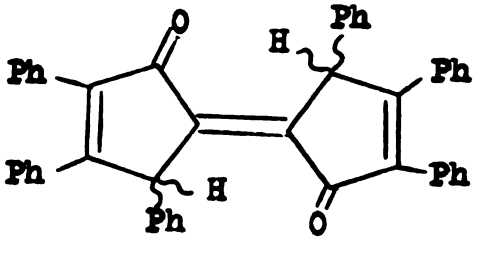
Although the alternate synthesis was not achieved the proposed structure has been well substantiated by spectral data. The reaction of pyrrolidine with hydroxy-ketone 29 represents a novel synthesis of a new theoretically interesting molecule.

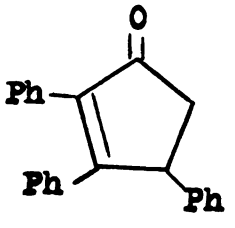
Structure Determination of (E)-3,3',4,4',5,5'-hexaphenyl-[bi-3-cyclopenten-1-ylidene]-2,2'-dione (31)

The minor, yellow product (31) which resulted from the 10% sulfuric acid-acetic acid dehydration of hydroxy-ketone 29 was identified as (E)-3,3',4,4',5,5'-hexaphenyl[bi-3-cyclopenten-1-ylidene]-2,2'-dione (31). The dimeric nature



31

of biscyclopentenylidene 31 is apparent from the elemental analysis and the parent peak at mass 616 in the mass spectrum. The nmr of compound 31 consists of an aromatic multiplet (15H) at δ 7.24-6.91 and a singlet at δ 5.19 (1 H). The aliphatic singlet is suggestive of a symmetrical molecule. The presence of identical carbonyls in the two halves of the molecule is supported by the presence of a single carbonyl absorption in the infrared spectrum. The position of this absorption at 1674 cm^{-1} is best rationalized by a carbonyl conjugated with both an α,β-endocyclic double bond and an α,β-exocyclic double bond. For comparison, the absorption of the carbonyl of 2,3,4-triphenyl-2-cyclopentenone (40) appears at 1702 cm^{-1}.



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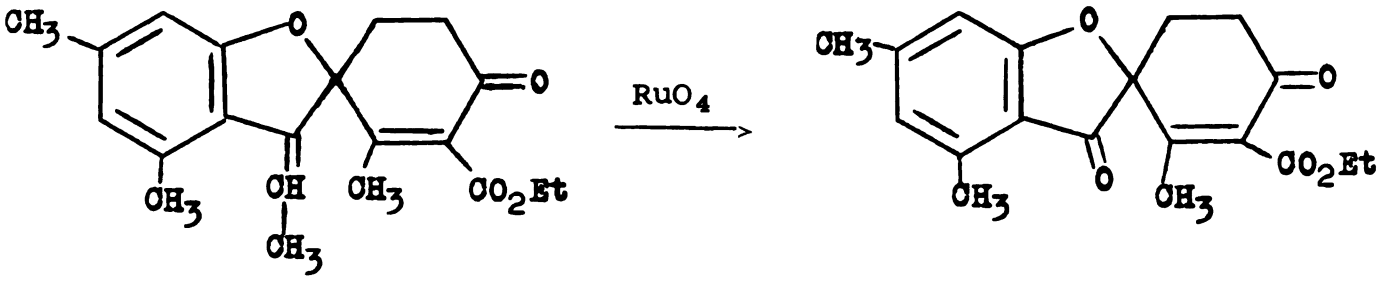
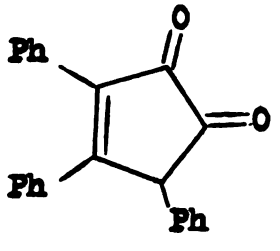
Biscyclopentenylidene 31 is also supported by its reaction with ruthenium tetroxide. Ruthenium tetroxide has been employed for the oxidative cleavage of double bonds to carbonyl compounds. For example, this reagent has been used for the oxidation of 3-alkylidene-2'-gresenes (41) to grisene-3-ones (42) (33). When biscyclopentenylidene 31 was



41 42

allowed to react with ruthenium tetroxide, an orange crystalline product was obtained. A comparison of infrared spectra showed that the degradation product was identical with a known compound, 3,4,5-triphenyl-3-cyclopenten-1,2-dione (43) (31). In addition, a mixed melting point of an authentic sample of dione 43 and the degradation product was undepressed.

Biscyclopentenylidene 31 + RuO_4 ⟶



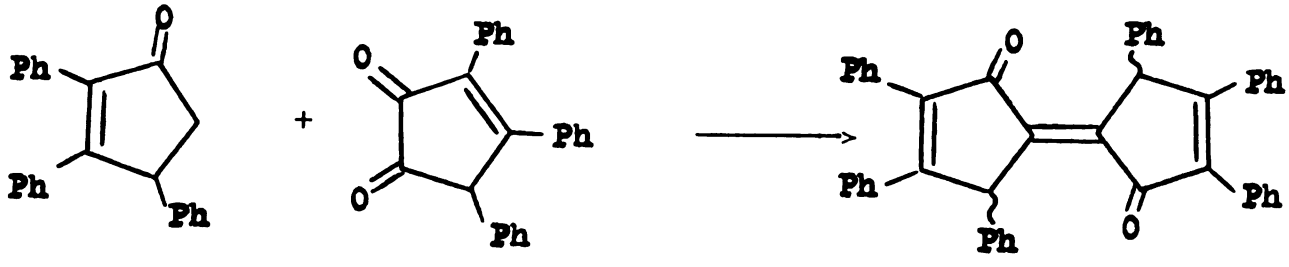
43

The identification of the degradation product and the spectral data, which establish the symmetrical nature of compound 31, are consistent with the proposed bicyclopentenylidene 31.

The formation of bicyclopentenylidene 31 can be rationalized by acid catalyzed rearrangement of the normal cyclone

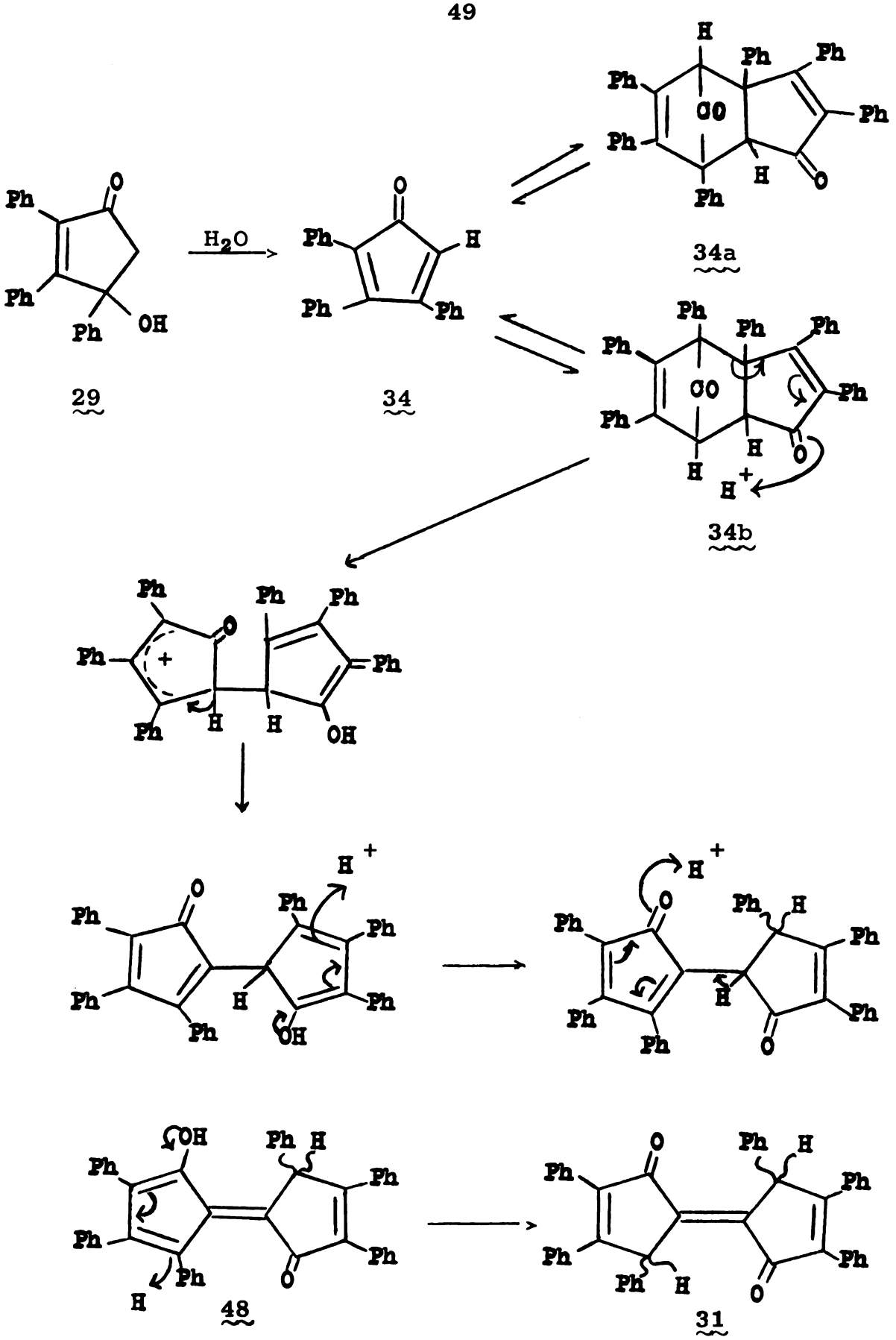
dimer. In strong acid a facile reaction which hydroxyketone 29 might undergo is dehydration to 2,3,4-triphenylcyclone (34). As discussed previously, cyclone 34 would be expected to exist either as a dimer or an equilibrium mixture of monomer and dimer. Subsequent rearrangement of dimer 34b under the strongly acidic conditions (Mechanistic Scheme II) would result in the formation of bicyclopentenylidene 31. Since there is free rotation about the central bond in some of the intermediates, the sterically most favorable product should result.

Since bicyclopentenylidene 31 was formed as a minor product in this reaction, an alternate synthetic route was sought. It was anticipated that dione 43 would be a useful starting material for this attempt. If dione 43 could be condensed with 2,3,4-triphenyl-2-cyclopenten-1-one (40) the desired product would result.



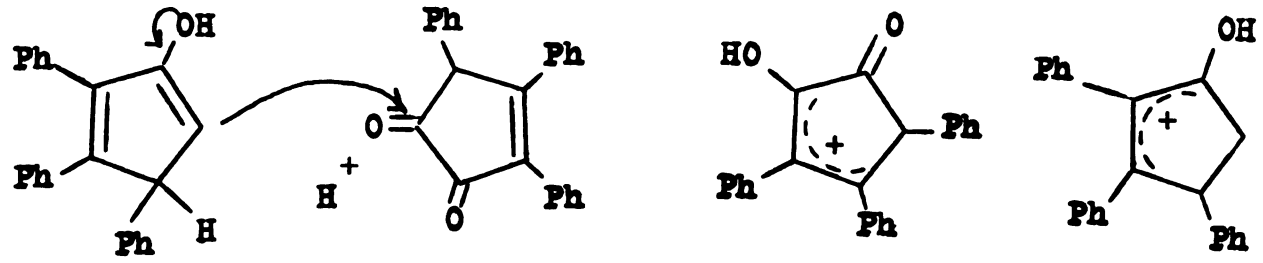
40 43 31

Condensation of these two compounds in strong acid solutions (trifluoroacetic acid or sulfuric acid -- acetic acid) failed to give any condensation product. If such condensation were to occur it would require the attack of the enol of



Mechanistic Scheme II. Formation of (E)-3,3',4,4',5,5'-hexaphenyl[bi-3-cyclopentenylidene]-2,2'-dione.

ketone 40 on the carbonyl of dione 43. However, in strong acid both ketone 40 and dione 43 should exist in the most stable protonated forms. Protonation of the ketone should give rise to the stabilized carbonium ion 40 H^+ whereas the dione should exist as a similar carbonium ion (43 H^+). Condensation of these carbonium ions is unlikely.



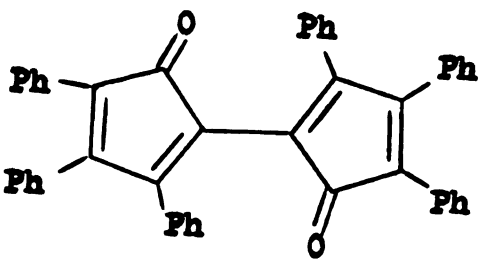
40 43 43 H^+ 40 H^+

Condensation also failed when base catalyzed reactions were attempted. Green solutions resulted when base was added to a solution of the two reactants. The color faded as the reaction progressed. Only ketone 40 was isolated from these reactions. No evidence for the presence of either dione 43 or a condensation product was apparent. Dione 43 apparently forms unstable green salts which decompose in basic solutions (32), thus removing the dione from further reaction. Appropriate conditions to accomplish the desired condensation could not be found.

Preparation of 3,3',4,4',5,5'-Hexaphenyl-2,2'-biscyclopentadienone (44)

Removal of two hydrogens from bicyclopentenylidene 31 would give rise to the theoretically interesting

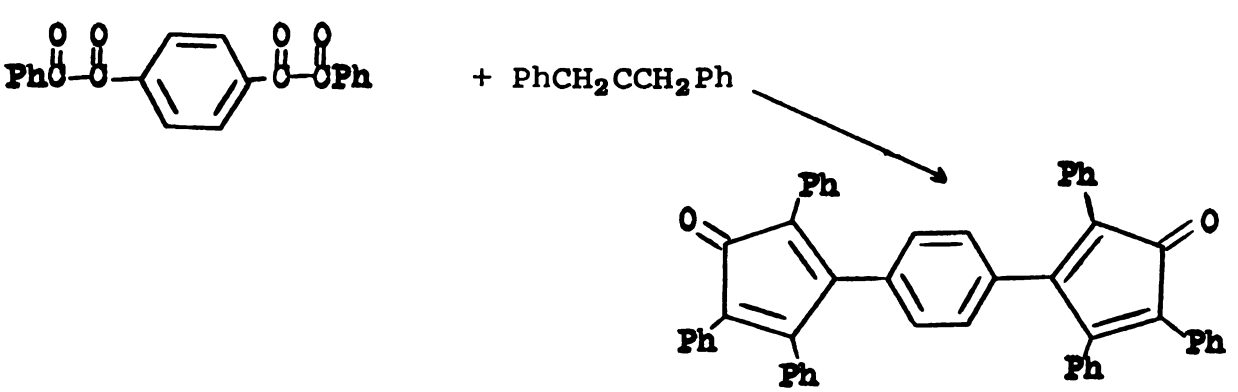
3,3',4,4',5,5'-hexaphenyl-2,2'-biscyclopentadienone (44). This conversion was, in fact, accomplished in low yield by



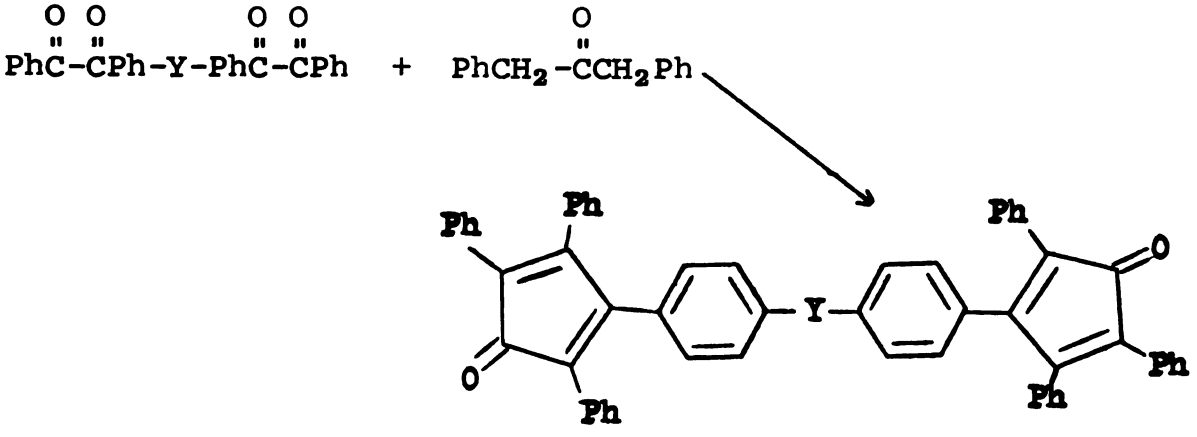
44

reaction of bicyclopentenylidene 31 with NBS. When 31 was reacted with chloranil the yield of biscyclone 44 increased to about 60%. Mass spectral and elemental analysis data were consistent with the dehydrogenation reaction. Biscyclone 44 exists as an almost black crystalline solid. Solutions of 44 are red-purple and absorb at 342 and 546 mμ in the ultraviolet and visible regions (benzene solvent).

Biscyclone 44 represents the simplest biscyclone known. The simplest biscyclone previously reported is one in which the two cyclopentadienone rings are connected to each other through a phenyl ring (20).



In addition, several biscyclones of the general type 45 are known (34).



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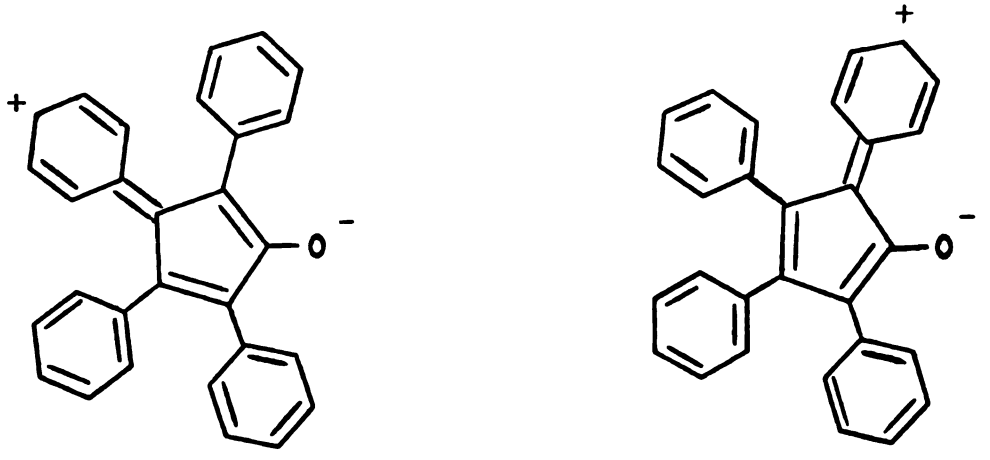
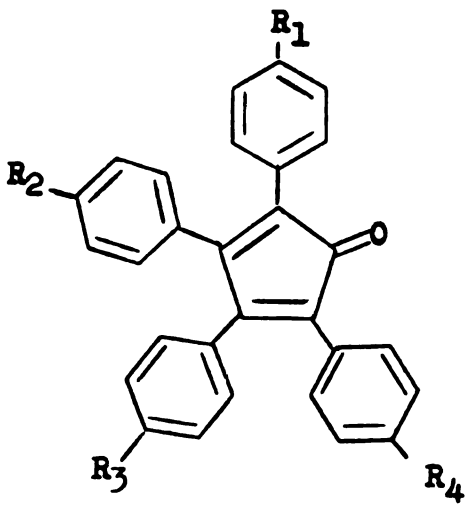
Biscyclones 45 in benzene have ultraviolet and visible absorptions at about 370, 463 and 505 mμ. In order to rationalize these absorptions of the biscyclones it is necessary to consider the absorptions of tetraarylcyclones. Benzene solutions of tetracyclone absorb at 342 and 512 mμ. The absorption maximum at 342 mμ has been attributed to an excited state of type II whereas, the absorption at 512 mμ has been attributed to an excited state such as III. This has been determined by placing various substituents at the para positions of the phenyl rings on tetracyclone (20). The 342 mμ absorption was affected most by R_2 and R_3 substituents whereas the 512 mμ absorption was dependent upon R_1 and R_4 substituents. The 341 mμ absorption was shifted to shorter wavelengths by electron withdrawing substituents at R_2 and R_3 and to longer wavelengths by electron releasing



II III

Figure 9. Excited states of tetracyclones.

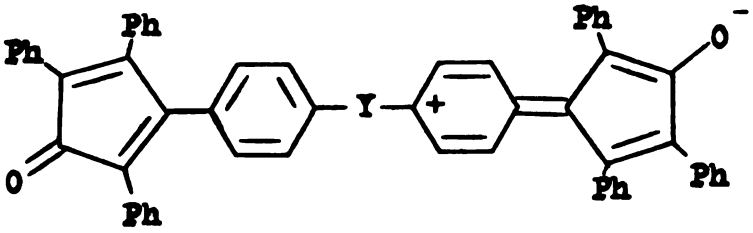
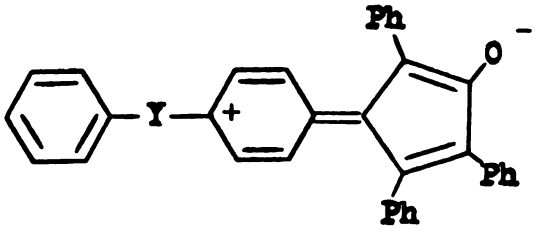


substituents, but was relatively unchanged by varying R_1 and R_4. Electron withdrawing groups at R_1 and R_4 caused hypsochromic shifts in the 512 mμ band and electron releasing groups caused bathochromic shifts. The 512 mμ band was only slightly affected by R_2 and R_3 substituents.

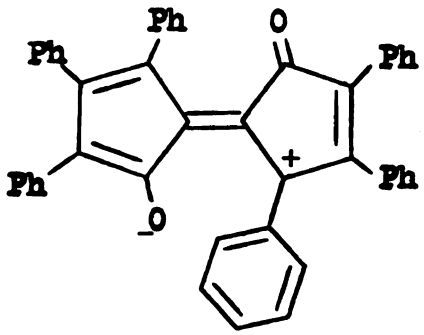
The bathochromic shift in the lower wavelength absorption of biscyclones 45 (Y = O, S) relative to the 342 mμ band of tetracyclone is consistent with these substituent effects. Table II compares the values for the biscyclones with the corresponding tetraarylcyclones. The additional absorption at 463 mμ in the biscyclones was attributed to simultaneous excitation of both cyclone moieties. This band decreased as atom Y became less effective as a transmitter of electronic effects between the two groups.

A similar effect is apparent with biscyclone 44. The absorption at 342 mμ is unchanged but the long wavelength maximum has shifted to 546 mμ. This indicates a stabilizing

Table II. Comparison of absorptions of biscyclones and tetraarylcyclones (20).

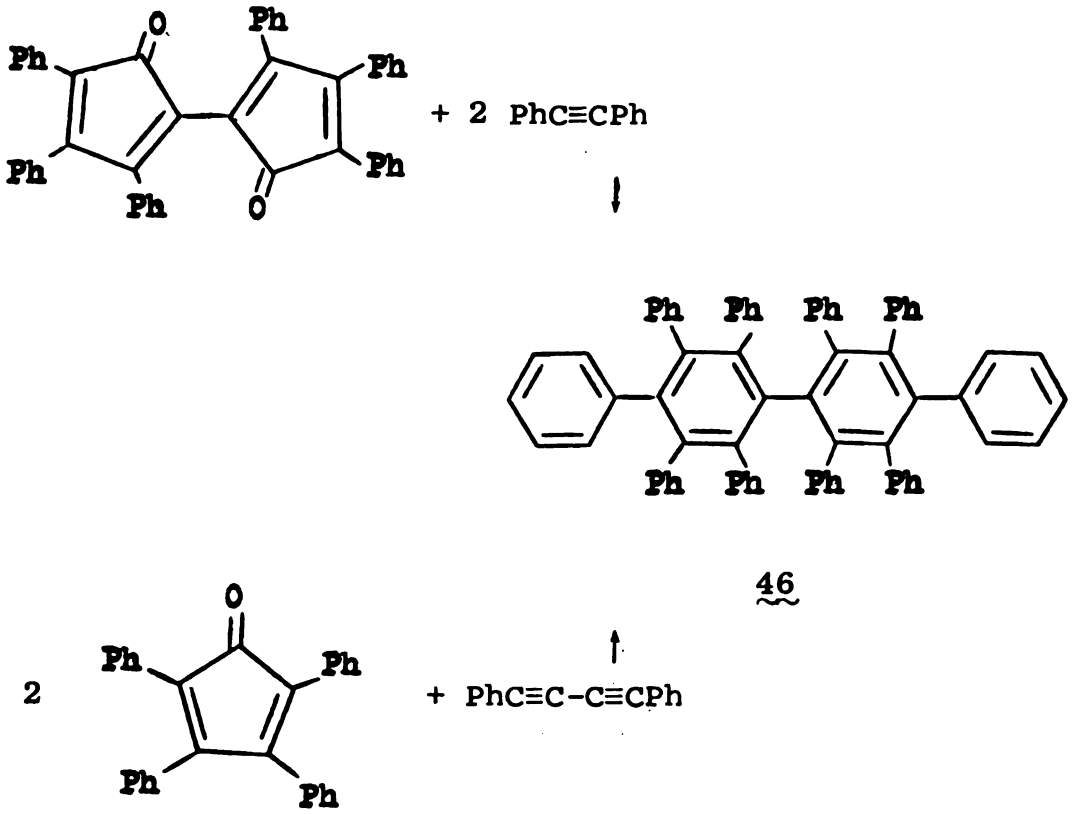
	Y	uv max (mμ)
	S	375 463 502
	O	368 463 507
	O	358 509
	S	378 516

effect such as IV in which the second cyclone ring is more effective than a phenyl group in stabilizing the positive charge in the excited state.

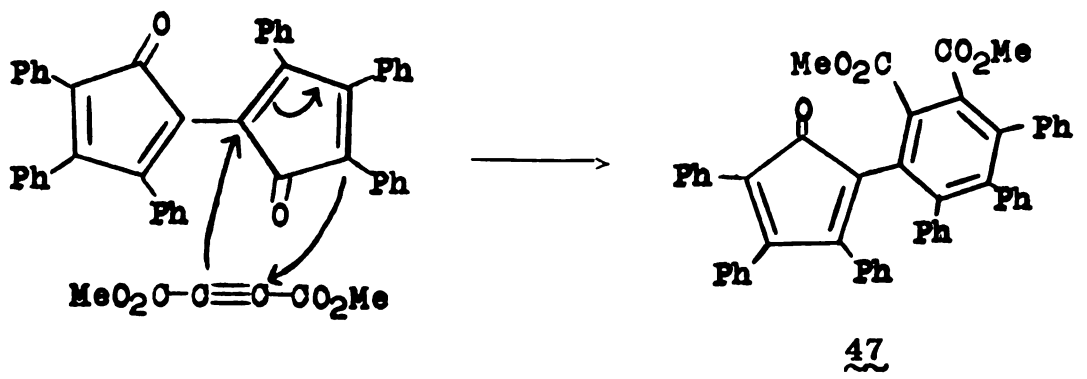


IV

Biscyclone 44 was found to undergo some interesting reactions. It was anticipated that biscyclone 44 would react with two moles of diphenylacetylene giving octaphenyl-quaterphenyl (46), the same product which results from reaction of two moles of tetracyclone with diphenyldiacetylene (35). However, the reaction did not occur as anticipated. When biscyclone 44 and diphenyl acetylene were heated together in refluxing benzophenone, a dark blue solution resulted. The same results were obtained when biscyclone 44 was heated alone in refluxing benzophenone. Within 15 minutes a blue solution resulted, from which a 70% yield of blue compound was obtained. It was found to be identical with blue compound 32 isolated from the dehydration of hydroxy-ketone 29. This facile rearrangement will be considered further in the discussion of blue compound 32.

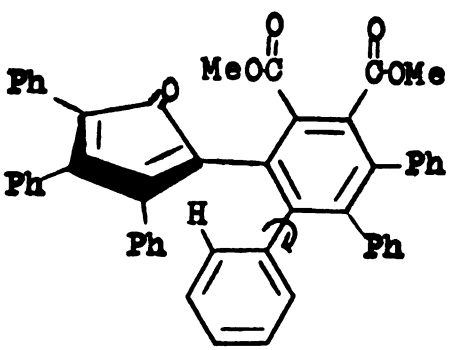


In refluxing benzene, biscyclone 44 readily reacted with dimethyl acetylene dicarboxylate giving tetraarylcyclone 47. Tetraarylcyclone 47 is a red crystalline compound which absorbs at 480 mμ in the visible region. The



elemental analysis and mass spectral data are consistent

with the addition of one mole of acetylenic ester to biscyclone 44 with subsequent loss of one mole of carbon monoxide. In addition to the ester absorption at 1735 cm^{-1} in the infrared another absorption was present at 1705 cm^{-1}. The addition of a single mole of acetylenic ester is reasonable considering the steric effects involved in the addition of a second mole of dienophile. The most favorable arrangement of cyclone 47 is one in which the plane of the cyclone ring is perpendicular to the plane of the hexasubstituted phenyl ring. The resulting effect is that the diene system



47

is completely blocked to further addition of a dienophile. The ester group interferes with addition on one face and a phenyl group interferes on the other face.

The hyposochromic shift of the 480 mμ band of 47 relative to the 512 mμ band of tetracyclone may be due to two factors. Perhaps the more important factor is that steric crowding forces the cyclone ring to approach a position in which its pi-orbitals are orthogonal to those of the phenyl group. Thus, very little, if any, interaction occurs. If,

however, any overlap is possible the presence of the electron withdrawing carbomethoxy groups on the phenyl ring will cause destabilization of the excited state.

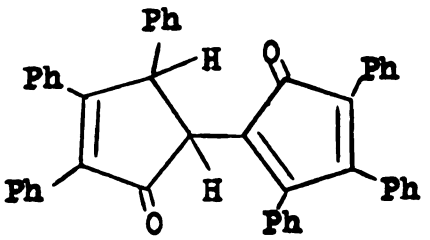
On the basis of these observations, cyclone 47 is a reasonable reaction product. Its stability to further attack of a dienophile is readily apparent from steric considerations.

Identification of 3,3',4,4',5,5'-Hexaphenyl-3,4-dihydro-2,2'-bicyclopentadienone (48).

In order to determine whether 2,3,4-triphenylcyclone (34) is an intermediate in the formation of 31 from the dehydration of hydroxy-ketone 29, the preparation of cyclone 34 was attempted. When dehydration was accomplished in benzene with p-toluene-sulfonic acid or in 2% sulfuric acid-acetic acid a red compound was obtained as the major product. There was no evidence for the presence of bicyclopentenylidene 31 and only a trace of blue compound 32 was obtained under these reaction conditions. In addition an unidentified colorless compound resulted.

At first the major product 48 was impure and appeared to be pink. Its solutions, however, were intense red. This was suggestive of the monomer-dimer equilibrium which exists in solutions of 2,3,5-triphenylcyclone. However, further purification gave a single, red crystalline product. Although it is tempting to suggest a 2,3,4-triphenylcyclone dimer or a monomer-dimer equilibrium, the spectral data lead to inconsistencies in interpretation.

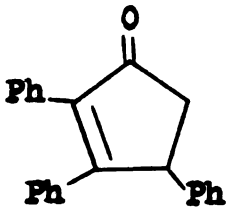
On the basis of spectral and chemical data, 3,3',4,4', 5,5'-hexaphenyl-2,3-dihydro-2,2'-biscyclopentadienone (48) is a more reasonable structure. The mass spectral data and



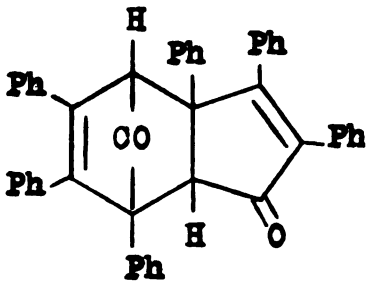
48

elemental analyses suggest a dimeric structure of molecular weight 616. The nmr in deuterochloroform consists of a 30 hydrogen multiplet at δ 7.93-6.4 and two doublets at δ 4.73 and 3.61 (J = 4 Hz) each representing one hydrogen. The nmr can be interpreted by either cyclone 48 or 2,3,4-triphenylcyclone dimer 34b. Dimer 34b, however, is the less favorable cyclone dimer. If cyclone 34 is present exclusively as a dimer, the more favorable dimer 34a would be more reasonable. The nmr is not consistent with dimer 34a.

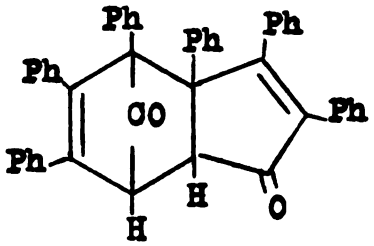
The infrared and ultraviolet spectra also favor cyclone 48 over 2,3,4-triphenylcyclone monomer 34 and dimers 34a and 34b. In the infrared only one carbonyl is present. This absorption is at 1700 cm^{-1}. If either cyclone dimer 34a or 34b is present a second carbonyl should absorb at 1775 cm^{-1}. In all dimers previously reported the bridge carbonyl appears at 1775 cm^{-1} (36). In fact, this carbonyl



34



34a



34b

absorption has been used as a diagnostic test for bridge carbonyls. The absence of the second carbonyl indicates either a structure such as 48 in which the similar carbonyls cannot be distinguished in the infrared, or an exclusively monomeric 2,3,4-triphenylcyclone.

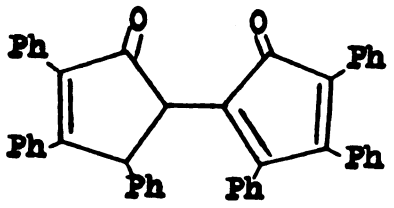
Cyclohexane solutions of 48 absorb in the visible at 480 mμ with log ϵ equal to 3.06 as compared with log ϵ equal to 3.20 for the corresponding absorption of tetracyclone. The similar extinction coefficient is reasonable for a cyclone of molecular weight 616 such as cyclone 48. If interpreted in terms of 2,3,4-triphenylcyclone the extinction coefficient would require the presence of essentially all

monomer. As previously discussed, existence of 2,3,4-triphenylcyclone in exclusively the monomeric form is very unlikely.

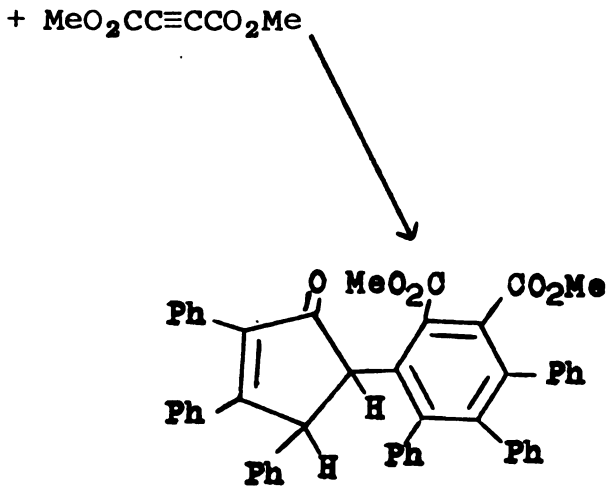
Thus, it is seen that in assuming 2,3,4-triphenylcyclone as the structure of 48, inconsistencies arise in the interpretation of the spectral data. In particular, extreme interpretations result from the nmr and ir spectra which were taken in essentially the same solvent. Cyclone 48, on the other hand, is totally consistent with all of the spectral data.

The presence of the cyclopentadienone portion of compound 48 was established by reaction of cyclone 48 with acetylenic ester. Addition of one mole of dienophile occurred with subsequent loss of one mole of carbon monoxide. The structure of the resulting cyclopentenone (49) is supported by its nmr spectrum which consists of an aromatic multiplet at δ 7.3-6.5 (30 H) and two doublets centered at δ 4.88 and 4.14 (J = 4 Hz) each representing one hydrogen. Two different methyl groups also appear at δ 3.62 and 3.40. In addition to the ester carbonyl at 1730 cm^{-1} another carbonyl is present at 1710 cm^{-1} in the infrared.

The formation of cyclone 48 can be rationalized by a carbonium ion rearrangement of the normal cyclone dimer (Mechanistic Sequence II) and it is a reasonable intermediate in the formation of bicyclopentenylidene 31. Apparently the weaker acid solution was ineffective in isomerizing cyclone 48 to bicyclopentenylidene 31. However, the intermediacy of cyclone 48

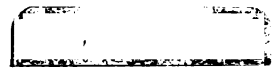


48

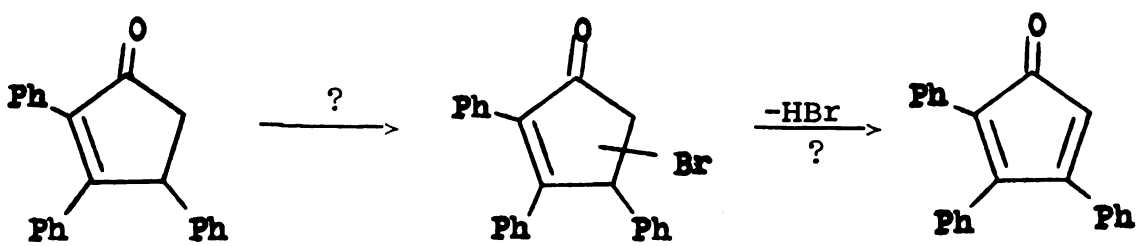


49

in the formation of 31 is supported by the conversion of cyclone 48 to the yellow bicyclopentenylidene 31 in 10% sulfuric acid-acetic acid. There was no evidence for the formation of blue compound 32 in this transformation. In addition, although cyclone 48 can be purified by chromatography on silicic acid, it is completely isomerized to the yellow bicyclopentenylidene (31) when chromatographed on alumina. In fact, a greater yield of the yellow compound could be obtained by chromatography of cyclone 48 than from dehydration of hydroxy-ketone 29. The same transformation also occurs in low yield when cyclone 48 is heated to 220°. Cyclone 48 appears to be a reasonable structure to account for these facile rearrangements to bicyclopentenylidene 31.



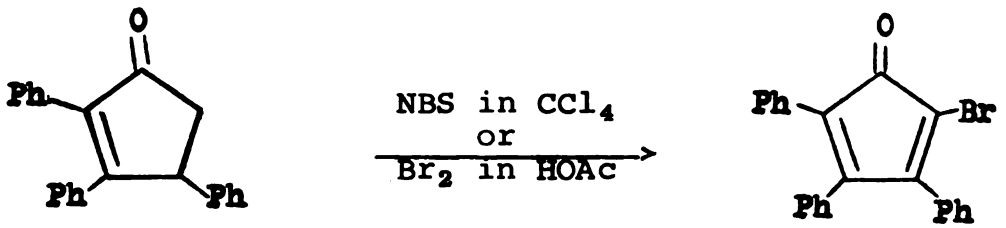
If a 2,3,4-triphenylcyclone dimer is the precursor to cyclone 48 and bicyclopentenylidene 31, its isolation from acid solutions is unlikely due to facile carbonium ion rearrangements. A synthetic route for preparing 2,3,4-triphenylcyclone in a nonacidic solution was sought. This attempt involved the bromination of 2,3,4-triphenyl-2-cyclopenten-1-one (40). If the monobromide could be formed, the elimination of hydrogen bromide would give the desired cyclone.



40 34

However, when either NBS in carbon tetrachloride or bromine in acetic acid was used a dark brown-red crystalline product was obtained. This compound has a very sharp carbonyl absorption at 1715 cm^{-1} in the infrared and has an absorption at 490 mμ in the visible. These results are suggestive of a cyclopentadienone. The molecular weight of 387 and elemental analyses give a molecular formula of $C_{23}H_{15}BrO$. A compound whose formation is readily rationalized is 2,3,4-triphenyl-5-bromocyclopentadienone (50). Either a dibromide is formed initially and spontaneously loses hydrogen bromide, or a monobromide forms with loss of hydrogen bromide to

give the desired cyclone which is then brominated. The value of log ϵ equal to 2.87 for the 490 mμ absorption suggests the presence of monomer.

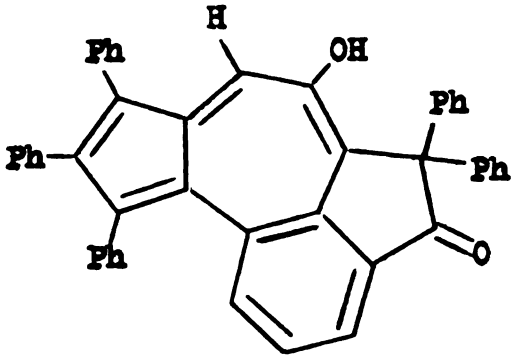


50

If 2,3,4-triphenylcyclone is formed in any of the reactions discussed, it is either very reactive or its dimer is very reactive under the reaction conditions. No further attempts at its synthesis were made.

Identification of 6-Hydroxy-5,5,8,9,10-pentaphenylbenzo-[cd]cyclopent[f]azulen-4-(5H)-one (32)

The major product resulting from the 10% sulfuric acid-acetic acid dehydration of hydroxy-ketone 29 was blue compound 32. The structure previously reported for this compound was 2,3,4-triphenylcyclone (34) (16). On the basis of spectral and chemical data now available, a more reasonable structure appears to be 6-hydroxy-5,5,8,9,10-pentaphenyl-benzo[cd]cyclopent[f]azulen-4-(5H)-one (32). The blue color of compound 32 is suggestive of an azulene chromophore. solutions of compound 32 in cyclohexane absorb at 620 mμ in the visible region as compared to the parent azulene which



32

absorbs at 670 mμ in the visible region (37).

The presence of the hydroxyl and carbonyl groups on hydroxy-azulene 32 are apparent from the infrared spectrum. The carbonyl absorption is present at 1681 cm^{-1} and the hydroxyl at 3150-3300 cm^{-1}. The presence of a relatively acidic hydroxyl is also evident from the nmr spectrum. There is a singlet (1H) at δ 10.2 and a multiplet at δ 7.60-6.92 (29H). The low field resonance can be washed out with D_2O.

This hydroxyl group was useful for converting hydroxy-azulene 32 to an acetate (51) or a trimethylsilyl derivative (52). The trimethylsilyl derivative showed a hypsochromic shift in the visible region to 532 mμ relative to the 620 mμ band of hydroxy-azulene 32. This substantial shift is in agreement with the proposed structure. Stabilization of hydroxy-azulene 32 by the free electrons on oxygen is decreased when the enol is converted to the trimethylsilyl derivative.

The trimethylsilyl derivative was used to obtain mass spectral data since the extremely low volatility of hydroxy-azulene 32 prevented its use. A computer analysis of the high

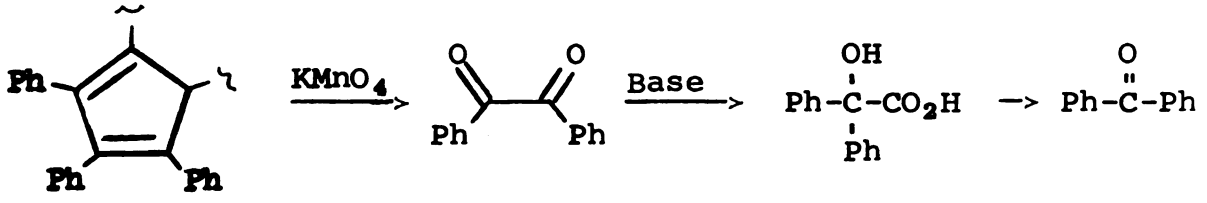
resolution mass spectrum shows that the molecular ion is present at mass 686 and corresponds to a molecular formula of $C_{49}H_{38}O_2Si$. In addition to the fragments due to the trimethylsilyl group, the loss of carbon monoxide and a phenyl group are also apparent. A $C_{13}H_{10}$ fragment which may be attributed to loss of a diphenylmethyl from hydroxy-azulene 32 is also present.

Several reactions were attempted in order to gain support for the suggested structure. However, many failed to give identifiable products. Reduction of the carbonyl of hydroxy-ketone 32 was attempted using sodium methoxyethoxy-aluminum hydride, but a complex mixture of products resulted. Hydroxy-azulene 32 might be expected to give such results. In addition to the carbonyl, the enol might be reduced by way of its keto form. Furthermore, the fulvenoid portion of compound 32 is also susceptible to hydride attack. Oxidation with ruthenium tetroxide also gave a complex mixture of products. This, too, is not surprising considering the many different double bonds which are available for oxidative cleavage. Catalytic hydrogenation with a platinum catalyst led to excessive hydrogen uptake. Partial reduction of the phenyl groups could account for such results. On the other hand, hydrogenation employing a paladium on carbon catalyst, led to negligible hydrogen consumption.

The isolation of oxidative degradation products was then attempted. The use of chromic acid as the oxidant gave benzoic acid as the only identifiable product. Several

unidentified products appeared to be only partially oxidized fragments. When a two phase oxidation was carried out using basic potassium permanganate as the oxidant, a second product was obtained. This product proved to be benzophenone by comparison of infrared spectra. In addition, the melting points and the infrared spectra of an authentic sample of benzophenone 2,4-DNP and the 2,4-DNP of the degradation product were identical.

Benzophenone would be expected to result from oxidative cleavage of the diphenylmethyl fragment on hydroxy-azulene 32. However, this evidence is ambiguous since benzophenone might also result from the oxidative cleavage of a group such as 54 if such a group is present in the molecule. Oxidation of fragment 54 should give benzil. In basic solution benzil can rearrange to benzilic acid which would give benzophenone on oxidation.



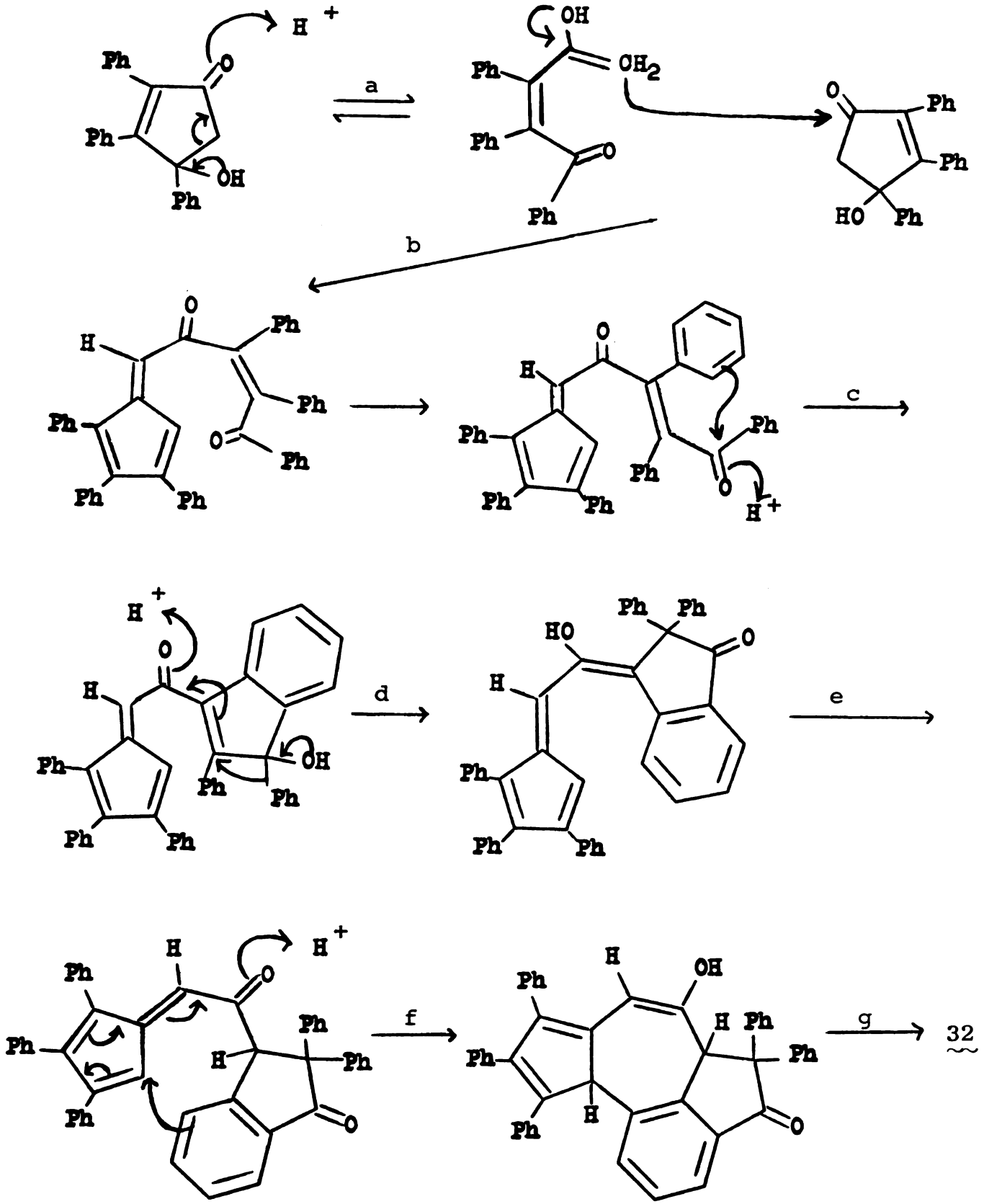
54

However, the presence of the diphenylmethyl group on hydroxy-azulene 32 is also suggested from the fragmentations in the mass spectrum of trimethylsilyl derivative 52.

Although a conclusive structure determination cannot be made from the available evidence, hydroxy-azulene 32 is fully consistent with all of the data presented. The formation of hydroxy-azulene 32 can be rationalized by mechanistic scheme III. In acidic solution, hydroxy-ketone 29 may undergo the following conversions to blue compound 32: (a) a reversible aldol reaction, (b) condensation of the retro-aldol product with either hydroxy-ketone 29 or 2,3,4-triphenylcyclone 34, (c) an acid catalyzed condensation of the benzoyl group with a phenyl ring in the formation of a five membered ring, (d) protonation of the remaining carbonyl with subsequent phenyl migration, (e) conversion of the enol to the keto form, (f) protonation of the ketone, followed by acid catalyzed addition of the fulvenoid system to the phenyl ring, and finally (g) oxidation to azulene 32.

No reaction path for the isomerization of biscyclopentadienone 44 to azulene 32 is readily apparent. If the blue compound is indeed azulene 32, this conversion represents an unusual rearrangement.

Since no blue compound was found in the 2% sulfuric acid-acetic acid reaction or in the conversion of cyclone 48 to bicyclopentenylidene 31, the stronger 10% sulfuric acid-acetic acid solution must provide conditions for an additional reaction path. In both cases the reverse aldol probably could occur. In the weaker acid ring closure to starting material may be favored. On the other hand, use of stronger

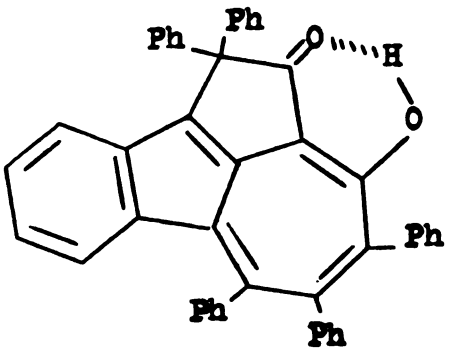


Mechanistic Scheme III. The formation of 6-hydroxy-5,5,8,9,10-pentaphenylbenzo[cd]cyclopent[f]azulen-4-(5H)-one.

acid may provide an additional path for the condensation of the retro-aldol product with either hydroxy-ketone 29 or with 2,3,4-triphenylcyclone (34).

Due to the uncertainty of the structure of hydroxy-azulene 32 the suggested mechanism for its formation is at best speculative. The identification of the other novel products are supported by chemical and spectral data but the mechanisms for their formation are also speculative. However, these routes do show that reasonable reaction paths are available which can account for the novel reaction products of hydroxy-ketone 29.

After discussing the structure of hydroxy-azulene 32 with Dr. D. G. Farnum, another possible structure, 3-hydroxy-1,1,4,5,6-pentaphenylbenzo[a]cyclopent[cd]azulen-2-(1H)-one (32a) was apparent.

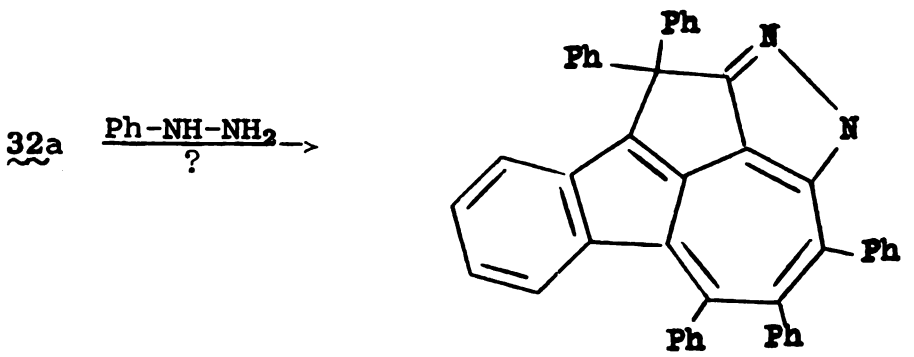


32a

This structure is consistent with the spectral data discussed previously for hydroxy-azulene 32. In addition, the carbonyl absorptions in the infrared spectra of the acetate and trimethylsilyl derivatives of 32 appear at 1701 cm^{-1} as compared to the 1681 cm^{-1} carbonyl absorption of the parent hydroxy-azulene 32. This shift could be rationalized by the loss of the chelate type structure in conversion of the hydroxy group to the derivatives.

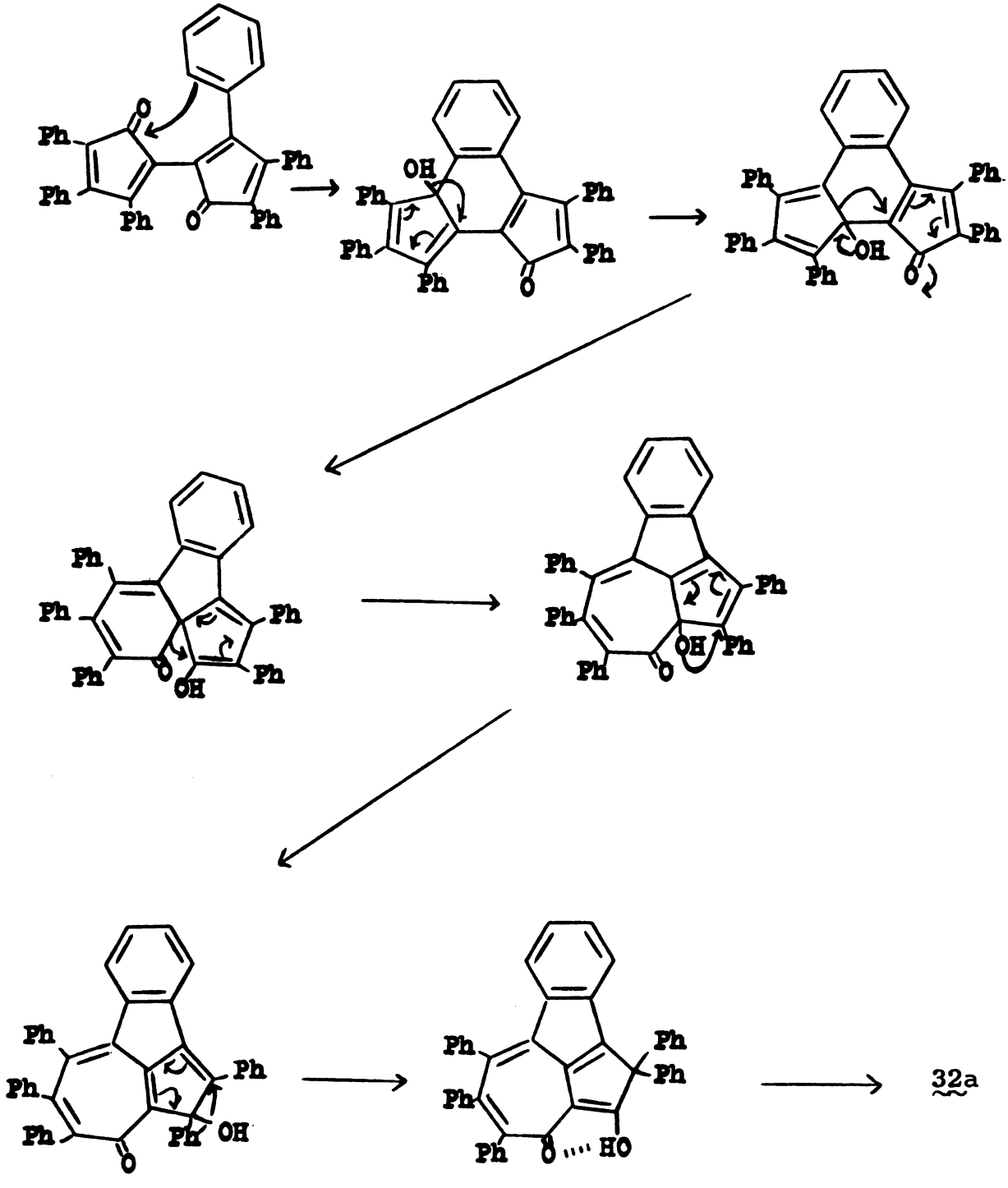
Two different approaches may be useful in attempting to distinguish between structures 32 and 32a. If the chelate structure is present it may be possible to convert it to a copper chelate by use of copper acetate.

A second approach involves the reaction of 32a with phenylhydrazine. This may result in condensation of the phenylhydrazine with both carbonyl positions in the formation of a 1-H-pyrazole.



If either of these two reactions is successful 32a would be a more satisfactory structure. However, failure of either of these reactions could result from steric factors. Thus, failure of either reaction would not eliminate structure 32a from consideration.

The formation of 32a from biscyclopentadienone 47 can be rationalized by the sequence of the following page.



Rearrangement of biscyclone 47 to azulene 32a.

EXPERIMENTAL

1. General Procedures

These are the same as those used in Part I.

2. 1,2,3-Triphenyl-4-azazulene (30)

A mixture of 1.7 g (0.0052 mole) of 4-hydroxy-2,3,4-triphenylcyclopent-2-en-1-one, 0.7 g (0.01 mole) of pyrrolidine and 0.1 g of toluenesulfonic acid in 10 ml of toluene was refluxed overnight with continuous removal of water by means of a Dean-Stark trap. The solvent was then removed under reduced pressure to give a tarry black residue which was chromatographed on Alcoa F-20 alumina with benzene. Initially a yellow band began to separate but before it could be eluted it had turned green. Upon removal of the solvent from this green fraction a dark green solid remained which was crystallized from heptane giving 80 mg of azazulene 30: mp 224-226°; uv max (CH_3CN) 285 (log ϵ 4.51), 325 (log ϵ 4.48), 380 (log ϵ 3.64), 610 (log ϵ 2.35), 654 (log ϵ 2.43ϵ, and 710 mμ (log ϵ 2.35); ir ($CHCl_3$) 1535, 1570, 1590 (arom), and (hexachlorobutadiene) 3020 cm^{-1} (arom C-H); nmr ($CDCl_3$) δ 8.33-8.08 (m, 1H), 8.07-7.82 (m, 1H), and 7.32-6.82 (m, 17H); mass spectrum (70 eV) m/e 357 (Parent)

Anal. Calcd for $C_{27}H_{19}N$: C, 90.80; H, 5.33.

Found: C, 90.70; H, 5.50.

3. 1,2,3-Triphenyl-4-azatetrahydroazulene

A mixture of tetrahydroazulenes could be obtained if the tarry mixture from the previous mixture was chromatographed on Baker neutral alumina packed in a nylon column (26). In packing the column the best results were obtained when the nylon column was supported in a glass sleeve and packed wet. When sufficient separation had occurred the column was cut apart and extracted with ether. The ether solution was concentrated to about 10 ml. After the solution was cooled in a freezer, yellow crystals appeared. The solution upon standing at room temperature decomposed but the crystals when isolated were stable. In this manner from 30 g of hydroxy-ketone 29, 100 mg of the tetrahydroazulene was obtained. This low yield was due to the many difficulties in isolation: nmr ($CDCl_3$) was not straightforward due to the many isomers which are possible but the ratio of phenyl protons to all others is 15:8; mp - not sharp.

Anal. Calcd for $C_{27}H_{23}N$: C, 89.70; H, 6.38.

Found: C, 89.60; H, 6.64.

4. (E)-3,3',4,4',5,5'-hexaphenyl[bi-3-cyclopenten-1-ylidene]-2,2'-dione (31)

a) From hydroxy-ketone 29

Compound 31 was prepared by the method of Pauson (16): mp softens at 256-258°, then solidifies and does not melt

up to 310°; uv max (cyclohexane) 267 (log ε 4.46), 342 (log ε 4.13), and 460 mμ (log ε 2.60); ir ($CHCl_3$) 1674 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.24-6.91 (m, 15) and 5.69 (s, 1); mass spectrum (70 eV) m/e 616 (Parent).

Anal. Calcd for $C_{46}H_{32}O_2$: C, 89.60; H, 5.30.

Found: C, 89.60; H, 5.34.

b) Thermal decomposition of 3,3',4,4',5,5'-hexaphenyl-3,4-dihydro-2,2'-biscyclone (48).

When a 500 mg sample of cyclone 48 was heated to 220° for 5 minutes gas evolution occurred from the melt and then the melt resolidified. After cooling the sample to room temperature 10 ml of benzene was added. The yellow solid which separated was filtered and washed with benzene to give 300 mg of a highly insoluble yellow solid which did not melt up to 310°.

From the benzene filtrate was isolated 60 mg of yellow compound having an ir identical with that of compound 31.

c) 10% Sulfuric acid-acetic acid reaction of cyclone 48

A solution of 100 mg (0.33 mmol) of cyclone 48 in 5 ml of 10% sulfuric acid in acetic acid was refluxed for 30 min and then poured into water and extracted with benzene. The benzene was washed with sodium carbonate solution and dried with $MgSO_4$. The yellowish residue was chromatographed on alumina with benzene to give 80 mg (80%) of yellow compound 31. The ir was identical with that of compound 31. No blue product was found.

d) From chromatography of cyclone 48

A sample of 0.5 g of cyclone 48 was chromatographed on an Alcoa F-20 alumina column with benzene. The only fraction eluted gave 0.45 g (85%) of bicyclopentenylidene 31.

5. Ruthenium Tetroxide Oxidation of Bicyclopentenylidene (31)

A solution of 300 mg (0.5 mole) of yellow compound in 20 ml of chloroform (washed well with water to remove traces of alcohol) was added dropwise to a mixture of 10 ml of chloroform, 30 ml of water, 10 gm of ruthenium dioxide, and 0.64 g of sodium periodate. The resulting mixture was stirred overnight at room temperature. The resulting black ruthenium dioxide was filtered and washed with chloroform. The water and chloroform layers of the filtrate were separated and the combined chloroform layers dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue chromatographed on Mallinckrodt silicic acid with benzene-methylene chloride (10:12). From the first yellow fraction 140 mg (47%) of starting material was recovered. From the second fraction 80 mg (49% based on unrecovered starting material) of orange needles was obtained. The ir spectrum was identical with that of 3,4,5-triphenylcyclopent-3-ene-1,2-dione (43) and a mixed melting point was undepressed; mp 160-162°; ir ($CHCl_3$) 1705 (C=O) and 1760 cm^{-1} (C=O); mass spectrum (70 eV) m/e 324 (Parent).

6. 3,3',4,4',5,5'-Hexaphenyl-2,2'-biscyclopentadienone (47)

a) From reaction of bicyclopentenylidene 31 with chloranil.

A mixture of 100 mg (0.17 mmol) of yellow compound 31 and 200 mg (0.1 mole) of chloranil in 10 ml of xylene was refluxed for 4 hrs. The solvent was removed under reduced pressure and chloroform added to the residue. The solution was filtered from insoluble material and the solvent removed from the purple solution. The residue was chromatographed on Baker neutral alumina with benzene to give 60 mg of black solid (60%). An ir and melting point showed this to be identical with the product from the NBS reaction.

b) From reaction of bicyclopentenylidene 31 with NBS.

A mixture of 200 mg (0.34 mmol) of yellow compound 31 and 400 mg (0.3 mole) of NBS was refluxed in carbon tetrachloride for 20 hrs. The solution was then cooled, washed with cold water, and dried ($MgSO_4$). The solvent was removed and the residue was chromatographed on Baker neutral alumina with benzene. The first fraction gave 130 mg of yellow starting material. A purple-black band was then eluted from which was isolated 20 mg of black solid which was crystallized from chloroform-isopropanol: mp 288-289°; uv max (benzene) 332 (log 4.23), and 546 mμ (log ϵ 3.46); ir ($CHCl_3$) 1705 cm^{-1} (C=O); mass spectrum (70 eV) m/e 614 (Parent).

Anal. Calcd for $C_{46}H_{30}O_2$: C, 90.00; H, 4.90.

Found: C, 90.15; H, 5.09.

7. Reaction of Biscyclopentadienone 47 with Acetylenic Ester

A mixture of 50 mg (0.08 mmol) of bistriphenylcyclopentadienone and 200 mg of dimethyl acetylenedicarboxylate in 5 ml of benzene was refluxed for 24 hrs. The solvent was removed from the bright red solution to give a red oil which was chromatographed on Mallinckrodt silicic acid with benzene-methylene chloride (10:12). A red oil was obtained which crystallized after addition of methanol giving 47.5 mg (82.5%) of red crystals. Recrystallization from methanol gave bright red crystals: mp 174-175°; uv max (cyclohexane) 248 (log ϵ 4.63), 325 (log ϵ 393), and 480 mμ (log ϵ 3.01); ir ($CHCl_3$) 1710 (C=O), 1730 cm^{-1} (ester C=O); mass spectrum (70 eV) m/e (rel intens) 728 (8) (Parent), 697 (100).

Anal. Calcd for $C_{51}H_{36}O_5$: C, 84.10; H, 4.95.

Found: C, 83.91; H, 5.06.

8. Conversion of Biscyclopentadienone 47 to Blue Compound 32

A mixture of 100 mg (0.33 mmol) of biscyclone 47 in 500 mg of benzophenone was heated to gentle reflux. Within 15 min an intense blue solution resulted. The reaction flask was allowed to cool and 10 ml of methanol was added. Upon standing overnight the solution deposited blue crystals. The solution was filtered and 70 mg (70%) of product identical with blue compound 32 (ir and melting point) was obtained.

9. 3,3',4,4',5,5'-Hexaphenyl-2,3-dihydro-2,2'-biscyclopentadienone (48)

a) From p-toluenesulfonic acid dehydration of hydroxyketone 29.

A mixture of 2 g (0.0015 mole) of 4-hydroxy-2,3,4-triphenylcyclopent-2-en-1-one and 1 g of p-toluene sulfonic acid in 25 ml of benzene was refluxed 1 hr. The solution was washed well with water and dried ($MgSO_4$). The benzene was removed under reduced pressure and the residue chromatographed on Mallinckrodt silicic acid with chloroform. Only a trace of blue compound was eluted followed by 180 mg of an unidentified yellow compound, 140 mg of another unidentified yellow compound, and 350 mg of a colorless compound which analyzed for a dimer: mp 264°.

Anal. Calcd for $C_{46}H_{32}O_2$: C, 89.60; H, 5.20.
Found: C, 89.55; H, 5.41.

Finally 320 mg of red compound was obtained. Recrystallization from chloroform-methanol gave a red crystalline product: mp 264-265°; uv max (cyclohexane) 245, 270, 332, 460, and 490 mμ; ir ($CHCl_3$) 1702 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.4-7.41 (m, 30H), 4.72 (d, 1, J = 4 Hz), and 3.61 (d, 1, J = 4 Hz); mass spectrum (70 eV) m/e (rel intensity) 616 (100), 598 (9), 588 (13), 570 (4), 539 (6), 525 (4), 521 (3), 511 (23), 510 (3), 498 (8), 493 (4), 433 (4), 308 (46), 280 (12), 267 (12) and 178 (19).

Anal. Calcd for $C_{46}H_{32}O_2$: C, 89.60; H, 5.20.
Found: C, 89.47; H, 5.26.

b) From 2% sulfuric acid-acetic acid dehydration of hydroxy-ketone 29.

To a solution of 10 g (0.03 mole) of 4-hydroxy-2,3,4-triphenylcyclopent-2-en-1-one in 50 ml of acetic acid was added 1 ml of concentrated sulfuric acid and the mixture heated to boiling for 5 minutes. The resulting solution was poured into water. The solid which separated was filtered and dried ($MgSO_4$). When ether was added 2 g of unidentified yellow compound separated. The remaining ether solution was evaporated and the residue chromatographed on silicic acid. The first fraction (carbon tetrachloride-benzene, 10:2) was blue and gave 0.3 g of product identical with compound 32. The second fraction (methylene chloride-benzene, 10:12) gave 3.4 g (35%) of cyclone 48. The final fraction consisted of an additional 1.4 g of unidentified yellow product.

The cyclone was identical with the product from the toluene sulfonic acid dehydration.

10. Reaction of Cyclone 48 with Acetylenic Ester

A mixture of 200 mg (0.33 mmol) of cyclone dimer and 300 mg of dimethyl acetylenedicarboxylate in 10 ml of benzene was refluxed overnight. The resulting solution was slightly yellow. The solvent was removed under reduced pressure and the residue chromatographed on silicic acid with benzene-methylene chloride (10:12). An oil was obtained which crystallized upon addition of methanol.

Recrystallization from methanol gave 150 mg (62%) of colorless crystals: mp 264-265°; ir ($CHCl_3$) 1735 (ester C=O) and 1705 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.32-6.23 (m, 30), 4.86 (d, 1, J = 4 Hz), 4.15 (d, 1, J = 4 Hz), 3.62 (s, 3), and 3.40 (s, 3); mass spectrum (70 eV) m/e 730 (Parent).

Anal. Calcd for $C_{51}H_{38}O_5$: C, 83.70; H, 5.2.

Found: C, 83.45; H, 5.20.

11. 2,3,4-Triphenyl-5-bromocyclopentadienone (50)

a) Bromination of 2,3,4-triphenylcyclopent-2-en-1-one.

To a stirred suspension of 9 g (0.03 mole) of 2,3,4-triphenylcyclopent-2-en-1-one in 150 ml of acetic acid was added 6 g (0.035 mole) of bromine in 15 ml of acetic acid. The mixture was heated to dissolve the starting material and then allowed to stand at room temperature overnight. The solvent was removed under reduced pressure leaving an oily red residue which was chromatographed on silicic acid with carbon tetrachloride-benzene (10:2). The product was eluted first as a dark red band. Upon removal of the solvent the remaining red solid was crystallized from ethanol giving 2.8 g (41.5%) of dark red crystals: mp 188-189°; uv max (cyclohexane) 245 (log ε 4.19), 270 (log ε 4.24), 332 (log ε 3.93), 460 (log ε 2 90), and 490 mμ (log ε 2.87); ir ($CHCl_3$) 1715 cm^{-1} (C=O); mass spectrum (70 eV) m/e (rel intensity) 388 (100), 386 (100), 360 (36), 358 (36), 307 (45.5), 279 (100), 278 (73), 277 (54.5), 276 (54.5), 202 (32), 178 (45.5), and 139 (50).

Anal. Calcd for $C_{23}H_{15}BrO$: C, 71.40; H, 3.88.

Found: C, 71.36; H, 4.06.

b) N-bromosuccinimide bromination of 2,3,4-triphenyl-cyclopent-2-en-1-one.

A mixture of 0.9 g (.003 mole) of 2,3,4-triphenyl-cyclopent-2-en-1-one and 0.5 g (0.0028 mole) of N-bromo-succinimide in 25 ml of carbon tetrachloride was refluxed for 1 hour during which time the solution became dark red. The mixture was cooled in an ice bath and then filtered. The filtrate was washed with cold water and then dilute sodium thiosulfate and dried ($MgSO_4$). Upon removal of the solvent a red oily residue remained. The remaining work-up was the same as in part a giving 120 mg (11%) of product having the same mp and ir as in part a.

12. 6-Hydroxy-5,5',8,9,10-pentaphenylbenzo[cd]cyclopent[f]-azulen-4-(5H)-one (32)

This was prepared by the method of Pauson (16): mp 294-295°; uv max (cyclohexane) 265 (log ϵ 4.20), 305 (log ϵ 4.25), 345 (log ϵ 3.34), and 620 mμ (log ϵ 3.34); ir ($CHCl_3$) 3150-3300 (OH) and 1681 cm^{-1} (C=O); nmr ($CDCl_3$) δ 10.2 (s, 1), and 7.60-6.92 (m, 29).

Anal. Calcd for $C_{46}H_{30}O_2$: C, 90.00; H, 4.90.

Found: C, 90.38; H, 5.23.

13. Trimethylsilyl Derivative of 32

A mixture of 100 mg of compound 32 in 8 ml of acetonitrile (freshly distilled from P_2O_5) and 1 ml of bistrimethylsilylacetamide was refluxed under nitrogen for 30 minutes during which time the color changed from blue to purple. Upon standing at room temperature the trimethylsilyl derivative crystallized: mp 257-258°; uv max (cyclohexane) 255 (log ε 4.57), 295 (log ε 4.73), and 532 mμ (log ε 3.72); ir ($CHCl_3$) 1701 cm^{-1} (C=O); mass spectrum (70 eV) m/e 686 (Parent).

Anal. Calcd for $C_{49}H_{38}SiO_2$: C, 85.50; H, 5.54.
Found: C, 85.41; H, 5.57.

14. Acetate of 32

A mixture of 100 mg of compound 32, 5 ml acetic anhydride, and 2 ml pyridine was refluxed under nitrogen for 30 minutes during which time the color changed from blue to purple. When poured into water the acetate crystallized and was filtered. Recrystallization from hexane gave 60 mg (62%) of acetate: mp 300-301°; ir ($CHCl_3$) 1701 (C=O) and 1760 cm^{-1} (ester C=O); UV_{max} (cyclohexane) 525 and 290 mμ.

Anal. Calcd for $C_{48}H_{32}O_3$: C, 87.70; H, 4.87.
Found: C, 87.59; H, 5.02.

15. Potassium Permanganate Oxidation of 32

A mixture of 0.6 g (0.001 mole) of blue compound 32 in 50 ml of heptane and 20 ml of water in a three-necked

(stirrer, thermometer, dropping funnel) flask was heated to 100°. To this was added dropwise a hot solution of 4 g of $KMnO_4$ and 3 g of sodium carbonate in water. When the permanganate was consumed another 2-g portion (in water) was added. This process was repeated until a total of 8 g was added. The heptane layer was drawn off and the solvent removed. The residue was chromatographed on silicic acid with CCl_4-benzene. The third and fourth fractions collected contained a total of 75 mg of an oil. The ir was identical with that of benzophenone; mp 2,4-DNP, 236-238°; benzophenone 2,4-DNP 237-238°. The ir spectra of the 2,4-DNP's were identical.

The aqueous layer from the oxidation was saturated with sulfur dioxide until all of the black MnO_2 was gone. Acid was added to dissolve most of the salts and the acidic solution was extracted for three days in a continuous extractor with ether. The ether was dried and the solvent removed. The residue was chromatographed on silicic acid with CCl_4-benzene. All factions eluted with CCl_4-benzene or with chloroform were found to contain benzoic acid (350 mg unpurified). The remaining fraction gave oils which appeared to be only partially oxidized fragments.

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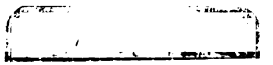

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APPENDIX

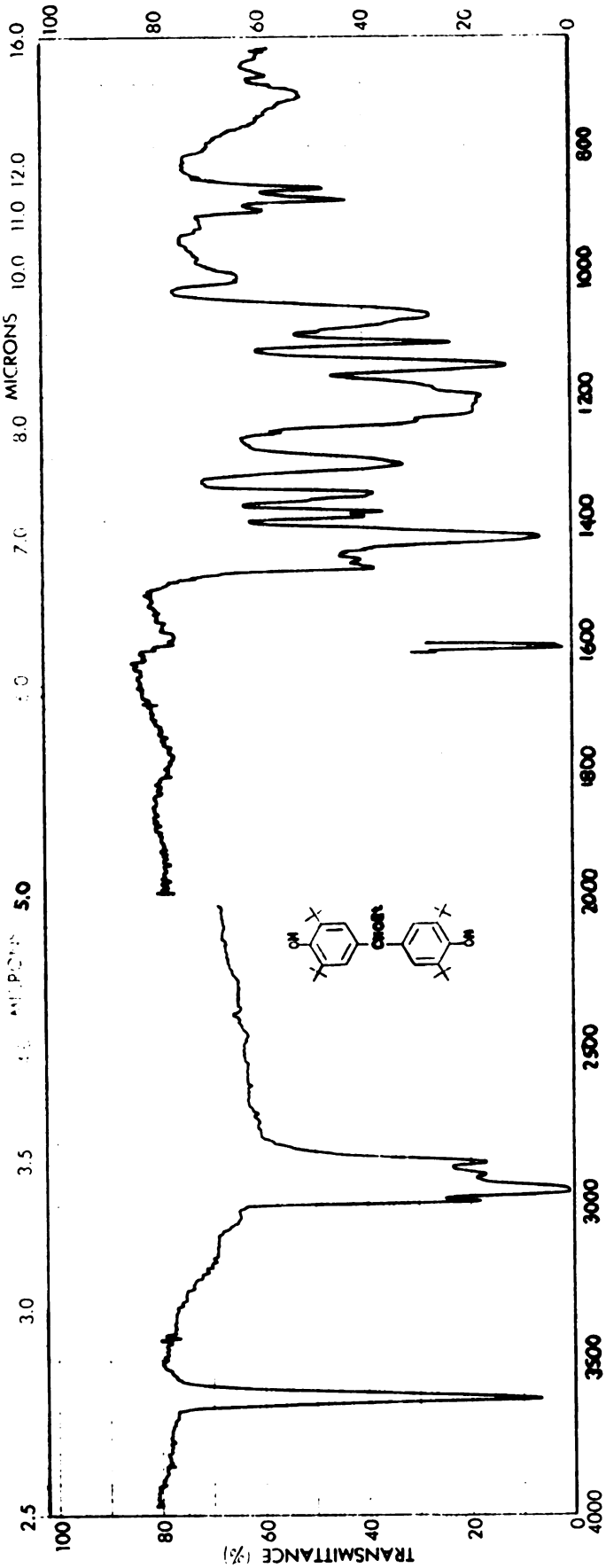

Figure 10. Infrared spectrum of ethoxy compound 19 (in $CHCl_3$).

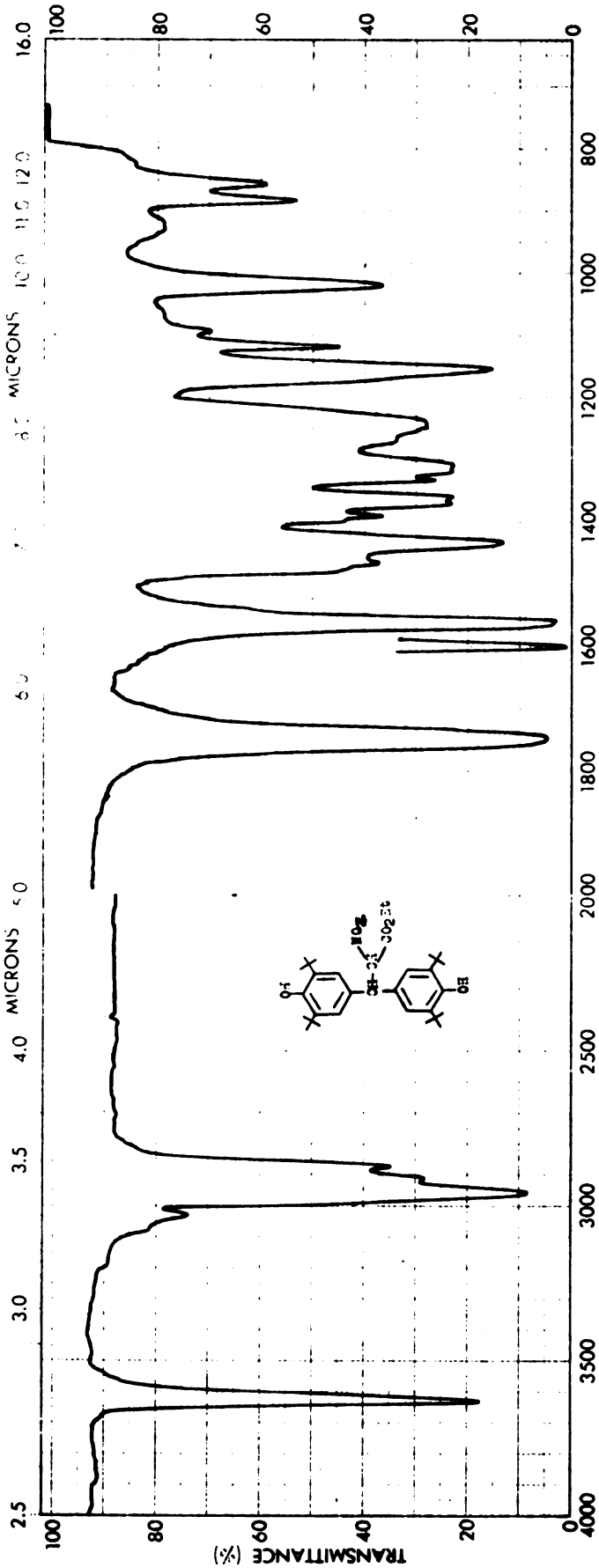

Figure 11. Infrared spectrum of nitro ester 18 (in $CHCl_3$).

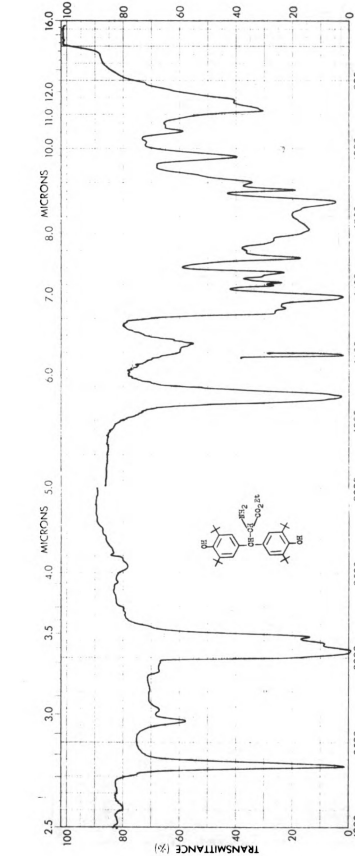

Figure 12. Infrared spectrum of amino ester 20 (in $CHCl_3$).

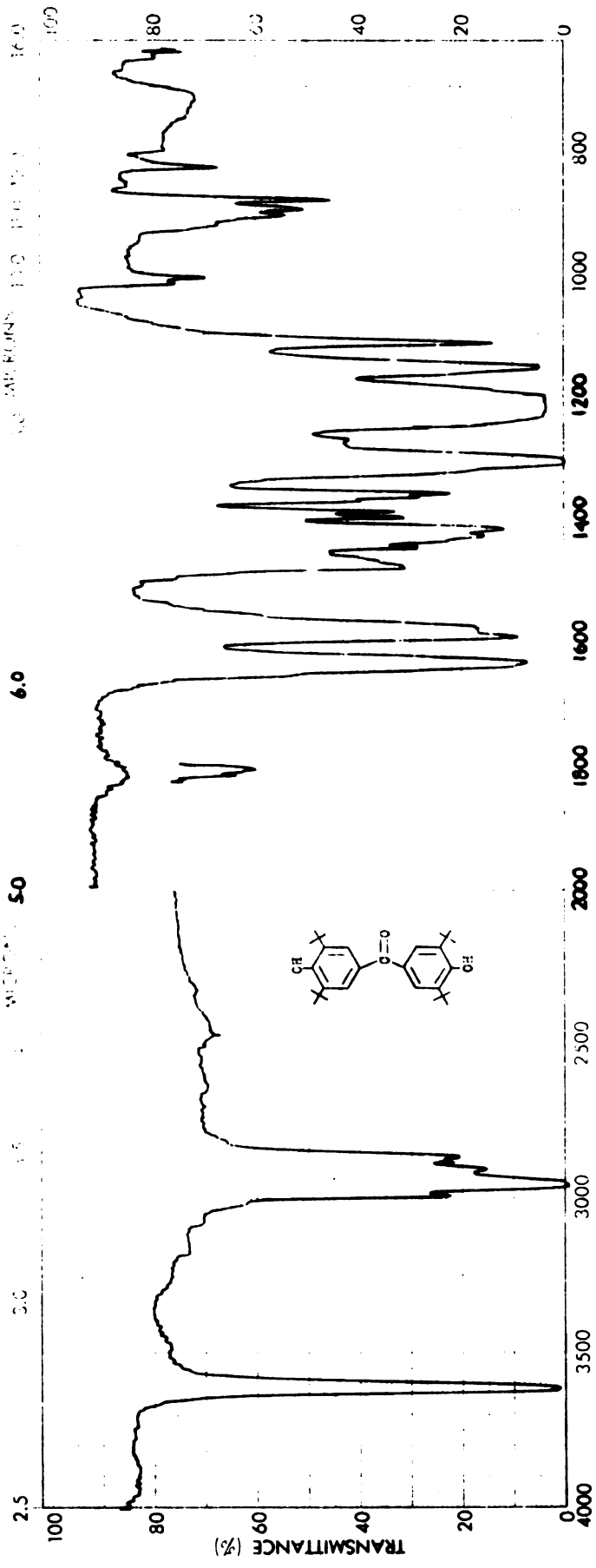

Figure 13. Infrared spectrum of benzophenone 28 (in $CHCl_3$).

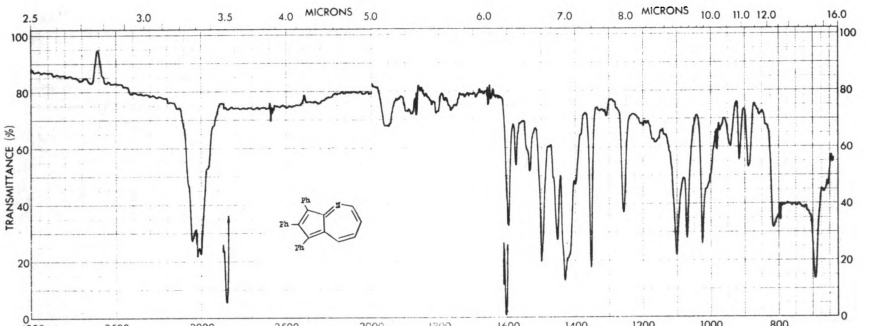

Figure 14. Infrared spectrum of azazulene 30 (in $CHCl_3$).

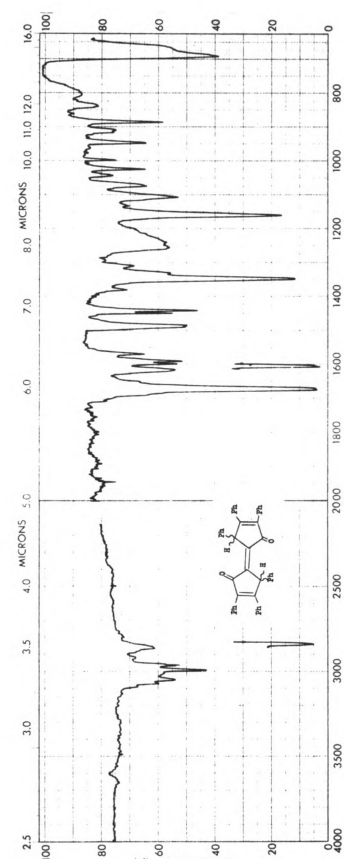

Figure 15. Infrared spectrum of bicyclopentenylidene **31** (in $CHCl_3$).

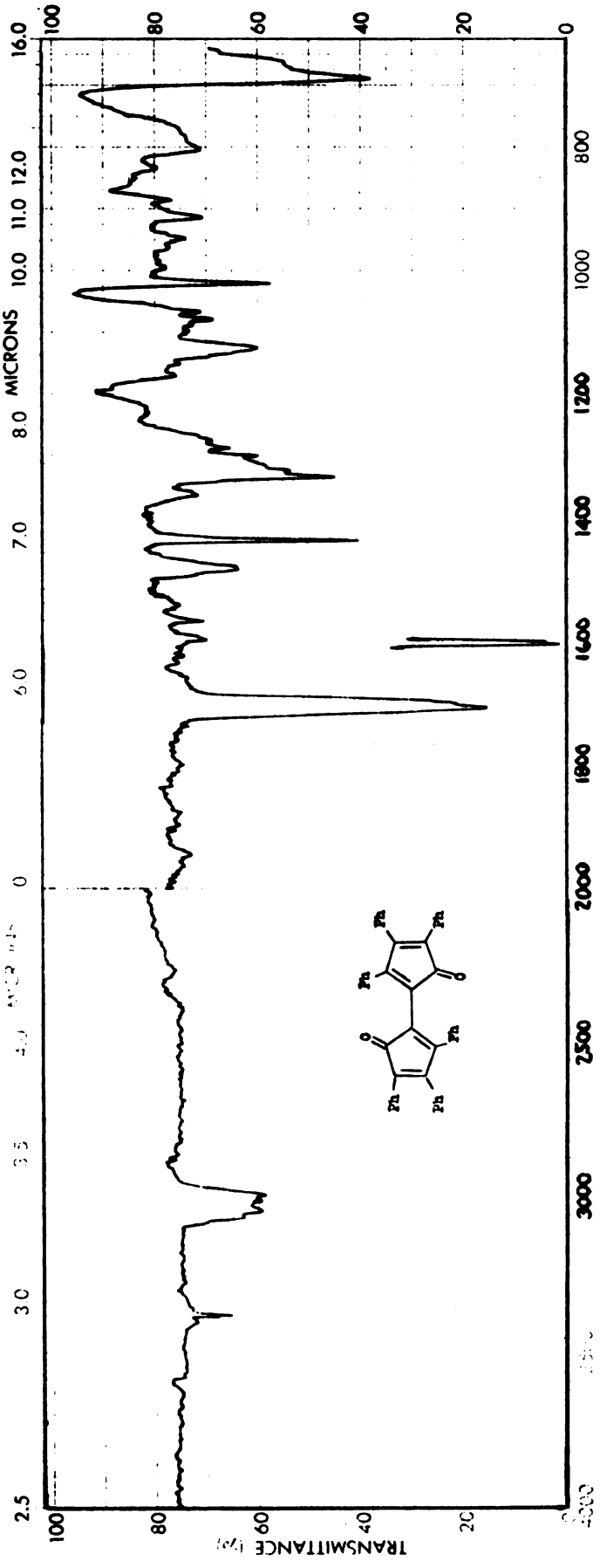

Figure 16. Infrared spectrum of biscyclone 44 (in $CHCl_3$).

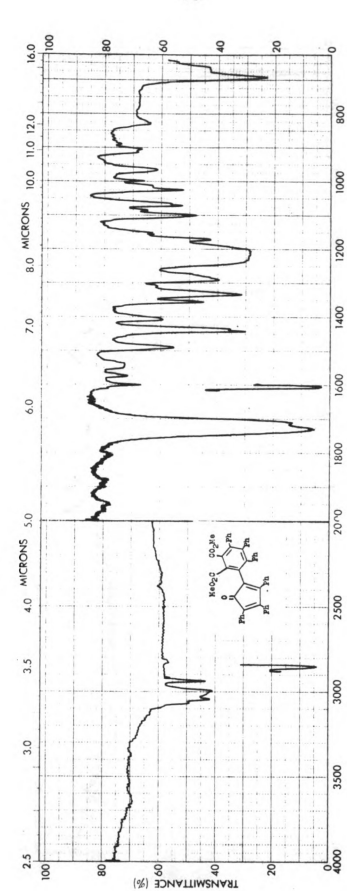

Figure 17. Infrared spectrum of acetylenic ester adduct of biscyclone **44** (in $CHCl_3$).

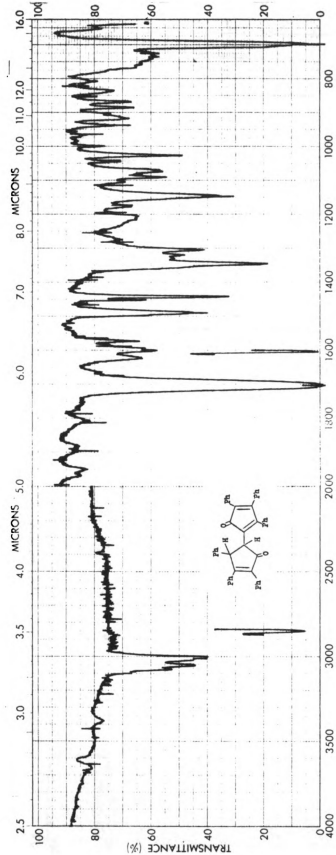

Figure 18. Infrared spectrum of cyclone 48 (in $CHCl_3$).

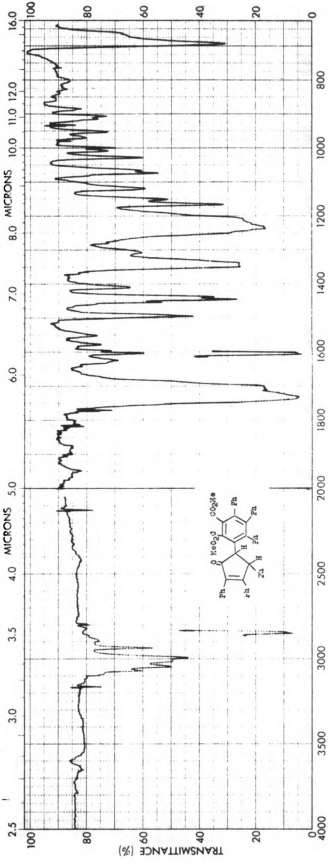

Figure 19. Infrared spectrum of acetylenic ester adduct of cyclone 48 (in $CHCl_3$).

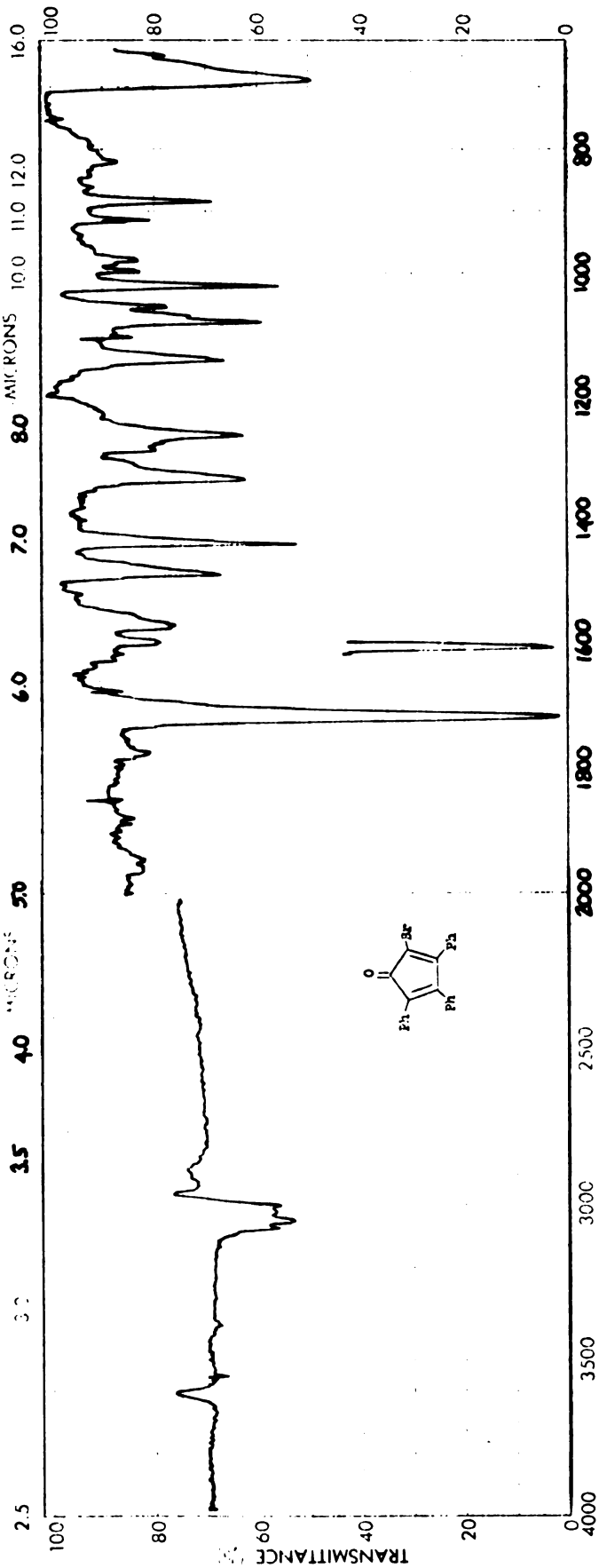

Figure 20. Infrared spectrum of triphenylbromocyclone 50 (in $CHCl_3$).

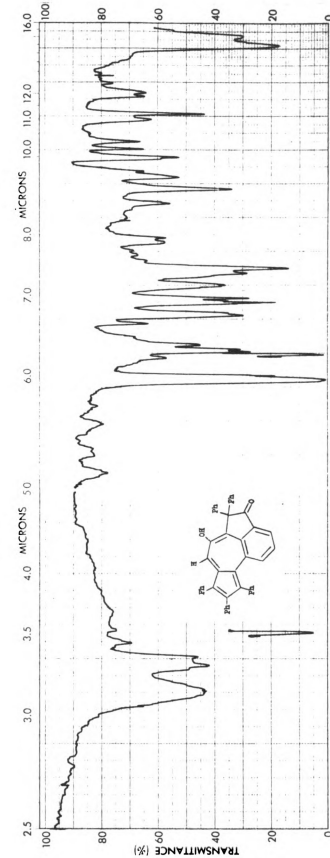

Figure 21. Infrared spectrum of azulene 32 (in $CHCl_3$).

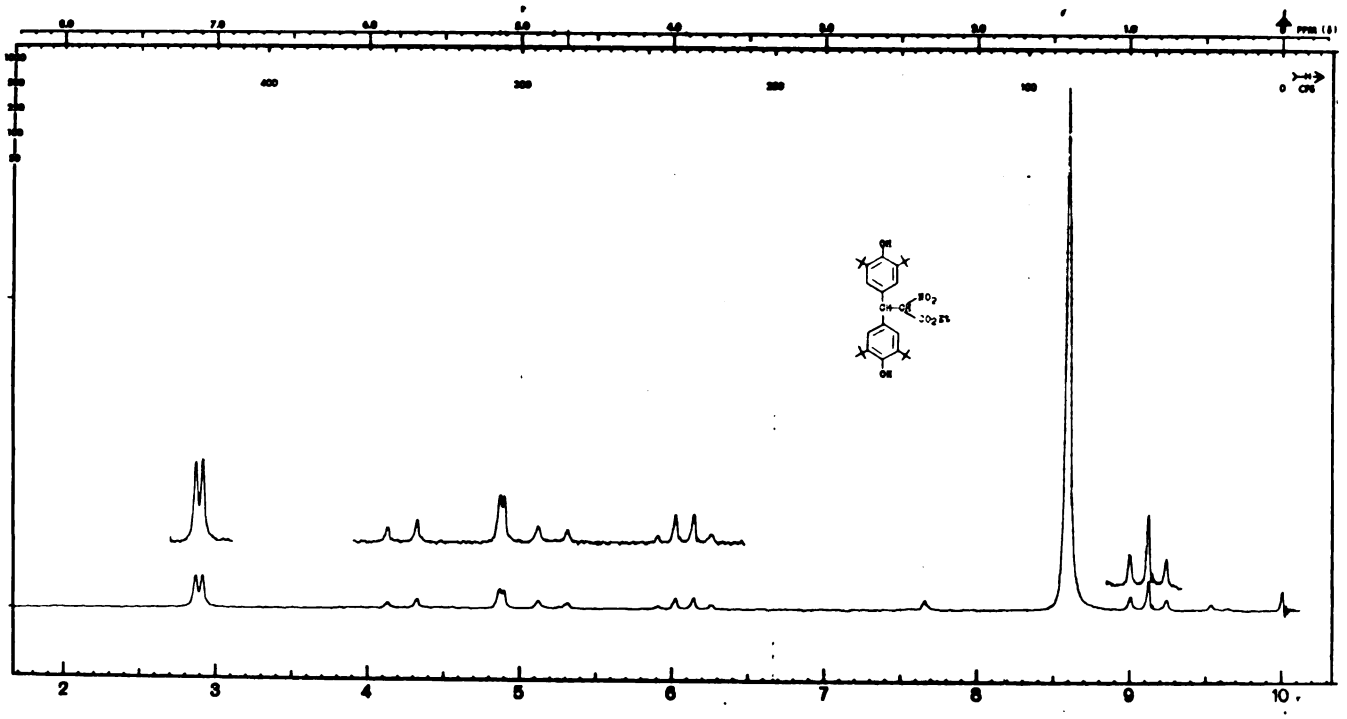

Figure 22. Nmr spectrum of nitro ester 18 (in $CDCl_3$).

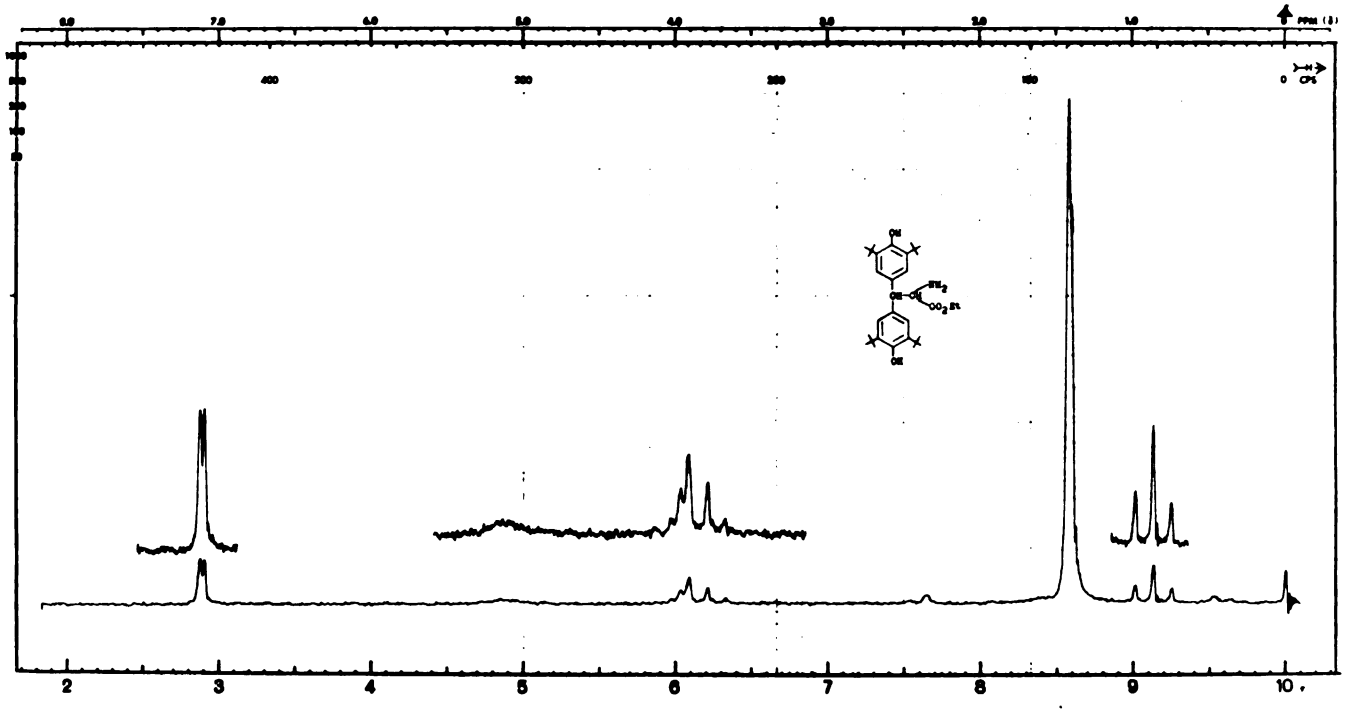

Figure 23. Nmr spectrum of amino ester 20 (in $CDCl_3$).

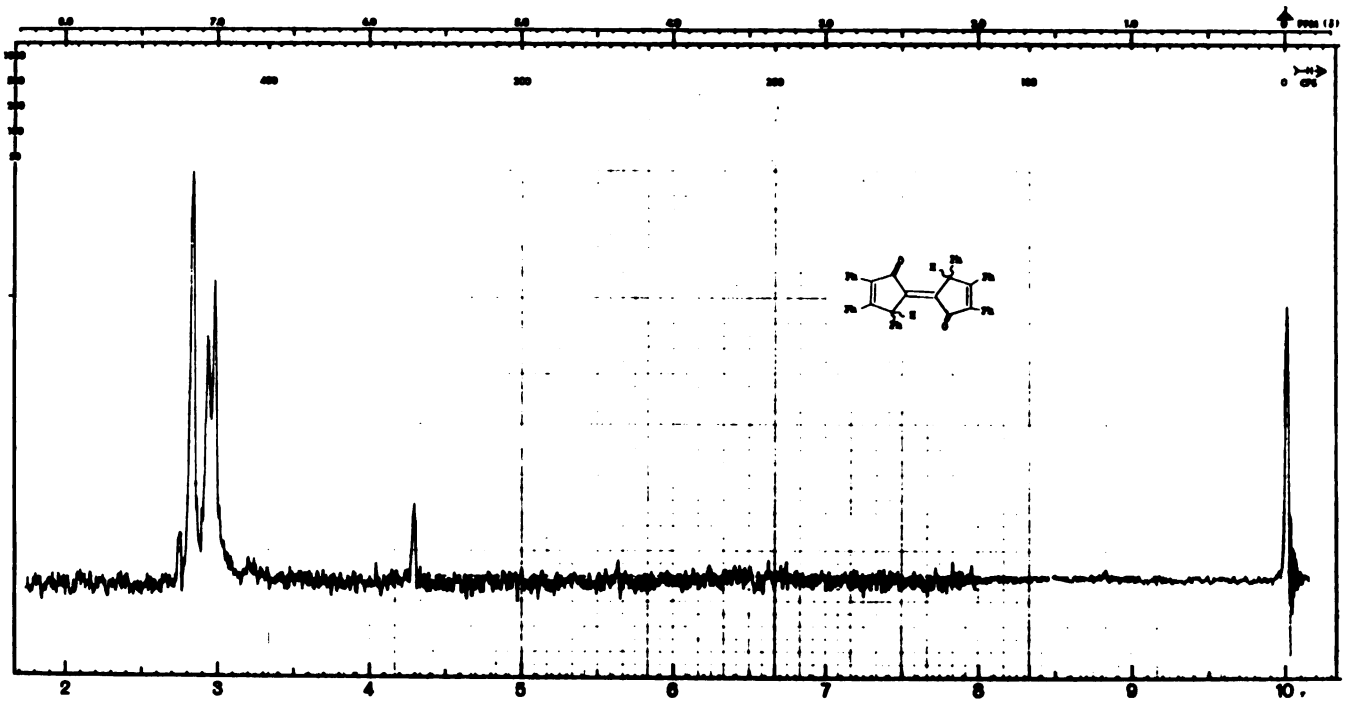

Figure 24. Nmr spectrum of biscyclopentenylidene 31 (in $CDCl_3$).

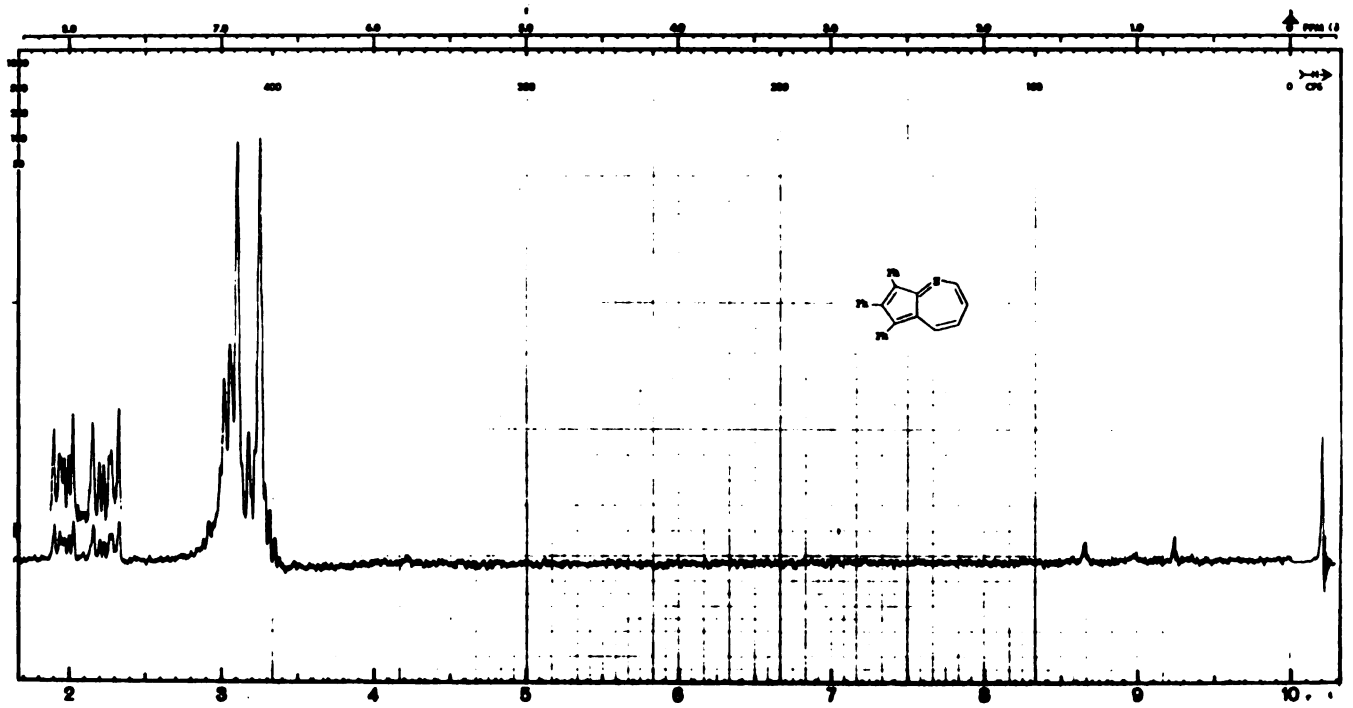

Figure 25. Nmr spectrum of azazulene 30 (in $CDCl_3$).

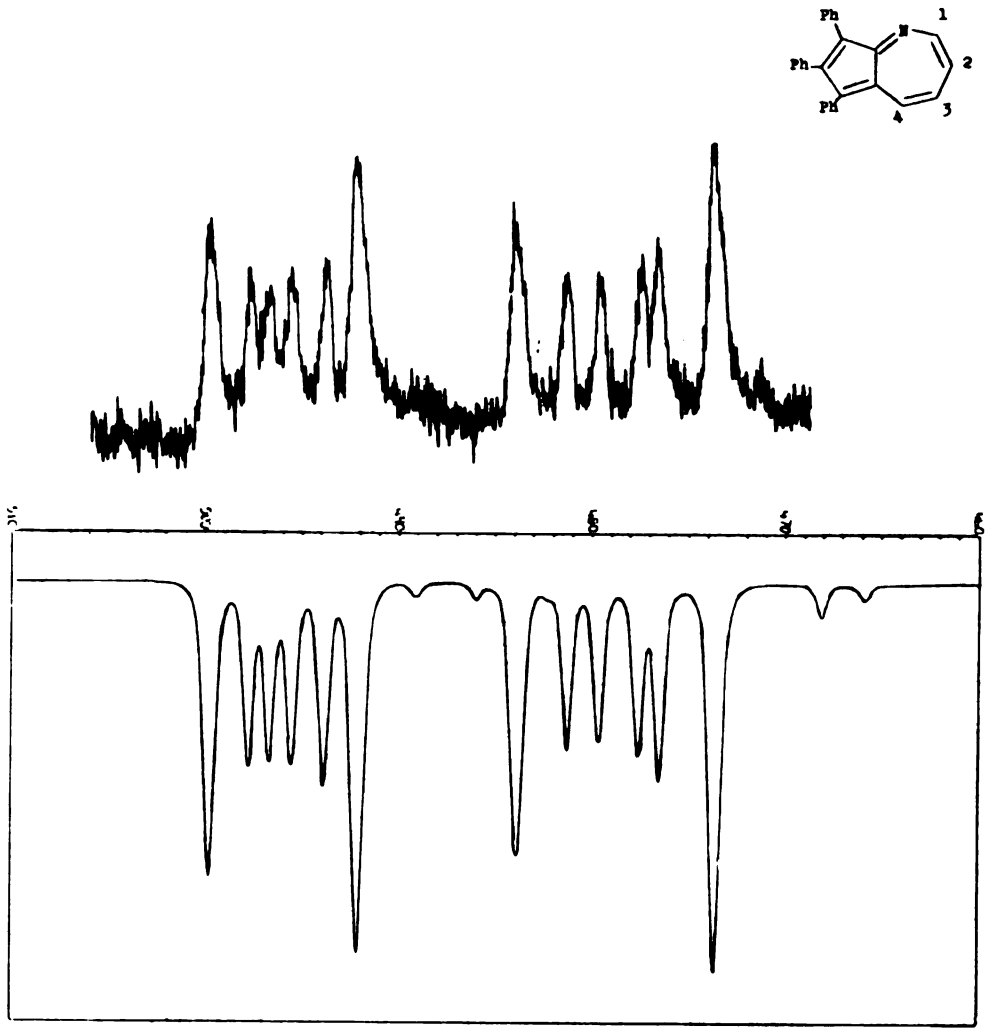

Figure 26. Comparison of calculated and observed spectra of H_1 and H_4 of azazulene 30.

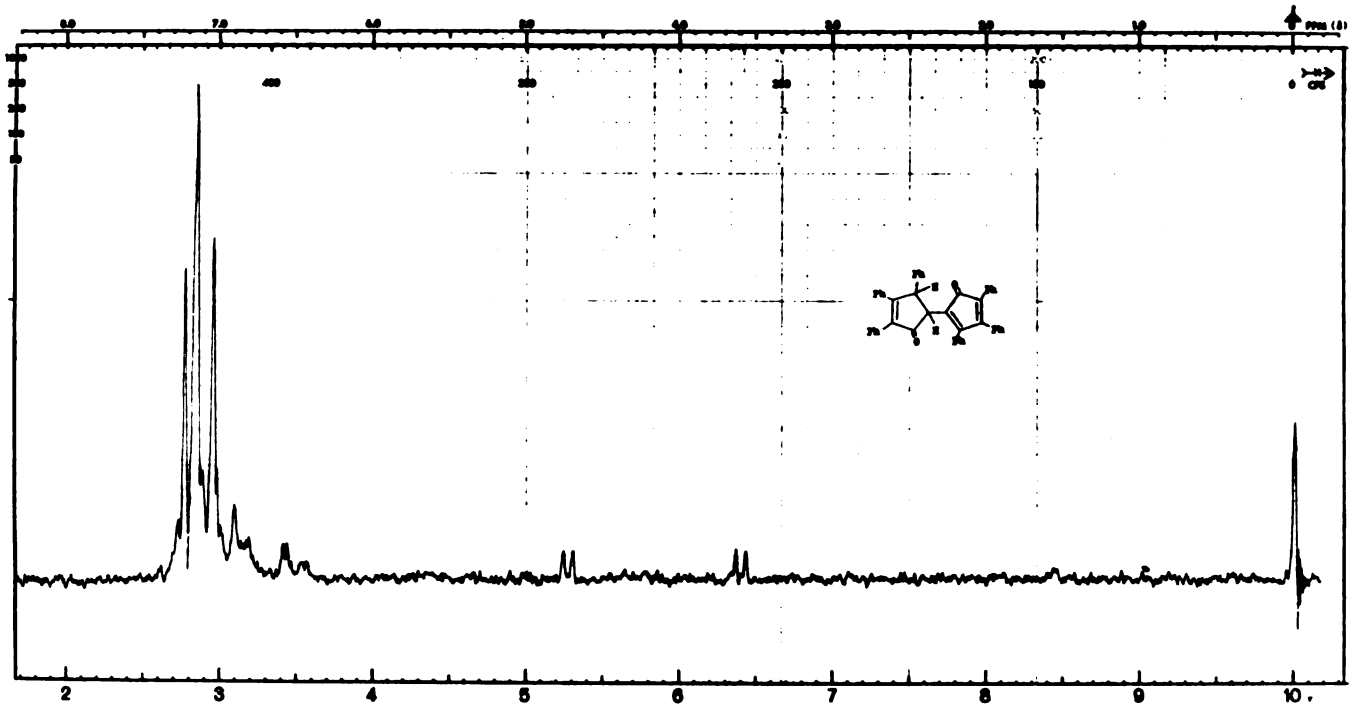

Figure 27. Nmr spectrum of cyclone 48 (in $CDCl_3$).

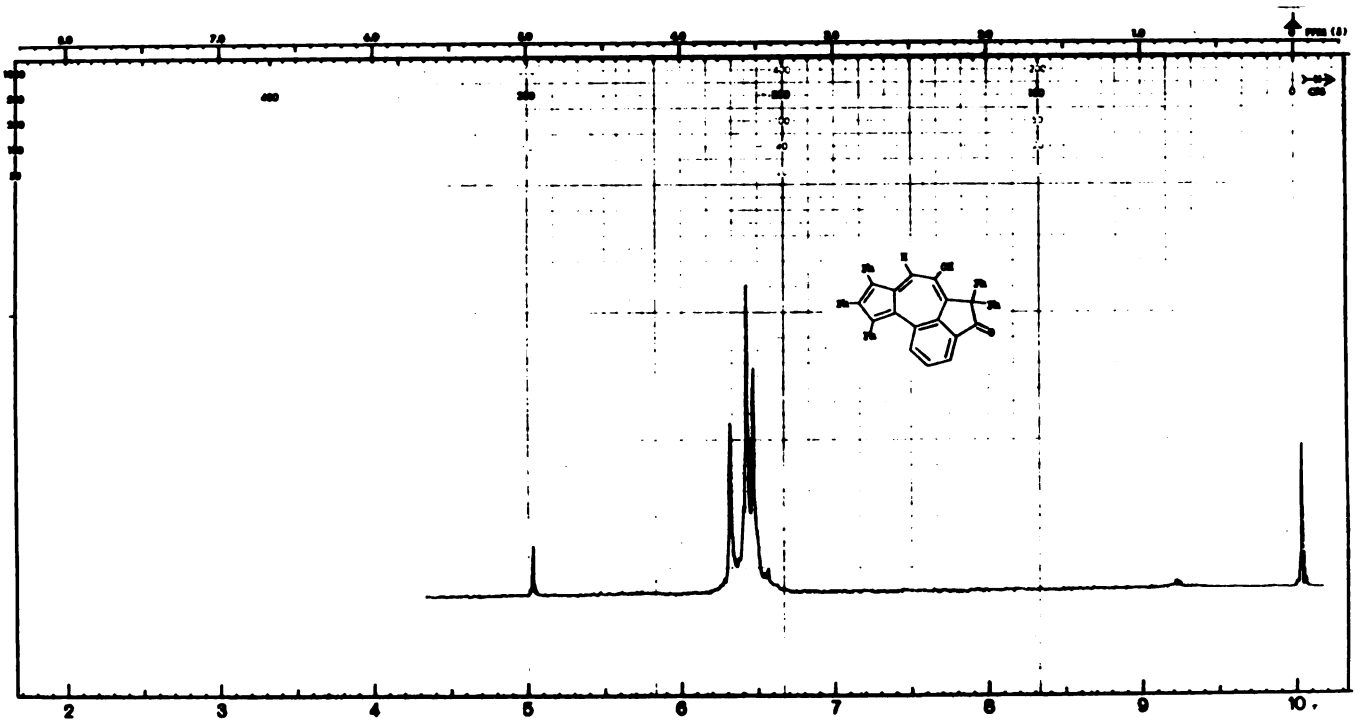

Figure 28. Nmr spectrum of azulene 32 (in $CDCl_3$ at 1000 Hz sweep width).

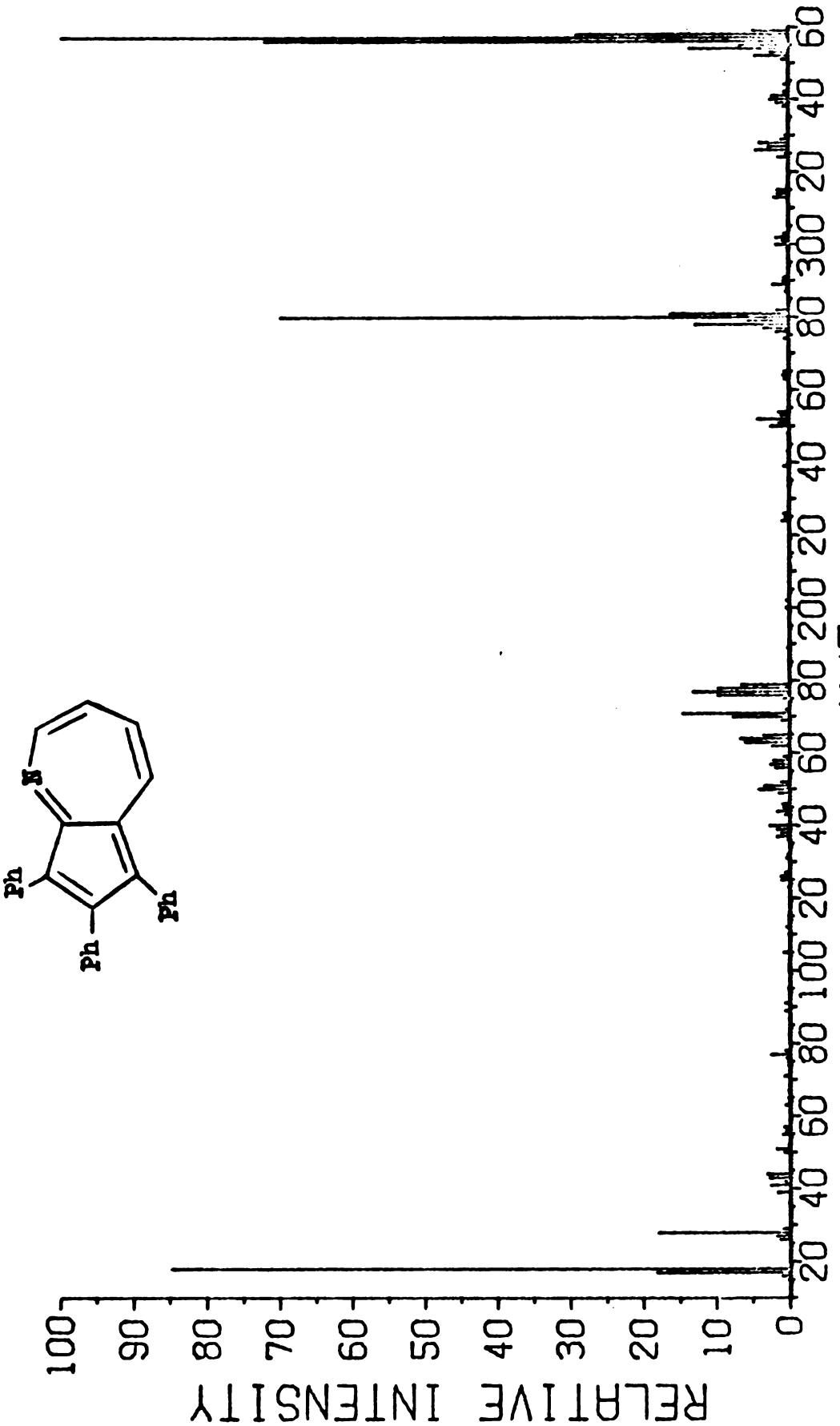

Figure 29. Mass spectrum plot of azazulene 30.

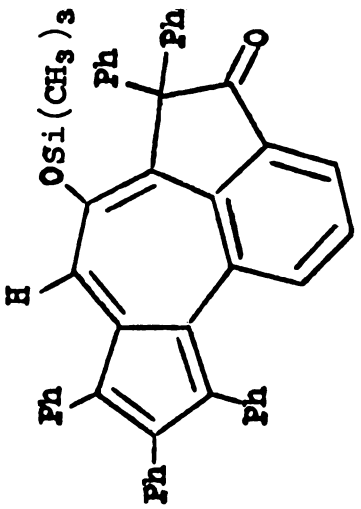

Figure 30. Mass spectrum plot of azulene 32 (22).

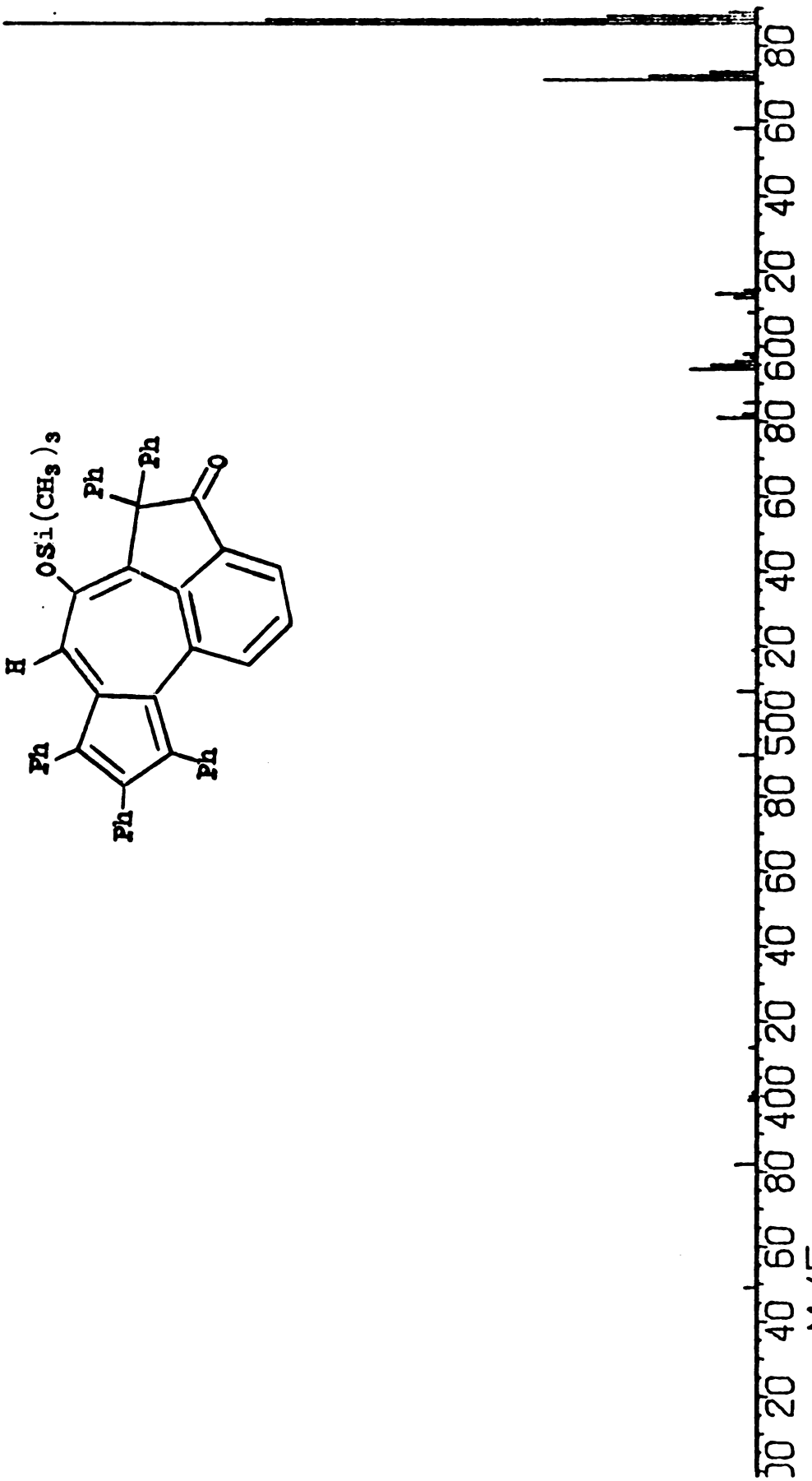

Figure 30. (Cont.).

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SAMPLE INTRODUCED VIA DIRECT INSERTION PROBE, TEMPERATURE 220 C.
IONIZING VOLTAGE- 70 V. ACCELERATING VOLTAGE- 8 KV.
NOMINAL RESOLVING POWER 10 K
BACKGROUND HAS NOT BEEN SUBTRACTED FROM THIS SPECTRUM

CALCULATION LIMITS

ERROR	N	O	F	CL	BR	I	S	P	SI	D	C13
.000021	1	0	0	0	0	0	0	0	0	0	0

RELATIVE INTENSITY OF WEAKEST PEAK= .119 PER CENT
SUM OF INTENSITIES OF ALL PEAKS= 679 PER CENT

MEASURED MASS	REL. INTENSITY ACTUAL	REL. INTENSITY THEOR.	CALCULATED MASS	ERROR PPM	INTENSITY STD DEV	MOLECULAR FORMULA.	
15.0231	.30		15.0235	25.3		C H3	
15.9948	.94		15.9949	4.2		O	
16.0309	.33		16.0313	26.8		C H4	
17.0024	18.22		17.0027	19.6		H O	
18.0106	85.01		18.0106	.0		H2 O	
26.0166	1.47		26.0156	35.2		C2 H2	
27.0113	.74		27.0109	14.8		C H N	
27.0243	1.44		27.0235	30.7		C2 H3	
27.9950	16.98		27.9949	1.8		C O	
28.0323	1.09		28.0313	34.9		C2 H4	
29.0394	1.18		29.0391	10.8		C2 H5	
35.9767	.20						NO SATISFACTORY FIT
39.0232	1.77		39.0235	6.2		C3 H3	
41.0393	2.72		41.0391	5.5		C3 H5	
42.0473	.80		42.0469	7.2		C3 H6	
43.0189	.70		43.0184	12.9		C2 H3 O	
43.0547	2.22		43.0548	1.2		C3 H7	
43.9898	3.29		43.9898	.0		C O2	
50.0169	.74		50.0156	25.9		C4 H2	
51.0240	1.88		51.0235	10.4		C4 H3	
52.0321	.28		52.0313	14.6		C4 H4	
55.0555	1.09		55.0548	14.1		C4 H7	
56.0630	.66		56.0626	6.7		C4 H8	
57.0702	.99		57.0704	3.5		C4 H9	
63.0232	.58		63.0235	4.7		C5 H3	
65.0400	.31		65.0391	12.9		C5 H5	
67.0559	.32		67.0548	17.2		C5 H7	
71.0872	.78		71.0861	15.5		C5 H11	
74.0165	.31		74.0156	11.8		C6 H2	
75.0249	.28		75.0235	19.4		C6 H3	
76.0303	.46		76.0313	12.9		C6 H4	
77.0388	2.63		77.0391	3.7		C6 H5	
78.0468	.70		78.0469	2.5		C6 H6	
89.0393	.54		89.0391	1.4		C7 H5	
91.0541	.54		91.0548	7.6		C7 H7	
95.0863	.19		95.0861	2.7		C7 H11	
105.0335	1.00						NO SATISFACTORY FIT
109.7053	.20						NO SATISFACTORY FIT

Table 3. Computer analysis of the mass spectrum of 1,2,3-triphenyl-4-azazulene (30).

112.0323	.37	112.0313	9.2		C9 H4	
113.0370	.19	113.0391	19.0		C9 H5	
114.0442	.16					NO SATISFACTORY FIT
115.0539	.13	115.0548	7.3		C9 H7	
123.0253	.14	123.0235	14.6		C10 H3	
125.0380	1.23	125.0391	9.3		C10 H5	
125.5368	.16					DOUBLY IONIZED 251.0830
126.0444	1.10	126.0469	20.1		C10 H6	
127.0506	.57					DOUBLY IONIZED 254.0992
130.5359	.18					NO SATISFACTORY FIT
131.0397	.21					NO SATISFACTORY FIT
131.5405	.32					DOUBLY IONIZED 263.0842
136.0365	.23					NO SATISFACTORY FIT
137.0392	1.71	137.0391	.5		C11 H5	
137.5434	.35					DOUBLY IONIZED 275.0783
138.0476	.97	138.0469	4.7		C11 H6	
138.5442	.21					DOUBLY IONIZED 277.0905
139.0514	1.63					DOUBLY IONIZED 278.0984
139.5524	1.87					DOUBLY IONIZED 279.0991
140.0542	.84					DOUBLY IONIZED 280.1106
142.5366	.55					NO SATISFACTORY FIT
143.5423	1.72					DOUBLY IONIZED 287.0930
144.0479	.13					DOUBLY IONIZED 288.0959
144.5470	.91					DOUBLY IONIZED 289.1059
145.5539	1.04					DOUBLY IONIZED 291.1153
149.0409	1.64	149.0391	12.3		C12 H5	
149.5401	.49					DOUBLY IONIZED 299.0768
150.0472	3.73					DOUBLY IONIZED 300.0923
150.5488	.73					DOUBLY IONIZED 301.0966
151.0500	2.76					DOUBLY IONIZED 302.1047
151.5524	.21					DOUBLY IONIZED 303.1127
152.0600	1.13	152.0626	17.4		C12 H8	
155.5454	1.74					NO SATISFACTORY FIT
156.0443	.33					NO SATISFACTORY FIT
156.5504	2.34					DOUBLY IONIZED 313.1032
157.0541	.45					DOUBLY IONIZED 314.1021
157.5554	2.10					DOUBLY IONIZED 315.1077
158.0561	.24					DOUBLY IONIZED 316.1086
158.5600	.71					NO SATISFACTORY FIT
161.5455	.12					NO SATISFACTORY FIT
162.0469	2.35					DOUBLY IONIZED 324.0941
162.5492	.99					DOUBLY IONIZED 325.0898
163.0514	5.09	163.0548	20.9	1.000	C13 H7	
163.5530	2.25					DOUBLY IONIZED 327.1132
164.0571	4.53					DOUBLY IONIZED 328.1180
164.5611	2.65					DOUBLY IONIZED 329.1208
165.0691	1.00	165.0704	8.3		C13 H9	
168.5473	.31					NO SATISFACTORY FIT
169.0519	.92					DOUBLY IONIZED 338.1033
169.5553	5.32					DOUBLY IONIZED 339.1141
170.0570	2.50					DOUBLY IONIZED 340.1182
170.5619	11.03					DOUBLY IONIZED 341.1245
171.0638	3.77					DOUBLY IONIZED 342.1307
171.5665	.50					NO SATISFACTORY FIT
175.0487	.87					NO SATISFACTORY FIT
175.5555	1.44					DOUBLY IONIZED 351.1073

176.0579	8.46						DOUBLY IONIZED 352.1117
176.5611	5.61						DOUBLY IONIZED 353.1193
177.0632	7.69						DOUBLY IONIZED 354.1259
177.5660	5.88						DOUBLY IONIZED 355.1323
178.0712	4.06						DOUBLY IONIZED 356.1421
178.5749	3.95						DOUBLY IONIZED 357.1507
179.0774	2.61						DOUBLY IONIZED 358.1561
189.0699	.24		189.0704	3.0		C15 H9	
200.0597	.51		200.0626	14.3		C16 H8	
202.0727	.50						NO SATISFACTORY FIT
224.0595	1.08		224.0626	14.0		C18 H8	
225.0705	.62		225.0704	.2		C18 H9	
226.0735	.73		226.0782	20.9		C18 H10	
239.0897	.72		239.0861	15.2		C19 H11	
240.0892	.12		240.0939	19.4		C19 H12	
242.9949	.17						NO SATISFACTORY FIT
248.0658	.19		248.0626	12.8		C20 H8	
250.0829	2.66		250.0782	18.6	1.000	C20 H10	
251.0830	1.39	.59					ISOTOPE PEAK OF C20 H10
			251.0861	12.3	1.000	C20 H11	
252.0969	4.37		252.0939	11.9	1.000	C20 H12	
253.0990	1.31	.96					ISOTOPE PEAK OF C20 H12
254.0992	1.39		254.0970	8.8	.553	C19 H12 N	
255.1063	.13	.29					ISOTOPE PEAK OF C19 H12 N
263.0842	.65		263.0861	7.2		C21 H11	
264.0847	.91		264.0813	12.7		C20 H10 N	
265.0963	.62		265.1017	20.5		C21 H13	
274.0790	.65		274.0782	2.9		C22 H10	
275.0783	.19		275.0735	17.6		C21 H9 N	
276.0873	2.01						NO SATISFACTORY FIT
277.0905	3.50		277.0891	4.9	1.000	C21 H11 N	
278.0984	12.98		278.0970	5.3	1.000	C21 H12 N	
279.0991	5.54	3.00					ISOTOPE PEAK OF C21 H12 N
			279.1048	20.4	1.000	C21 H13 N	
280.1106	69.91		280.1126	7.0	.015	C21 H14 N	
281.1159	16.27	16.15					ISOTOPE PEAK OF C21 H14 N
282.1181	1.84						NO SATISFACTORY FIT
287.0930	.45						NO SATISFACTORY FIT
288.0959	.21		288.0939	7.0		C23 H12	
289.1059	2.31		289.1017	14.4	1.000	C23 H13	
290.1107	.74	.59					ISOTOPE PEAK OF C23 H13
291.1153	.69		291.1174	7.0		C23 H15	
299.0768	.12		299.0735	11.2		C23 H9 N	
300.0923	1.87		300.0939	5.4	1.000	C24 H12	
301.0966	.94	.49					ISOTOPE PEAK OF C24 H12
302.1047	1.84		302.1095	16.0	.235	C24 H14	
303.1127	.60	.49					ISOTOPE PEAK OF C24 H14
313.1032	2.07		313.1017	4.6	1.000	C25 H13	
314.1021	1.54		314.0970	16.3	1.000	C24 H12 N	
315.1077	1.60	.41					ISOTOPE PEAK OF C24 H12 N
			315.1048	9.3	1.000	C24 H13 N	
316.1086	.15		316.1126	12.6		C24 H14 N	
324.0941	1.59		324.0939	.5	1.000	C26 H12	
325.0998	.42		325.0891	2.0		C25 H11 N	
326.1096	4.67		326.1095	.2	1.000	C26 H14	
327.1139	2.96	1.34					ISOTOPE PEAK OF C26 H14

			327.1174	12.6	1.000	C26 H15	
328.1180	4.11		328.1126	16.3	1.000	C25 H14 N	
329.1209	1.09	1.13					ISOTOPE PEAK OF C25 H14 N
330.1305	.46		330.1283	6.7		C25 H16 N	
338.1033	.74		338.1095	18.3		C27 H14	
			338.0970	18.9		C26 H12 N	
339.1141	1.83		339.1174	9.8	1.000	C27 H15	
340.1182	2.66	.54					ISOTOPE PEAK OF C27 H15
			340.1126	16.4		C26 H14 N	
341.1245	2.31		341.1204	11.9	1.000	C26 H15 N	
342.1307	.62	.66					ISOTOPE PEAK OF C26 H15 N
344.1589	.68		344.1565	7.1		C27 H20	
351.1073	1.09		351.1048	7.2	1.000	C27 H13 N	
352.1117	4.80	.32					ISOTOPE PEAK OF C27 H13 N
			352.1126	2.6	1.000	C27 H14 N	
353.1193	2.68						NO SATISFACTORY FIT
354.1259	13.86		354.1283	6.6	1.000	C27 H16 N	
355.1323	6.55	4.12					ISOTOPE PEAK OF C27 H16 N
			355.1361	10.5	1.000	C27 H17 N	
355.2114	.16						NO SATISFACTORY FIT
355.8029	.19						NO SATISFACTORY FIT
356.0515	.20		356.0500	4.2		C28 H6 N	
356.1421	71.68						NO SATISFACTORY FIT
357.1507	100.00		357.1517	2.8	.998	C27 H19 N	
358.1561	29.14	29.70					ISOTOPE PEAK OF C27 H19 N
359.1613	5.07		359.1674	17.0	1.000	C27 H21 N	