

carboxylate, 20 ml of methyl alcohol-*O-d*, and a petroleum ether solution of photoproducts **2a**, **b**. Three grams (0.05 mol) of perdeuterioacetic acid was added, and the mixture was stirred under a nitrogen atmosphere for several hours. The solution was filtered, and the solvent was removed. The dicyclopentyl isolated from the residue exhibited a molecular ion at mass 142 indicating four deuterium atoms per molecule.

Preparation of Authentic *meso*- and *d,l*-3-(3'-Cyclopentenyl)-cyclopentenes. In a dry 100-ml round-bottomed flask maintained under nitrogen were placed 2.43 g (0.100 mol) of triply sublimed magnesium, 30 ml of anhydrous ethyl ether, and 2.17 g (0.200 mol) of 3-chlorocyclopentene.¹⁸ The reaction mixture was stirred overnight at room temperature. The preparation was extracted several times with water, and the ether layer was dried over sodium sulfate. The ether was removed by rotary evaporator, and the residue was chromatographed on neutral alumina (petroleum ether eluent). Authentic *meso*- and *d,l*-3-(3'-cyclopentenyl)cyclopentenes were collected separately in pure form by preparative vpc (1/4 in. × 2 m, succinate polyester of diethylene glycol, oven at 74°). The two products were formed in equal amounts.

Coinjection of a mixture of the authentic *meso*- and *d,l*-3-(3'-cyclopentenyl)cyclopentenes with a mixture of photoproducts **2a**, **b** on vpc gave only two peaks. The nmr and mass spectra of the authentic compounds were identical with the spectra of photoproducts **2a**, **b**.

Perdeuteriocyclopentadiene. A solution of 10 g of potassium deuterioxide dissolved in 10 ml of deuterium oxide was maintained under nitrogen. In a 250-ml round-bottomed flask (maintained under nitrogen) were placed 15 ml (0.75 mol) of deuterium oxide, 12 g (0.18 mol) of cyclopentadiene, 2 ml of the stock potassium deuterioxide solution, and 100 ml of diglyme (refluxed for 24 hr over sodium and distilled). The solution was stirred for 40 min, and the cyclopentadiene was transferred from the homogeneous exchange medium in a bulb-to-bulb vacuum distillation. Infrared analysis (Perkin-Elmer 137) indicated that deuterium had been exchanged into the cyclopentadiene. The C-H absorption bands at 2880 and 3090 cm⁻¹ were less than half as strong, and C-D absorption bands appeared at 2310 and 2180 cm⁻¹.

The partially deuterated cyclopentadiene was degassed on the vacuum line and then distilled into a new exchange medium. The

solution was stirred for 40 min, and the cyclopentadiene was again removed. Another exchange medium was prepared, and the procedure was repeated. A total of five exchanges was done (the last four entirely on the vacuum line), and each time the reaction medium, consisting of 15 ml of deuterium oxide, 2 ml of potassium deuterioxide solution, 100 ml of diglyme, and cyclopentadiene, was stirred for 40 min. Approximately 10 ml of perdeuteriocyclopentadiene was distilled from the last exchange solution into 400 ml of tetrahydrofuran.

Photolysis of Perdeuteriocyclopentadiene. Perdeuteriocyclopentadiene was prepared in the usual manner using 200 ml of the tetrahydrofuran solution of perdeuteriocyclopentadiene (0.35 M). Immediately before transfer to the photolysis vessel 50 ml of *tert*-butyl alcohol-*O-d* was added. A 160-ml portion of the solution was irradiated for 2 hr. The solution was worked up and chromatographed in the usual manner, and a mixture of the dimeric photoproducts, *meso*- and *d,l*-3-(3'-cyclopentenyl)cyclopentenes, was isolated by preparative vpc (1/4 in. × 2 m, succinate polyester of diethylene glycol, oven at 75°). Mass spectral analysis (Atlas CH-4) of the mixture of photoproducts revealed that they were perdeuterated.

Exchange of Deuterium into *meso*- and *d,l*-3-(3'-Cyclopentenyl)-cyclopentenes. In a 25-ml round-bottomed flask were placed 50 mg of a 50:50 mixture of the *meso*- and *d,l*-3-(3'-cyclopentenyl)-cyclopentenes, 0.5 g (0.004 mol) of potassium *tert*-butoxide, and 15 ml of *tert*-butyl alcohol-*O-d*. The solution was stirred under nitrogen for 3 hr and then neutralized with perdeuterioacetic acid. The solution was worked up by adding water and extracting with ethyl ether. The ether layer was washed with water and dried over anhydrous sodium sulfate. The mixture of *meso*- and *d,l*-3,3'-dicyclopentenyls was collected by preparative vpc. The mass spectrum (Atlas CH-4) of the dicyclopentenyls was identical with the spectrum of authentic material indicating that no deuterium had been incorporated.

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(18) "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 238.

Photolysis of Carbocationic Species. Nonbenzenoid Aromatics

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Abstract: In this and an accompanying article, the first studies of product formation from excited carbonium ion systems are reported. Of the cases investigated, only one isomerization of a carbocationic aromatic to a valence bond isomer was uncovered, the photolytic conversion of tropylium ion to the bicyclo[3.2.0] system **4**, **6**, **7**. Under conditions of less acidity in similar irradiations, ditropyl (**8**), photoditropyl (**9**), an ethoxylated ditropyl (**11**), and other products are formed. In the presence of oxygen, phenyltropylium ion is converted to biphenyl, while in acetonitrile, light induces conversion to 2- and 4-phenylbenzaldehydes, along with *cis*- and *trans*-2,2'-diphenylstilbenes. Upon irradiation, azulenum ion is transformed by means of an unusual, obscure reaction to 2,2-di-(1'-azulenyl)propane (**19**) and the related species **20**. Ultraviolet light effects conversion of triphenylcyclopropenium ion to hexaphenylbenzene, under conditions where di-*n*-propylcyclopropenium ion is not affected. Possible mechanisms for most of these changes are presented and discussed.

Chemical investigation of excited aromatic carbocationic systems was initiated for two reasons: (1) generation of valence bond isomeric systems might be expected, as was observed in the irradiation of certain benzenoid chromophores, and (2) to our knowl-

edge, product formation during photolysis of carbonium ions had not been treated in any previous system. In this contribution are recounted the photochemical explorations of selected cationic nonbenzenoid aromatic cases, *viz.*, substituted cyclopropenium

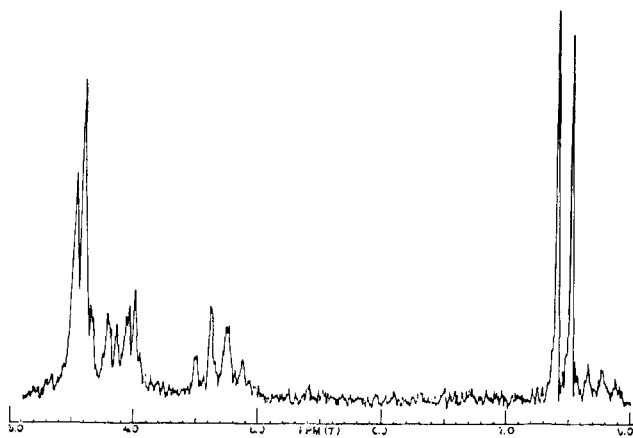
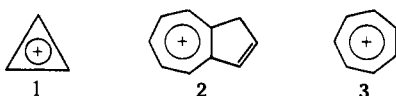
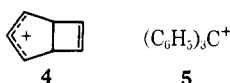


Figure 1. Nmr spectrum of photoditropyl (9) (room temperature in CCl_4 , 60 MHz).

1, azulanium ion 2, and tropylium ion 3, including for-



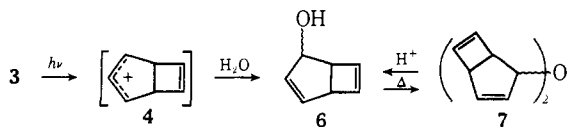
mation from the last of the valence bond isomeric "Dewar tropylium ion" 4. In the accompanying



article,¹ the behavior of excited triphenylcarbonium ion 5 is discussed.

In addition to providing for formation of new valence bond isomers, photolysis of stabilized, nonbenzenoid aromatics of the carbonium ion type also permits execution of the irradiation in a medium not excessively low in pH, an advisable condition for survival of any less stable product. As in our carbanion studies,² parallel investigations featuring both the carbonium ion *per se* and also the covalent counterpart seemed advisable, in order that one could be certain that identified products did in fact evolve from the former system. Such studies were carried out in the parent tropylium ion case.

Irradiation of tropylium ion,³ as provided from tropylium fluoroborate,⁴ was carried out for 10 min in 5% (v/v) aqueous sulfuric acid with a Hanovia medium-pressure lamp equipped with a Vycor filter. Two major products were formed in 58% yield (based on unrecovered starting material): bicyclo[3.2.0]hepta-3,6-dien-2-ol (6) and the derived ether 7, both colorless



liquids partially insoluble in the irradiation medium. Treatment of ether 7 with dilute sulfuric acid induced

(1) E. E. van Tamelen and T. M. Cole, Jr., *J. Amer. Chem. Soc.*, **93**, 6158 (1971). For other information and publications from this laboratory, see ref 1-4 in this paper.

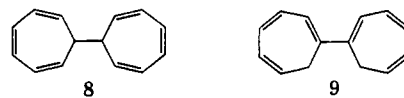
(2) See, e.g., E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *ibid.*, **93**, 6145 (1971).

(3) W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

(4) H. J. Dauben, F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *ibid.*, **79**, 4557 (1957).

formation of the parent alcohol 6, while the latter, in benzene at room temperature for some days, was converted to the former. The general structural character of the ether was established by mass spectral analysis, supplemented by other spectral behavior. Likewise, ir, uv, and nmr methods suggested the constitution of alcohol 6, which was confirmed by oxidation to the corresponding, known ketone, bicyclo[3.2.0]hepta-3,6-dien-2-one.⁵ No effort was made to determine the stereochemical nature of the alcohol and ether functions.

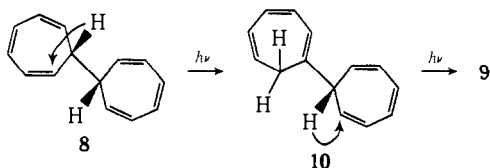
From all indications, photolysis of tropylium ion produces the valence bond isomer 4 (Dewar tropylium ion), a relatively simple allylic carbonium ion which readily captures solvent water, producing initially the bicyclic alcohol 6. That the bicyclic material in fact arises by irradiation of tropylium ion, and not the corresponding alcohol, is indicated first of all by the relative concentration of the two species. The equilibrium constant calculated for 5% aqueous sulfuric acid indicates an alcohol content of $2.7 \times 10^{-4}\%$, much too low to account for any detectable photochemical transformation of this covalent member. In support of the above, neither alcohol 6 nor ether 7 is apparently generated when irradiations were carried out on solutions made up by adding tropylium salt to ethanol or ethanol-water, without added acid, under which conditions the nearly exclusive species present is troyl ethyl ether (λ_{\max} 206 and 254 $m\mu$). After being photolyzed for 10-15 min, the starting material was almost all converted to a mixture of various products, which were isolated by extraction from a basified reaction medium and subjected to tlc separation. Hydrocarbon material consisted of a mixture of ditropyl (8) and its secondary irradiation product, "photoditropyl." After a 10-min initial photolysis, about 80% of the hydrocarbon portion consisted of ditropyl, whereas after a 3-hr irradiation, no ditropyl was left, and only the photoisomer could be detected. Ditropyl was identified by ir, uv, and melting point/mixture melting point ($59-60^\circ/58-60^\circ$) comparison with authentic material.⁶ Photoditropyl was secured as a very light yellow oil, reducible catalytically to bicycloheptyl. In the mass spectrum the



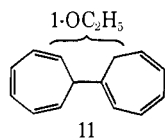
molecular ion appeared at 182, and in the uv λ_{\max} were located at 212, 264.5, and 339 $m\mu$ (ϵ 13,400, 3200, 7300). Main ir absorptions fell at 3005 (s), 2915 (m), 2835 (m), 1620 (w), 1580 (m), 1520 (ms), 1440 (s), 1370 (s), 1290 (s), 1260 (m), and 845 (ms) cm^{-1} . Structural assignment 9 is consistent with the above as well as the nmr properties (Figure 1): eight $\text{C}=\text{C}$ H's τ 3.6 (triplet) and 3.9 (two doublets); two $\text{C}=\text{C}$ H's τ 4.7 (quartet); two CH_2 's τ 7.45 and 7.7 (doublets). Thus hexaene 9 emerges as a reasonable photoproduct, formed from ditropyl by a twofold suprafacial 1,7-hydrogen migration, undoubtedly involving unsymmetrical isomer 10 as an intermediate. Further overall coupling was evidenced by formation of an ethoxylated ditropyl isomer in substantial amount. The general constitution of this material was indicated by M^+ 226

(5) P. R. Story and S. Fahrenholz, *ibid.*, **87**, 1623 (1965).

(6) W. von E. Doering and L. H. Knox, *ibid.*, **79**, 352 (1957).

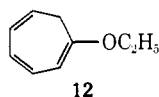


and maximal uv absorption at 229 and 258 m μ . In the nmr spectrum, signals appeared in the regions τ 3.4–3.6 (2 H), 3.6–4.2 (4 H), 4.6–5.0 (4 H), 6.0–6.4 (2 H), 7.2–7.6 (1 H), 7.8–8.3 (1 H), and 8.6–8.9 (4 H). Although these data are not sufficient to permit unique structural assignment, it is evident that the substance must conform to the type 11. There were observed, in



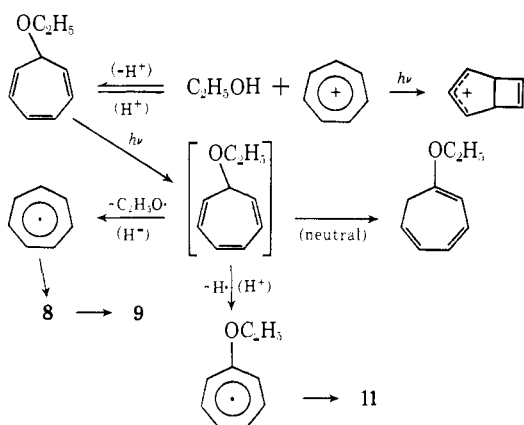
addition, tropryl ethyl ether and some troponoid material (unidentified) as products from the original reaction mixture. None of the aforementioned substances was formed detectably during irradiation of troprylium ion in 5% aqueous acid, and thus it seems certain that it is indeed troprylium ion *per se* that acts as a precursor of bicyclic alcohol 6 and ether 7.

Tropryl ethyl ether is reported to produce on irradiation in *neutral* alcoholic medium the isomer 12, also



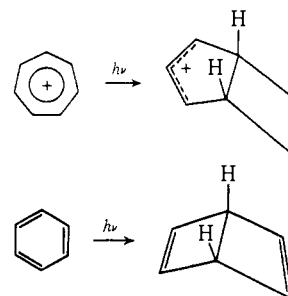
the result of a 1,7-hydrogen shift.⁷ In our reaction system, such a product, if formed, would be expected to afford the parent 3,5-dienone, unobserved in our experiments, but conceivably a precursor of tropone. Accepting provisionally that three pH- and/or solvent-dependent reaction courses are followed, one can rationalize the events by assuming that Dewar troprylium ion is generated directly from troprylium ion 3, whereas excited tropryl ethyl ether can undergo either an acid-catalyzed or noncatalyzed chemical change. From the nature of the products evolving in the acid-controlled reaction, it appears that tropryl radicals are formed and subsequently dimerize. From these considerations the tentative relationships shown in Chart I emerge.

Chart I

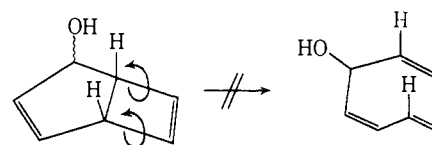


(7) G. W. Borden, O. L. Chapman, R. Swindell, and T. Tezuka, *J. Amer. Chem. Soc.*, 89, 2979 (1967).

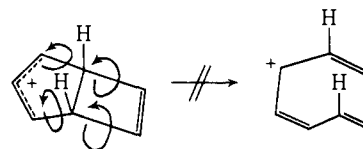
Troprylium ion, with its sextet of electrons in a cyclic system, possesses aromatic character and therefore might be expected to behave, on irradiation, similarly to the more traditional aromatic, benzenoid system. This appears to be the case, in that the conversion to the [3.2.0] skeleton parallels exactly the established isomerization of a benzenoid to a Dewar benzenoid.⁸ In the



latter reaction, the sequence of events is concluded by the appearance of stable, nonplanar bicyclo[2.2.0]hexadiene. In the troprylium series, solvation is superimposed, and a stable, nonplanar bicyclo[3.2.0]heptadienol results. It is possible that solvation of excited Dewar troprylium ion occurs, with the direct formation of observed ground-state product. Alternatively, formation of ground-state Dewar troprylium ion can be imagined, followed by normal interaction of allyl-carbonium ion with solvent to give final product. In either interpretation, the stability of ground-state products presents no problem, in that nonphotochemical isomerization to the cycloheptatrienyl system is disallowed by the Woodward–Hoffmann rules.⁹ The restrictions obviously apply to the bicycloheptadienol, a cyclobutene for which thermal conrotatory ring opening is not structurally possible. Similarly, ground-state



Dewar troprylium ion is restrained, for orbital symmetry reasons, from isomerization to troprylium ion, despite the potential energy gain implied. In this case, two dissimilar π - σ moieties are present, and seemingly can be

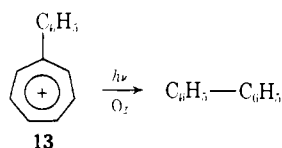


treated as functions independent of each other. One unit is the cyclobutene ring, subject to the reaction and structural constraints discussed for Dewar benzene. Furthermore, Woodward and Hoffmann have demonstrated that the pentadienyl cation–cyclopentenyl cation structure should be interconvertible thermally by conrotatory means, again signifying permitted change of the allylcarbonium ion portion of Dewar troprylium ion to a mono *trans*-troprylium ion, a structure of energy prohibited in the system under consideration.⁹

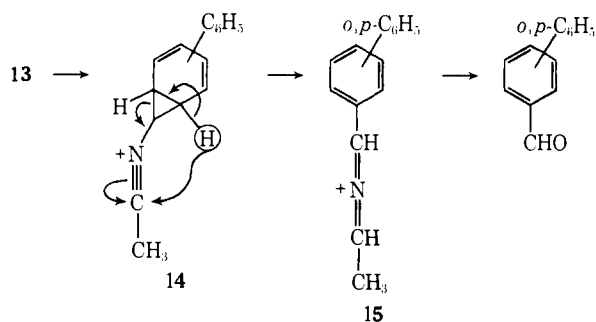
(8) E. E. van Tamelen and S. P. Pappas, *ibid.*, 84, 3789 (1962).

(9) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 797 (1969).

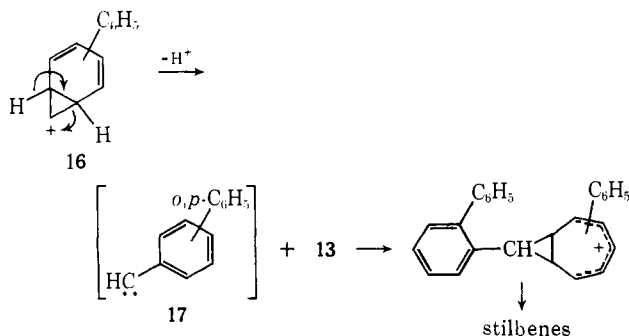
On irradiation, phenyltropylium ion **13** differs significantly from the parent aromatic. Photolysis under anaerobic conditions of a solution made up from phenyl tropylium fluoroborate in aqueous sulfuric acid led only to recovery of starting material. In the presence of oxygen, the aromatic ion was converted to biphenyl, known to be formed from **13** by the action of hydrogen



peroxide.¹⁰ In acetonitrile, light induces other changes. In the monomeric category, 2- and 4-phenylbenzaldehydes are formed, while coupling products are *cis*- and *trans*-2,2'-diphenylstilbenes. Structures of the latter pair were established by mass spectral analysis and by cleavage of the compounds to 2-phenylbenzoic acid, identical with an authentic specimen. Stereochemistry was assigned by nmr comparison of vinyl hydrogen chemical shifts with those observed for *cis*- and *trans*-stilbenes. The mechanisms by which these products are evolved are not clear, but may involve reaction of a norcaradiene, possibly produced either in a secondary, thermal reaction from vibrationally excited



phenyltropylium ion (formed from photoexcited **13**) or by photoexcitation of norcaradiene in *thermal* equilibrium with **13**. If solvent intervenes, there might be produced norcaradiene in which nitrogen is covalently bound (**14**); aromatization would then lead to progenitor **15** of the aldehyde product. Alternatively, if norcaradienyl cation **16** undergoes aromatization by proton

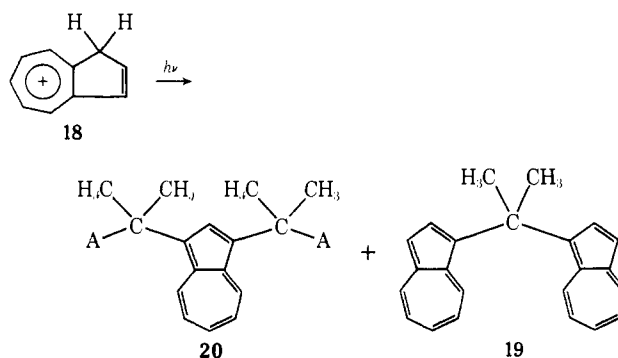


loss, as shown, carbene **17** becomes available for reaction, e.g., with ground-state **13** and ultimate conversion to observed stilbenes.

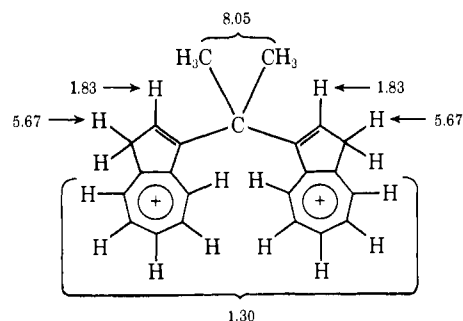
Azulenium ion **18** represents an interesting variation on the tropylium ion theme, and by reason of the double bond conjugated with the aromatic nucleus might be ex-

(10) C. Jutz and F. Voithenleiter, *Chem. Ber.*, 97, 29 (1964).

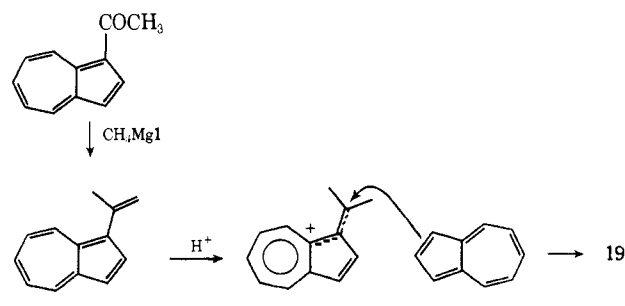
pected to display characteristically different chemical behavior on photolysis. Flash photolysis studies had already revealed formation of an excited state of greatly increased acidity.¹¹ Irradiation of azulenum cation in 50% (w/w) aqueous sulfuric acid solution, carried out with a Hanovia lamp and a Pyrex filter, resulted in the formation of two isolable products, assigned structures **19** and **20** (yields 11 and 7%, respectively), in addition to much polymer. Visible and ultraviolet light properties suggested early the azulenoic character of the photolysis products, and high-resolution mass spectral behavior revealed molecular weight as well as structural symmetry properties. The nmr spectrum of **19** in sulfuric acid was disarmingly simple: ten azulene (tro-



pylium) H's at τ 1.30; two azulene (olefinic) H's at 1.83; two CH_2 's at 5.67; and two CH_3 's at 8.05. As expected for azulenes, the photoproducts were soluble in



strong sulfuric acid, revealing the anticipated spectral changes. The structures suggested by the chemical and spectral data accumulated at this point were so surprising, in terms of derivation from starting material, that corroboration by synthesis was regarded as necessary. Toward that end, azulene and the known 1-isopropenylazulene (2:1 ratio) were treated with sulfuric acid in ether, with the result that hydrocarbon **19**,

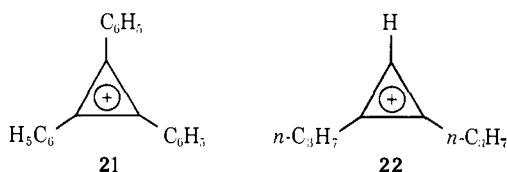


(11) K. H. Grellman, E. Heilbronner, P. Seiler, and A. Weller, *J. Amer. Chem. Soc.*, 90, 4238 (1968).

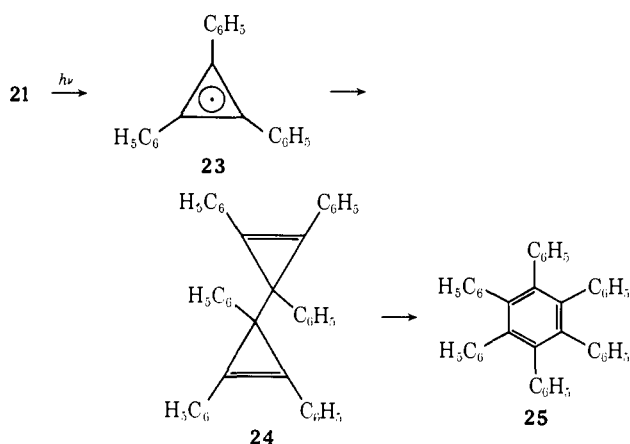
identical with the irradiation product, was secured in 27% yield (overall from 1-acetylazulene). In addition, traces of the triazulenyl derivative were formed, probably by interaction of diazulene **19** with protonated 1-isopropenylazulene.

Although the mechanism of this bizarre photoreaction is unknown, it was definitely determined that neither product **19** nor **20** could have been produced by dark reaction of acetone and azulonium ion under the conditions used in the photolysis. The precise source of the isopropylidene unit in **19** has not been determined, but since extraneous organic sources were apparently definitely excluded, the three-carbon unit must find its origin in the azulene system, presumably the five-membered ring moiety. However, no evidence for the fate of the remaining seven-carbon unit was forthcoming.

Despite its inability to valence bond isomerize, the cyclopropenium cation **1** seemed eminently worthy of photochemical study in that it is the simplest of the few stable, aromatic carbonium ion types available.¹² Two known cyclopropenium ion cases were selected for investigation, triphenylcyclopropenium ion **21** and di-*n*-propylcyclopropenium ion **22**.



A 4-hr photolysis of the triphenyl case **21** ($2.0 \times 10^{-3}\%$ covalent) in 10% aqueous sulfuric acid with a Hanovia lamp (Corex filter) gave hexaphenylbenzene (**25**) in 49% yield (92% yield, based on starting material consumed). Methanol-water-sulfuric acid or acetonitrile were even more suitable media for the irradiation, providing yields of **25** in the range 75–95%. The overall reaction is presumably initiated by charge transfer to produce cyclopropenyl radical **23**, which couples to the bisbicyclopropenyl **24**, the *in situ* pre-



cursor of final product by a reason of a second, ultra-violet-induced transformation. Subsequent to formation of radical **23**, the conversion to hexaphenylbenzene finds close analogy in previously recorded behavior.

(12) (a) R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Amer. Chem. Soc.*, **87**, 5139 (1965); (b) R. Breslow and H. W. Chang, *ibid.*, **83**, 2367 (1961); (c) R. Breslow, H. Hoever, and H. W. Chang, *ibid.*, **84**, 3168 (1962).

When generated by other means, *viz.* reduction with zinc of the cyclopropenyl cation **21**, radical **23** dimerizes irreversibly. It is also known that dimer **24** rearranges photochemically to hexaphenylbenzene, possibly *via* hexaphenylprismane as an unisolated intermediate.¹³

Attempts to induce photochemical reaction of di-*n*-propylcyclopropenium fluoroborate proved unsuccessful, either in aqueous acid or organic solvents, and with or without sensitizers. This failure accords with the calculated energy difference between parent cyclopropenyl cation and the corresponding radical, 1.00 β or 32 kcal/mol. By contrast, the difference between triphenylcyclopropenyl cations and triphenylcyclopropenyl radicals is 0.5 β , or 16 kcal/mol, based on calculated delocalization energies of the two species. Thus, ready excitation and conversion to radical **23** are reasonable in the triphenyl case **21**. In regard to the photostability of the di-*n*-propyl species, the primary reason may be lack of sufficiently low-lying excited states, thus accounting for lack of excitation with or without sensitizers.

In the aromatic carbanion series, such phenomena as hydrogen abstraction from solvent and enhanced basicity of excited states were detected, while no example of valence bond isomerization was uncovered.¹⁴ As described herein, valence bond isomerization of the aromatic tropylium system seemingly operates, while cyclopropenium ion is subject to electron-transfer reaction. Coupling phenomena are also in evidence in both studies, but not always as reactions of aromatic carbanion or carbonium ion systems *per se*. On the other hand, coupling as well as other chemical behavior is characteristic of excited triphenylcarbonium ion, a subject treated elsewhere.¹

Experimental Section

Nuclear magnetic resonance analyses (nmr) were made with a Varian A-60 NMR spectrometer, a Varian T-60 NMR spectrometer, or a Varian HA-100 NMR spectrometer at 35° unless otherwise indicated. Chemical shifts are given in τ units in parts per million with an internal reference of tetramethylsilane at τ 10.00. Infrared (ir) spectra were taken on a Perkin-Elmer 421 grating spectrophotometer or on a Perkin-Elmer 137 sodium chloride spectrophotometer employing 0.1-mm pathlength sodium chloride cavity cells. Ultraviolet (uv) spectra were taken on a Bausch and Lomb 505 spectrophotometer or on a Cary Model 14 recording spectrophotometer.

Melting points were taken on a Büchi melting point apparatus and are uncorrected. Analyses for carbon, hydrogen, and nitrogen were made by the Stanford Analytical Laboratory. Mass spectral analyses were carried out on an Atlas CH-4 mass spectrometer.

Analytical thin-layer chromatographic separations were carried out using Merck silica gel H on 5-cm glass plates or with Mallinckrodt ChromAR 500 silica gel-glass fiber matrix. Preparative scale separations were performed on 20 \times 20 cm glass plates using Merck silica gel GF₂₅₄, Merck silica gel HF₂₅₄, Merck silica gel HF₂₅₄ with Rhodamine 6G dye, or with Mallinckrodt ChromAR 1000 silica gel-fiber glass matrix. Analytical detections were made by means of iodine or uv fluorescence. Column chromatography separations were made using Grace desiccant silica gel with 15% by weight of water added.

General Procedures. Most photochemical reactions in these studies were carried out either in aqueous sulfuric acid or in aprotic organic solvents such as acetonitrile or methylene chloride, although acetic acid-water and dioxane-water systems were used when cationic species were not involved. Two separate photochemical reaction systems were used in these studies. The first employed a Rayonette low-pressure mercury lamp system (254 nm) surrounding quartz reaction vessels. The starting material was then irradiated under N₂ or argon for the desired period with air

(13) A. W. Krebs, *Angew. Chem., Int. Ed. Engl.*, **4**, 10 (1965).

(14) See ref 1, footnote 1.

cooling to maintain a temperature of 30–35°. In the second system a Pyrex reaction vessel was employed with a water-cooled quartz insert designed to hold a Hanovia 450-W medium-pressure lamp.

Irradiation of Tropylium Fluoroborate in 5% Sulfuric Acid. A solution of 1.00 (5.6 mmol) of tropylium fluoroborate was prepared in 500 ml of 5% (v/v) sulfuric acid–water, and the system was degassed with nitrogen. The resulting solution was then irradiated with a Hanovia medium-pressure lamp and Vycor filter for a period of 10 min. The water-insoluble material was extracted with ether, and the organic phase was dried (MgSO₄) and concentrated to yield 0.136 g (23%) of product. Tlc analysis with 1:4 chloroform–carbon tetrachloride solvent showed that only two components were present. Treatment of the aqueous phase with sodium hydroxide until basic and extraction with ether yields 0.321 g (58%) of a single product identified as ditropyl ether by comparison with authentic material (ir (neat) 3000, 2800, 1625, 1530, 1390, 1290, 1110 cm⁻¹). The total yield of photoproducts, based on unrecovered starting material, was 58%.

The two products were identified as bicyclo[3.2.0]hepta-3,6-dien-2-ol (6) and bis(bicyclo[3.2.0]hepta-3,6-dien-2-yl) ether (7) on the basis of spectral characteristics and chemical derivatives. Bicyclo[3.2.0]hepta-3,6-dien-2-ol possessed the following spectral properties: nmr (acetone-*d*₆) τ 3.48 (d, *J* = 3 Hz, 1 H, vinyl), 3.77 (d, *J* = 3 Hz, 1 H, vinyl), 3.88 (m, 1 H, vinyl), 4.22 (m, 1 H, vinyl), 5.49 (m, 1 H, HOCH=), 6.21 (m, 1 H, methyne), 6.75 (s, 1 H, -OH), 6.88 (m, 1 H, methyne); uv had no maxima above 220 nm; ir (CCl₄) 3325, 3115, 3040, 2925, 1603, 1553, 1345, 1310, 1275 cm⁻¹. The bis(bicyclo[3.2.0]hepta-3,6-dien-2-yl) ether was characterized by the following properties: mass spectrum (70 eV) *m/e* 198 (rel intensity 0.4), 91 (100.0); uv had no maxima above 220 nm; nmr (CDCl₃) τ 3.48 (d, *J* = 2.5 Hz, 2 H, vinyl), 3.78 (m, 4 H, vinyl), 4.12 (m, 2 H, vinyl), 5.52 (m, 2 H, HOCH=), 6.15 (m, 2 H, methyne), 6.68 (m, 2 H, methyne); ir (CCl₄) 3110, 3035, 2990, 2920, 1600, 1550, 1348, 1310, 1272 cm⁻¹.

Under similar conditions, but in the absence of added acid, completely different photolysis products were formed. Irradiations were carried out on solutions prepared by solution of tropylium bromide in ethanol, or in ethanol–water (10–20%). After 10–15-min irradiation, a dark green or brown solution with shoulders at 253–254 μ in the uv resulted. After being treated with 2 *N* aqueous sodium bicarbonate to neutralize, the reaction solution was extracted with petroleum ether (30–50°). After evaporation, the resulting dark yellow oil weighed approximately half that of the starting material. Tlc analysis (silica gel with CCl₄ or CCl₄–CHCl₃) showed the presence of four major, and as many as five minor, components. Preparative tlc was carried out with silica gel G or GF–CCl₄ or CCl₄–CHCl₃. The following description of components is taken up in the order of increasing polarity.

The least polar material was represented by a tlc spot, constituting a 5–15% yield of a mixture of ditropyl (8) and photoditropyl (9). After 10 min of original irradiation of the tropyli starting material, the mixture was composed of 80% ditropyl, whereas after a 3-hr photolysis, only photoditropyl was present in this fraction. By a combination of further tlc purification and crystallization, pure ditropyl (8) (mp 59–60°) was obtained from a mixture originally rich in this component. A mixture melting point with authentic ditropyl¹⁶ (mp 59–60°) was undepressed. Likewise, uv and ir spectra of product and authentic specimen were indistinguishable.

Photoditropyl was obtained as a very pale yellow oil from fractions resulting from prolonged original photolysis reactions. It exhibited mass, ir, uv, and nmr spectral properties detailed and discussed earlier in this article.

The material of next highest polarity was found to be principally the ethoxylated ditropyl isomer (10–20% yield) assigned the generalized structure 11 on the basis of spectral properties already presented. Isolation of the most nearly pure material was achieved by preparative tlc with CCl₄–cyclohexane. Very sensitive to acid, the ether in solution could be stored no longer than a few weeks in the refrigerator.

Products of greater polarity were revealed as two major and two minor components in a tlc (35–45% total yield), but did not yield to isolation and purification attempts.

Interconversion of Bis(bicyclo[3.2.0]hepta-3,6-dien-2-yl) Ether (7) to Bicyclo[3.2.0]hepta-3,6-dien-2-ol (6). A total of 0.056 g of bis(bicyclo[3.2.0]hepta-3,6-dien-2-yl) ether purified by tlc was dissolved in 1 ml of methanol and added to 100 ml of 5% (v/v) sulfuric acid–water. The mixture was shaken for 10 min, and the organic material was extracted into ether. The product was concentrated and fractionated by tlc with 2:1 carbon tetrachloride–chloroform. The fraction at the expected position for the alcohol was eluted

with methylene chloride, and analysis by ir showed that this product was indeed bicyclo[3.2.0]hepta-3,6-dien-2-ol.

A solution of 0.023 g of bicyclo[3.2.0]hepta-3,6-dien-2-ol was prepared in 5 ml of benzene and allowed to stand in the dark for 8 days. The product was concentrated and fractionated by tlc with 1:4 chloroform–carbon tetrachloride. The material corresponding to the expected ether was eluted with methylene chloride, and was confirmed to be bis(bicyclo[3.2.0]hepta-3,6-dien-2-yl) ether by comparison of the ir spectra.

Oxidation of Bicyclo[3.2.0]hepta-3,6-dien-2-ol (6) to Bicyclo[3.2.0]hepta-3,6-dien-2-one. A solution of 0.050 g of bicyclo[3.2.0]hepta-3,6-dien-2-ol in 50 ml of pentane was treated with 0.5 g of activated manganese dioxide, and the solution was stirred for 48 hr. Filtration and concentration of the product gave 0.040 g of material which was then fractionated by tlc with chloroform for 2 hr. The uv-active band was eluted with methylene chloride and concentrated to give 0.010 g of bicyclo[3.2.0]hepta-3,6-dien-2-one. Identification was made by comparison of the spectral properties with those of the authentic material:¹⁵ nmr (CCl₄) τ 2.45 (m, 1 H, vinyl), 3.47 (m, 1 H, vinyl), 3.62 (m, 1 H, vinyl), 3.99 (d, *J* = 6 Hz, 1 H, vinyl), 6.10 (m, 1 H, methyne), 6.60 (m, 1 H, methyne); ir (CCl₄) 3030, 2920, 1710, 1600, 1550, 1330, 1260 cm⁻¹.

Irradiation of Phenyltropylium Ion (13) in 3% Sulfuric Acid. A total of 0.30 g of phenyltropylium fluoroborate was dissolved in 285 ml of 3% (v/v) sulfuric acid–water and subsequently irradiated for 2 hr with a medium-pressure Hanovia lamp and Vycor filter. The system was then extracted with ether after neutralization with dilute sodium hydroxide, and the ether phase was dried and concentrated.

The product mixture was fractionated by tlc with chloroform solvent to yield two main products. The first (*R*_f 0.72) was identified as phenyltropylium ethyl ether, which was no doubt formed by reaction of the bis(phenyltropylium) ether with the ethanol in the chloroform, and was identified by comparison of the nmr spectrum with that of authentic material. The second product (*R*_f 0.84) was shown to be biphenyl by comparison of the nmr with that of authentic material¹⁸ and by mp 68–69° (lit. 69–70°).¹⁸

Irradiation of Phenyltropylium Ion (13) in Acetonitrile. A solution of 0.53 g of phenyltropylium fluoroborate in 200 ml of acetonitrile was prepared and degassed with argon. The system was subsequently irradiated with a Hanovia medium-pressure lamp and Pyrex filter for 2.5 hr. The product was concentrated to 25 ml and extracted with aqueous sodium chloride solution and ether to remove the fluoroborate residues. The resulting system was dried (MgSO₄) and concentrated.

The product was fractionated on tlc with petroleum ether to yield two easily separable components and several less easily separable fractions. The first two components were identified as 2-phenylbenzaldehyde and 4-phenylbenzaldehyde 3:1 by comparison of the nmr spectra with those of authentic samples.

Of the other products, two major components were easily separable and purified by repeated tlc. These substances were analyzed by mass spectral means and shown to have molecular weights of 332. Cleavage of both these products with potassium permanganate–sodium periodate in neutral solution yielded pure 2-phenylbenzoic acid, which was identified by nmr comparison with authentic material. The less polar tlc component was assigned the *cis* configuration by comparison of the vinyl hydrogens (τ 3.68) with those of *cis*-stilbene (τ 3.45). Nmr analysis of the remaining products in their crude state indicated that there are probably also other isomers of diphenylstilbene, but absolute identification was not made.

Irradiation of Azulonium Ion 18. A solution of 0.35 g of azulene was prepared in 200 ml of 50% (w/w) sulfuric acid–water and degassed with argon. This solution was irradiated with a Hanovia medium-pressure lamp (Pyrex filter) for 4 hr. The product was poured into 1 l. of water and extracted with ether and then chloroform. The organic phase was collected, dried (MgSO₄), and concentrated. Continuous tlc gave three major components.

The first product was obtained in a yield of 0.049 g (14%) and was identified as azulene by comparison of the nmr with that of authentic material. The second product was identified as 2,2-bis(1-azulenyl)propane (20) by evaluation of the spectral and analytical data and the properties of the material in sulfuric acid:

(15) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "High Resolution NMR Spectra Catalog," National Press, New York, N. Y., 1962, no. 289.

(16) W. H. Zartman and H. Adkins, *J. Amer. Chem. Soc.*, **54**, 3398 (1932).

mass spectrum (70 eV) m/e 296.1514 (rel intensity 44.6) $C_{23}H_{20}$, 281.1233 (100.0) $C_{22}H_{17}$, 265.0994 (34.0) $C_{21}H_{13}$, 152.0610 (11.1) $C_{12}H_8$, 128.0610 (13.0) $C_{10}H_6$; metastable peak 252 (transition 279 – 265), 263 (296 – 279), 266.5 (296 – 281), 277 (281 – 279); nmr (CCl_4) τ 1.92 (d, $J = 4$ Hz, 2 H), 1.92 (d, $J = 9$ Hz, 2 H), 2.52 (d, $J = 10$ Hz, 2 H), 2.75 (d, $J = 4$ Hz, 2 H), 2.85 (t, $J = 10$ Hz, 2 H), 3.20 (t, $J = 9$ Hz, 2 H), 3.57 (t, $J = 10$ Hz, 2 H), 7.99 (s, 6 H, $-CH_3$); uv max 238 nm ($\log \epsilon$ 4.47), 276 (4.81), 607 (2.72); ir 1570, 1450, 1390 cm^{-1} .

This product could be dissolved in concentrated sulfuric acid and recovered quantitatively by dilution and extraction with ether. However, prolonged treatment with 50% (w/w) sulfuric acid–water resulted in decomposition of the material. Spectral studies in sulfuric acid indicated the strong similarity to azulene: nmr (H_2SO_4) τ (m, 10 H, 1.30 troyl), 1.83 (s, 2 H, $=CH-$), 5.67 (s, 4 H, $-CH_2-$), 8.05 (s, 6 H, $-CH_3$); uv (H_2SO_4) max 222 nm ($\log \epsilon$ 3.42), 263 (3.43), 357 (3.18).

Azulene itself had the following spectral properties: nmr ($CDCl_3$) τ 1.68 (d, $J = 9$ Hz, 2 H), 2.08 (t, $J = 4$ Hz, 1 H), 2.43 (t, $J = 10$ Hz, 1 H), 2.61 (d, $J = 4$ Hz, 2 H), 2.89 (t, $J = 9$ Hz, 2 H); uv max 274 nm ($\log \epsilon$ 4.79), 340 (3.67), 579 (2.51), 632 (2.51). Azulene in sulfuric acid possessed the following spectral properties: nmr (H_2SO_4) τ 1.09 (m, 5 H, troyl), 2.02 (1 H, vinyl), 2.38 (1 H, vinyl), 5.74 (2 H, $-CH_2-$); uv (H_2SO_4) max 220 nm ($\log \epsilon$ 3.07), 258 (3.26), 351 (2.95).

The third product was tentatively identified as 1,3-bis[1-methyl-1-(1-azulenyl)ethyl]azulene on the basis of the similarity of the nmr, mass spectral, and infrared spectral data to that of 2,2-bis(1-azulenyl)propane: mass spectrum (70 eV) m/e 464 ($C_{36}H_{32}$); ir 1565, 1445, 1385 cm^{-1} ; nmr (CCl_4) τ 1.62 (s, 1 H), 1.89 (d, $J = 4$ Hz, 2 H), 1.88 (d, $J = 10$ Hz, 2 H), 2.28 (d, $J = 9$ Hz, 2 H), 2.58 (d, $J = 10$ Hz, 2 H), 2.73 (d, $J = 4$ Hz, 2 H), 2.84 (t, $J = 9$ Hz, 2 H), 3.09 (t, $J = 9$ Hz, 1 H), 3.14 (t, $J = 10$ Hz, 2 H), 3.42 (t, $J = 9$ Hz, 2 H), 3.75 (t, $J = 10$ Hz, 2 H), 7.89 (s, 12 H); uv (EtOH) max 240 nm ($\log \epsilon$ 4.30), 278 (4.63), 608 (2.56).

Attempted Dark Reaction of Acetone and Azulene with 10% Sulfuric Acid. A total of 0.015 g of azulene was dissolved in 30 ml of ether and stirred with an equal volume of 10% sulfuric acid and 0.3 ml of acetone for 24 hr. Tlc of the product showed only the presence of azulene; no condensation products were noted. Confirmation of the identity of azulene was made by nmr means.

Similarly, a solution of 0.010 g of azulene was prepared in 100 ml of 50% (w/w) sulfuric acid–water, and 0.1 ml of acetone was introduced. The system was allowed to stand for 3 hr, and the product was isolated by dilution and extraction with ether as in the photolysis work-up procedure. No material other than azulene was noted by TLC, and nmr analysis confirmed the presence of azulene and the absence of any other product.

Synthesis of 2,2-Bis(1-azulenyl)propane (20). First, 1-acetylazulene was synthesized by the method of Hafner.¹⁷ This product was dissolved in ether and added to 1.0 mmol of methylmagnesium iodide in ether. The resulting system was hydrolyzed with saturated ammonium chloride solution and concentrated to give 0.0194 g (74% based on unrecovered azulene) of 1-isopropenylazulene.

A total of 0.0097 g of 1-isopropenylazulene and 0.020 g of azulene was dissolved in 10 ml of ether. This system was treated with 0.2 ml of sulfuric acid and stirred for 10 min. The product was extracted with water, and after ether extraction, 0.015 g of azulene was removed by sublimation. The residue was fractionated on TLC with a carbon tetrachloride solvent to give 0.004 g (23%) of 2,2-bis(1-azulenyl)propane, which was identical by nmr with the photoproduct attributed structure 20. A second component of 0.001 g (7.5%) was isolated which was identical with the material attributed the structure 1,3-bis[1-methyl-1-(1-azulenyl)ethyl]azulene by TLC.

Irradiation of Triphenylcyclopropenium Ion 21 in Aqueous Sulfuric Acid. A solution of 0.175 g of triphenylcyclopropenyl bromide in 0.5 l. of 10% (v/v) sulfuric acid–water was prepared and purged with nitrogen. This solution was then irradiated with a Hanovia medium-pressure lamp and Corex filter for a period of 4 hr. The product solution was isolated by repeated benzene extraction. The material resulting from the concentration of the benzene was treated with a small amount of ethanol to dissolve any extraneous material, and the residue was freed of solvent under vacuum to yield 0.066 g (49%) of hexaphenylbenzene. Isolation of the ethanol-soluble fraction yielded 0.068 g of triphenylcyclopropenyl ethyl ether (43%), which was identical with an authentic sample prepared from ethanolic sodium hydroxide and triphenylcyclopropenyl bromide: nmr ($CDCl_3$) τ 2.3–3.0 (m, 15 H, aromatic), 6.43 (q, $J = 7$ Hz, 2 H, OCH_2-), 8.85 (t, $J = 7$ Hz, 3 H, $-CH_3$).

The yield of hexaphenylbenzene, taking into account recovered starting material in the form of the ethyl ether, is 86%. Hexaphenylbenzene was identified by comparison of spectra with those of authentic material prepared by the condensation of tetraphenylcyclopentadienone with diphenylacetylene and thermal decarbonylation:¹⁸ uv max ($CHCl_3$) 249 nm ($\log \epsilon$ 4.48); ir 3080, 3060, 3025, 1601, 1496, 1443, 1402 cm^{-1} .

Anal. Calcd for $C_{42}H_{30}$: C, 94.38; H, 5.62. Found: C, 93.75; H, 5.74.

Irradiation of Triphenylcyclopropenium Ion 21 in Methanol–Sulfuric Acid–Water Solution. A solution of 0.150 g of triphenylcyclopropenyl bromide was prepared in 300 ml of 10% sulfuric acid, 40% water, 50% methanol (by volume) solution. This solution was degassed with nitrogen and irradiated with a Hanovia medium-pressure lamp and Corex filter for 40 min. The reaction gave 0.085 g (75%) of hexaphenylbenzene which was identified by comparison of the ir with that of authentic material. The product was isolated by concentration of the solution and collection of the solid by filtration.

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