Photolysis of Cyclopentadienide and Cyclopentadiene

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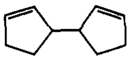
Abstract: In the first study of product formation from an excited carbanionic species, sodium cyclopentadienide in *tert*-butyl alcohol–tetrahydrofuran was found on ultraviolet irradiation to produce small yields of *meso*- and *dl*-3-(3′-cyclopentenyl)cyclopentenes (**2a, b**). Mechanistic studies suggest that these two products are formed from cyclopentenyl radicals, produced by protonation of radical anions generated by abstraction of hydroxylic hydrogen atoms of *tert*-butyl alcohol by excited cyclopentadienide. Ultraviolet irradiation of cyclopentadiene in neutral or weakly basic alcoholic solution leads to formation of the valence bond isomer, bicyclo[2.1.0]pent-2-ene (**4**), the smallest known unsaturated polycyclic hydrocarbon. The new isomer was characterized spectrally and was observed to undergo: (1) diimide reduction to bicyclo[2.1.0]pentane, (2) a Diels–Alder reaction with cyclopentadiene, and (3) thermal isomerization to cyclopentadiene. Theoretical aspects are discussed.

Despite the great variety and considerable number of organic substances which have been subjected to photochemical investigation, there have appeared no reports on the nature of products formed during ultraviolet irradiation of carbanions, a well-known and useful species in organic chemistry. In initiating work in this area, we have concentrated our attention thus far on the behavior of excited carbanions of the aromatic type, partly because of (1) their high order of ground-state stability and (2) the presence of chromophores well suited for irradiation and possible conversion to valance bond isomeric systems or other interesting products. The first true anionic case to be studied was cyclopentadienide (**1**).[1]

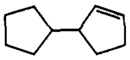
1

Since the planning of experimental details had in this study distinct ramifications in the entire body of chemistry which developed, we comment first on the reasons for selecting certain procedures used. In the absence of a proton source, the immediate product deriving from excited cyclopentadienide would likely be in itself a carbanion, probably corresponding to an acid considerably weaker than the original cyclopentadiene. In order to trap the anionic photoproduct and thereby forestall reversion to cyclopentadienide or formation of some still different transformation product, protonation immediately following chemical reaction of the excited cyclopentadienide seemed desirable. However, inclusion of an acid of the strength appropriate to ensure such protonation complicates the irradiation system in the sense that the presence of some amount of cyclopentadiene in equilibrium with the anion might now be permitted, with resultant ambiguity as to the true source of isolated final products. In order to remove absolutely such doubts, identification of products from *both* hydrocarbon and derived carbanion was made, the photoreactions being carried out under conditions closely similar, except for level of basicity. In consequence, not only were products definitely derived from excited anion isolated, but also formation of a novel valence bond isomer was shown to be a result of cyclopentadiene irradiation under the particular conditions used in these studies.

The ultraviolet irradiation of sodium cyclopentadienide in 20% *tert*-butyl alcohol–80% tetrahydrofuran gave in approximately 5% total yield equal amounts of the *meso*- and *dl*-3-(3′-cyclopentenyl)cyclopentenes (**2a, b**) (identified by vpc, nmr, and mass spectral comparison with authentic specimens).[2] The photolysis was carried out with a Hanovia quartz immersion well apparatus fitted with a 450-W Hanovia high-pressure mercury arc lamp. After completion of the reaction, volatile materials were analyzed by vpc methods, and nonvolatile products by column chromatography. In addition to the dicyclopentenyls, small amounts of unidentified colored hydrocarbons as well as considerable polymeric material were formed. Bicyclo[2.1.0]pent-2-ene (**4**) was not formed under these conditions; however, when excess cyclopentadiene was present, bicyclopentene was produced. Light transmission of the solution decreased rapidly during photolysis as a dark color developed, and the irradiated solution became dark brown on exposure to air or water. None of these substances was observed after work-up of the unirradiated solution of the anion.



2a, b
meso and *d, l*



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Carbon skeletons of the 3,3′-dicyclopentenyls were established by catalytic hydrogenation and diimide reduction to dicyclopentyl. The degree of unsaturation was found by mass spectral analysis of each photoproduct and of the dicyclopentyl-d_4 obtained by deuteriodiimide reduction. The mass spectra of photoproduct **2a** and **2b** were identical, with the major fragment having a mass of 67. Controlled diimide reduction of the mixture of photoproducts resulted in a single partial reduction product, 3-cyclopentylcyclopentene (**3**). The photoproducts **2a** and **b** exhibited only end absorption

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[1] Preliminary communications: (a) E. E. van Tamelen, L. E. Ellis, and J. I. Brauman, *J. Amer. Chem. Soc*, **89**, 5073 (1967); (b) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *ibid.*, **88**, 846 (1966).

[2] For our purposes, authentic *meso*- and *dl*-3-(3′-dicyclopentenyl)-cyclopentene were prepared by Grignard coupling of 3-chlorocyclopentene. The hydrocarbons were obtained previously by the benzophenone-sensitized photolysis of cyclopentene, presumed to generate cyclopentenyl radicals which couple to observed products: K. S. Sidhu, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, 44, 531 (1966). The configurational assignments suggested by these authors are opposite to those proposed herein.

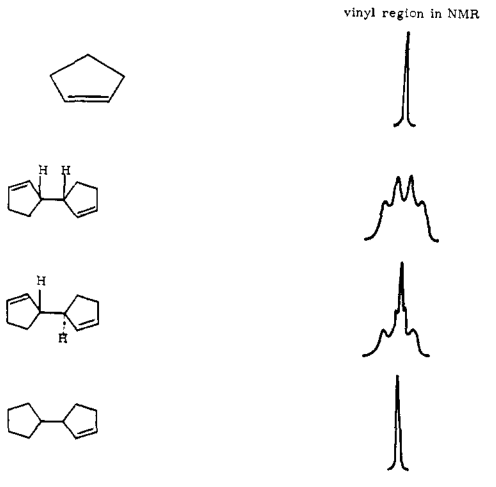
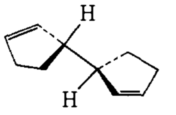


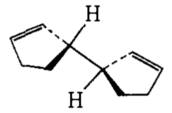
Figure 1.

in the ultraviolet, and the following peaks appeared in the nmr spectra: olefinic, δ 5.65 (4 H); methineallylic, 2.68 (2 H); allylic, 2.26 (4 H); and methylene, 1.2–2.0 (4 H). Nmr spectra of the photoproducts are identical except for fine splitting in the olefinic region. Significantly, the olefinic splitting of one isomer (**2a**) resembles that of the partial reduction product **3** (Figure 1).

In terms of the most favorable conformations (**2a**, **b**), the environment of the olefinic hydrogens of *meso*-3-(3′-dicyclopentenyl)cyclopentene, in which the double bonds lie on opposite sides of the molecule, resembles the environment of the olefinic hydrogens in **3**. On the basis of this argument, compound **2a** is the meso isomer. In the most stable conformation of the *d,l* isomer, the double bonds reside on the same side of the molecule (**2b**), and it is reasonable that because of their proximity the double bonds of the *d,l* isomer would exert greater influence on each other than those of the meso isomer. Thus **2b**, exhibiting greater olefinic fine splitting, is assigned the *d,l* configuration.



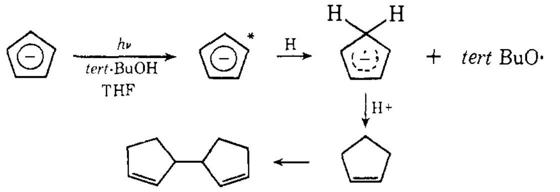
2a



2b

That of all possible dimeric photoproducts only these dicyclopentenyls are produced, and in equal amounts, suggests that the final step in product formation is coupling of cyclopentenyl radicals, perhaps produced *via* hydrogen abstraction by photoexcited cyclopentadienide to give an anion radical which is then protonated (Scheme I). Since the photochemical event occurring

Scheme I



2 (*meso* and *d, l*)

with cyclopentadiene in neutral or less basic solution differs entirely from that observed under the present, more strongly basic, conditions cyclopentadienide *per se* must be involved in conversion to the dicyclopentenyls.

In a series of experiments, the reaction medium was varied in order to elucidate the mechanism of product formation. Yields of **2a** and **b** are not enhanced when a 50:50 mixture of cyclopentadiene and cyclopentadienide is photolyzed; thus neither ground- nor excited-state cyclopentadiene is implicated in the reaction, nor are the yields enhanced when cyclopentadienide is photolyzed in the presence of cyclopentene. Furthermore, the photoproducts are not produced when *tert*-butyl alcohol is absent from a THF–sodium cyclopentadienide photolysis solution or when cyclopentadienide is absent from a THF–*tert*-butyl alcohol–cyclopentadiene photolysis solution. Photolysis of a more dilute solution of cyclopentadienide (0.03 *M*) gave reduced amounts of photoproducts. Finally, in an experiment designed to locate the source of the abstracted hydrogen atom, all exchangeable protons in the reaction system were replaced by deuterium. Perdeuteriocyclopentadienide was prepared from perdeuteriocyclopentadiene and photolyzed in the presence of 20% *tert*-butyl alcohol-O-*d*. The 3,3′-dicyclopentenyls obtained in this experiment were shown by mass spectral analysis to be perdeuterated (it was demonstrated by mass spectral analysis that photoproducts **2a** and **2b** were not subject to deuterium exchange on treatment with potassium *tert*-butoxide in *tert*-butyl alcohol-O-*d*). Since the 3,3′-dicyclopentenyls obtained in this experiment were shown by mass spectral analysis to be perdeuterated, it follows that, in the nonisotopic reaction, the hydrogen atom comes from an exchangeable proton position. Thus photoexcited cyclopentadienide is not abstracting hydrogen atoms from solvent in the customary fashion (*i.e.*, from the methyl groups of *tert*-butyl alcohol or from the α-methylenes of tetrahydrofuran). Abstraction of the hydrogen atom bonded to oxygen would not be expected on the basis of bond strengths. However, there is sufficient energy available from photoexcitation for this reaction, and this hydroxylic hydrogen may well be in an optimal position for abstraction. Close association in the ground state between exchangeable protons and cyclopentadienide may be favored because of either hydrogen bonding or solvation of sodium ions, which in turn are associated with cyclopentadienide. Thus, abstraction of hydrogen atoms from the hydroxyl position of *tert*-butyl alcohol, heretofore an unobserved photochemical event, is a possible explanation for the experimental observations.

A second, conceivable hydrogen atom source is ground-state cyclopentadiene. The abstraction by photoexcited cyclopentadienide of a hydrogen atom from ground-state cyclopentadiene would, again, generate a cyclopentadienyl radical anion and, on protonation, a cyclopentenyl radical. This pathway would be expected to lead to some dimeric products with a cyclopentadiene moiety; however, only dimers with a total of two olefinic bonds have been observed. Also, since photolysis in the presence of excess cyclopentadiene does not enhance the yield of dimeric photoproducts, this mechanism is not probable. Another pathway for the formation of perdeuterated cyclopentenyl radicals would involve electron transfer from photoexcited cyclopentadienide to ground-state cyclopentadienide or electron transfer in the reverse direction. Such a process would generate a cyclopentadienyl radical and a cyclopentadienyl dianion radical, which would become

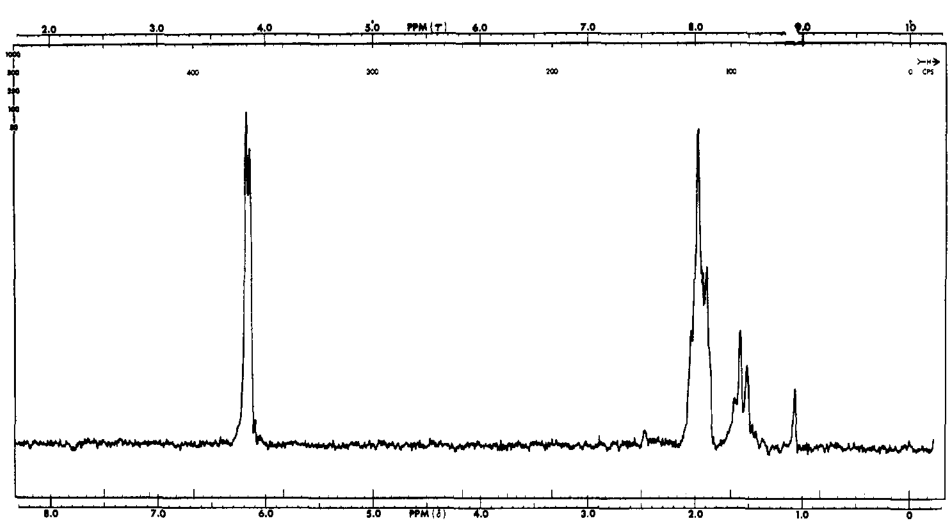


Figure 2. Nmr spectrum of bicyclo[2.1.0]pent-2-ene.

a perdeuterated cyclopentenyl radical on protonation by *tert*-butyl alcohol-O-*d*. This pathway, too, would be expected to lead to some dimers having more than two olefinic bonds because of the cyclopentadienyl radical generated initially. It is possible, however, that cyclopentadienyl radicals react to form other, unstable products. Of the three reaction mechanisms considered for formation of the 3,3′-dicyclopentenyls, the pathway which appears to be most consistent with the data is that which involves abstraction of a hydrogen atom from the hydroxyl position of *tert*-butyl alcohol.

The bicyclo[2.1.0]pent-2-ene system, in the past generally considered too unstable to exist independently, has been postulated as an intermediate in a number of reactions from which cyclopentadienes have been isolated.[3a-d] Barton reported in 1959 that attempted preparation of parent bicyclo[2.1.0]pent-2-ene (**4**) by ultraviolet irradiation of cyclopentadiene was unsuccessful because of rapid dimerization to dicyclopentadiene.[4] Hammond and Turro later observed that sensitized ultraviolet irradiation of cyclopentadiene produced equal amounts of three dimers: *endo*-dicyclopentadiene, *exo*-dicyclopentadiene, and *trans*[3.0.3.0]tricyclo-2,8-decadiene (**5**).[5] Our own endeavors in this area have been rewarded by the successful preparation, isolation, and identification of bicyclo[2.1.0]pent-2-ene ("homocyclobutadiene") (**4**).[1b] The new hydrocarbon, a valence bond isomer of cyclopentadiene, is the smallest unsaturated polycyclic hydrocarbon yet secured in the organic laboratory.

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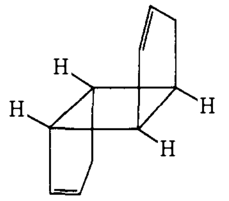

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Ultraviolet irradiation of cyclopentadiene in either neutral or mildly basic ethanol results in the generation of bicyclo[2.1.0]pent-2-ene (**4**). One of the more satisfactory preparations involves the 3-hr photolysis (450-W Hanovia high-pressure mercury arc lamp) of a 170-ml portion of a 0.3 *M* ice-cooled solution of cyclopentadiene in ethanol, under which circumstances as high as 15% of the starting material is converted to the bicyclopentene. The unstable photoproduct, isolated by vpc and conveniently stored at −78°, is a volatile colorless liquid with a distinctive penetrating odor. Photochemical formation of the bicycle from cyclopentadiene is not a naphthalene- or benzophenone-sensitized process.

The mass spectrum of the photohydrocarbon, similar to that of cyclopentadiene, reveals a molecular ion at 66 and major fragments at 65, 40, and 39. The nmr spectrum exhibits a slightly split olefinic hydrogen peak at δ 6.10–6.30 (2.0 H), a complex envelope at 1.90–2.17 (3.1 H), and a complex multiplet at 1.45–1.75 (1.1 H) (Figure 2). In the ultraviolet spectrum, there appears strong end absorption (ϵ_{210} 1600), in addition to peak absorption at 232 (ϵ_{max} 1000) and 245 mμ (ϵ_{max} 900), with tailing out to 290 mμ (Figure 3). The nmr spectrum of the photohydrocarbon (Figure 2) is in agreement with the proposed structure. The slightly split olefinic hydrogen peak compares favorably with that in cyclobutene (δ 5.97, $J = \mp 0.2$ Hz).[6] As expected, the splitting exhibited by the methine and (nonequivalent) cyclopropyl methylene hydrogens is extensive. The marked downfield shift of the cyclopropyl methylene hydrogens, one of which overlaps with the methine hydrogens, is consistent with trends noticeable in bicyclo[2.1.0]pentane and certain vinylcyclopropanes.[7] With reference to the ultraviolet spectrum, the cyclopropyl group is well known to exert conjugative effects intermediate between the hyperconjugation of alkyl groups and the true conjugation of the vinyl group (vinylcyclopropane, λ_{max} 210 mμ;[8a] cyclopropylbenzenes, λ_{max} 258 mμ;[8b] bicyclo-

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(3) (a) E. H. Farmer, C. K. Ingold, and J. F. Thorpe, *J Chem. Soc.*, **121**, 128 (1922); (b) L. Skattebøl, *Chem. Ind.* (*London*), 2146 (1926); (c) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **1**, 519 (1962); (d) P. M. Maitlis and M. L. Games, *J. Amer. Chem. Soc.*, **85**, 1887 (1963).

(4) D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959).

(5) N. J. Turro and G. S. Hammond, *J. Amer. Chem. Soc.*, **84**, 2841 (1962).

(6) K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).

(7) (a) W. v. E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963); (b) D. Forbess, Ph.D. Dissertation, Stanford University, 1965.

(8) (a) A. I. Scott, "Interpretations of Ultraviolet Spectra of Natural Products," Pergamon Press New York N. Y., 1964; (b) A. L. Goodman and R. H. Eastman, *J. Amer. Chem. Soc.*, **86**, 908 (1964).

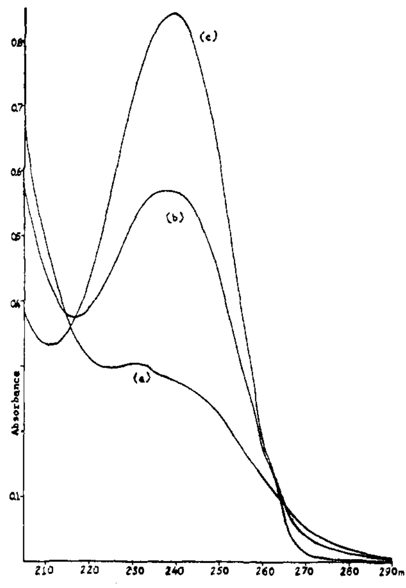
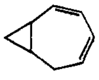


Figure 3. Ultraviolet spectra of bicyclo[2.1.0]pent-2-ene isomerizing to cyclopentadiene: (a) initial spectrum; (b) spectrum after 16 hr; (c) spectrum after 60 hr at room temperature.

[5.1.0]octa-2,4-diene (**6**), λ_{max} 258 mμ;[7a] bicyclo[5.1.0]-octa-2,5-diene (**7**) does not absorb above 215 mμ[7a]).



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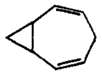

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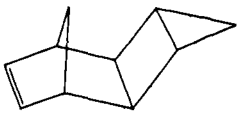
Diimide reduction[9a] of bicyclopentene (**4**) gave a nearly quantitative yield of bicyclo[2.1.0]pentane (**8**), identical with authentic bicyclo[2.1.0]pentane prepared by pyrolysis of 1,3-diazocyclopentane according to a procedure originally described by Criegee.[9b] The Diels–Alder adduct **9** of bicyclopentene and cyclopentadiene was isolated from the original photolysis solution and its structure assigned by spectral means.[10] The mass spectrum featured a molecular ion peak at 132. The nmr spectrum exhibited a triplet at δ 6.17 (2 H, olefinic), a complex multiplet at 2.6–3.0 (2 H), a complex multiplet at 1.9–2.2 (2 H), a complex envelope in the range 1.0–1.8 (4 H), and a complex multiplet at 0.6–0.9 (2 H, cyclopropyl). The hydrocarbon **9** was found to be a secondary thermolysis product of bicyclopentene (**4**) (cyclopentadiene is the primary thermolysis product) by following the change in the nmr spectrum of bicyclopentene with time.

8

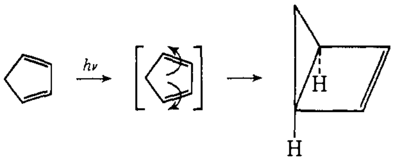


9, stereochemistry uncertain

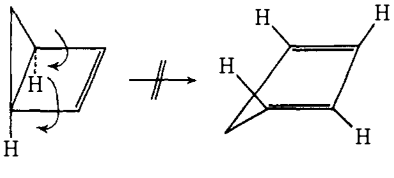
Bicyclopentane undergoes facile thermal isomerization to cyclopentadiene. The rates of isomerization, carried out in dilute heptane solutions in order to minimize the Diels–Alder reaction, were found to be about twice as fast as those in the gas phase.[11] The half-life for isomerization of bicyclopentene is 4 hr at 34° (in the presence of cyclopentadiene, the compound disappears faster because of the Diels–Alder reaction).

Conversion of excited cyclopentadiene to the valence bond isomer, bicyclopentene, appears to be a simple example of a well-known photoinduced 1,3-diene reaction subject to control by the Woodward–Hoffmann rules.[12] Because of the geometrical restrictions imposed by the cisoid nature of the [2.1.0] skeleton present in the product, the reaction must proceed in a disrotary fashion, the course anticipated for ring closure of 1,3-diene to cyclobutene. Although on irradiation 1,3-cyclohexadienes are subject to either cyclobutene ring closure or ring opening to 1,3,5-trienes, cyclopentadiene cannot undergo the latter type change, and, like 1,3-cycloheptadiene and 1,3-cyclooctadiene, is converted to cyclobutene.

In our experiments, carried out in the absence of added sensitizers, formation of photodimers could not be detected. In the general case of olefins, direct intersystem crossing is forbidden and thus, in the absence of a sensitizer, conversion to the triplet of the singlet formed by direct excitation is not possible.[13] Thus the cyclopentadiene → bicyclopentene transformation is probably a singlet process. In agreement with this interpretation, bicyclopentene apparently is not formed in the presence of sensitizers, and the isomerization reaction is insensitive to the presence of oxygen, a known triplet quencher.[14] In contrast to most cyclobutenes, bicyclopentene absorbs significantly in regions easily accessible to the ultraviolet frequencies used in our experiments, and thus a photoequilibrium between cyclopentadiene and bicyclopentene emerges as a sensible, but as yet untested, possibility.



The observed facile thermal isomerization of bicyclopentene to cyclopentadiene cannot occur by the electronically preferred conrotary process since an impossibly strained cis,trans ground-state product would necessarily result. Presumably because of the considerably internal strain present, the bicycle is forced into



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[9] (a) Review: S. Hünig, H. R. Müller, and W. Thier, *Angew. Chem., Int. Ed. Engl.*, 4, 271 (1965); (b) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

[10] The independent preparation and spectral analysis of Diels–Alder adduct **9** were reported recently by J. E. Baldwin and R. K. Pinschmidt, Jr., *J. Amer. Chem. Soc.*, 92, 5247 (1970). The microwave spectrum of bicyclopentene itself has been determined by S. L. Hsu, A. H. Andrist, T. D. Gierke, R. C. Benson, and W. H. Flygare, *ibid.*, 92, 5250 (1970).

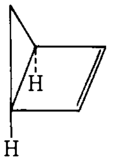
[11] J. I. Brauman and D. M. Golden, *ibid.*, **90**, 1920 (1968); D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969). Faster solution rates have been observed previously for reactions of similar compounds.

[12] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 87, 395 (1965).

[13] For a review of the photochemistry of dienes, see: W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

[14] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 117.

isomerization and thereby circumvention of the orbital symmetry requirements which normally control thermal ring-opening reactions of this type. It is undoubtedly true that whatever thermal stability bicyclopentene does possess is due to inhibition of simple isomerization by orbital constraints implied by electrocyclic theory.[15]



Experimental Section

Melting points were taken on a Büchi capillary tube melting point apparatus or a Reichart microscope hot stage and are uncorrected. Infrared (ir) spectra were obtained on a Perkin-Elmer 137 sodium chloride spectrophotometer or a Perkin-Elmer 421 grating spectrophotometer. Ultraviolet (uv) spectra were measured on a Bausch and Lomb spectronic 505 or Cary Model 14M spectrophotometer. Nuclear magnetic resonance (nmr) spectra were taken on a Varian A-60 spectrometer or a Varian HR-100 spectrometer in carbon tetrachloride with tetramethylsilane as an internal reference. Chemical shifts are given as δ in parts per million relative to tetramethylsilane at δ 0.00. Mass spectra were taken on a CEC 103-C mass spectrometer or an Atlas CH-4 mass spectrometer.

For vapor phase chromatography (vpc) a Perkin-Elmer Model 154D vapor fractometer (thermal conductivity detection with helium as carried gas) was used. Analytical thin layer chromatography (tlc) was carried out with Merck silica gel H using iodine for compound detection, while for preparative tlc Merck silica gel GF$_{254}$, 1 mm thick, using petroleum ether as eluent and uv light for compound detection, was used. Column chromatography was done on neutral aluminum oxide (Merck) using 30–60° petroleum ether as eluent.

Photolysis of Cyclopentadiene. Cyclopentadiene, bp 42°, was obtained by heating commercial 95% dicyclopentadiene (Matheson Coleman and Bell) under a reflux condenser maintained at 50° Stock solutions (0.28 M) of cyclopentadiene was prepared by distilling cyclopentadiene into absolute ethanol and were stored at $-78°$ until they were used. Portions of the stock solution ($\sim$170 ml) were photolyzed in the Hanovia immersion well photochemical apparatus described elsewhere.[16] No filters were used. Photolysis solutions were not maintained under nitrogen since the photochemical results were the same whether carried out in nitrogen or in air. The photolysis vessel was sealed to prevent evaporation of the extremely volatile photoproduct, and the solution was cooled for the duration of the photolysis by immersing the entire apparatus in a large Dewar flask filled with ice water. The decreasing concentration of cyclopentadiene (retention time 5.25 min) and appearance of a volatile photoproduct **4** (retention time 4.25 min) were conveniently followed during photolysis by vpc ($^1/_4$ in. × 2 m, UCON-Oil LB-550-X, oven at 50°). A trace of cyclopentene (retention time 4.80 min) was present both before and after photolysis. The concentration of the photoproduct **4** increased rapidly during the first hour of photolysis and continued to increase slowly during the second and third hours, reaching a maximum (as high as 15% of the original cyclopentadiene concentration, estimated by comparison of peak areas) by the end of the third hour, while the concentration of cyclopentadiene steadily decreased. If photolysis was continued for longer than 3 hr, the concentrations of both cyclopentadiene and photoproduct **4** rapidly decreased.

When the photolysis was ended, the yellow solution was quickly transferred to a 250-ml round-bottomed flask and cooled to $-78°$. The solution could be stored at $-78°$ for several days without appreciable loss of the unstable photoproduct **4**. (A sample of the solution stored at room temperature contained none of the photoproduct after 12 hr.) The solution was degassed at $-78°$ for 30 min on a vacuum line, and then approximately 10 ml was distilled from the 250-ml flask into a 50-ml round-bottomed flask containing 20 ml of dimethyl sulfoxide and 3 g of potassium *tert*-butoxide (MSA Corporation). Treatment with this basic medium removed most of the cyclopentadiene, thereby greatly simplifying subsequent preparative vpc collections. It was later learned that base treatment also removed a trace photoproduct having the same vpc retention time as photoproduct **4** and exhibiting nmr signals in the range δ 1.4–1.9. Approximately 0.5 ml was distilled from the 50-ml flask to a 0.5-ml container (constructed by forming a hemispherical seal $^3/_4$ in. below the joint of a 7/25 standard taper outer joint). The 0.5-ml container was removed from the vacuum line while still cold to a liquid nitrogen bath and quickly sealed with a special stopper (constructed by cutting a 7/25 inner joint $^1/_4$ in. above the joint, flaring the edge, and wiring on a silicone rubber serum cap). The stopper was wired in place because of pressure formed inside when the container was allowed to warm. The concentrated solution (composition $\sim$50% photoproduct **4**, 25% cyclopentadiene, and 25% ethanol) was conveniently stored at $-78°$ in the 0.5-ml containers. Loss of the extremely volatile photoproduct through evaporation was minimized by the use of these containers. Less enriched solutions of photoproduct **4** were obtained by distilling other 0.5-ml portions from the 50-ml flask.

When ethanolic solutions of cyclopentadiene were irradiated in the presence of sodium ethoxide (0.3 M) the photochemical results were essentially the same as in neutral ethanol.

Isolation of Photoproduct 4 by Vpc Collection. A 100-μl fixed needle syringe was cooled with Dry Ice before withdrawing 40-μl portions from the cold concentrated photoproduct solution (maintained at $-78°$) for injection into the Vapor Fractomer ($^1/_4$ in. × 2 m, UCON-Oil LB-550-X, oven at room temperature). The photoproduct **4** was condensed in a collection tube at $-78°$ as it came off the column. The photoproduct **4** is an extremely volatile colorless liquid with a distinctive penetrating odor.

Mass Spectrum. A sample of the photoproduct **4** was collected by preparative vpc from a base-treated concentrate. The mass spectrum (CEC 103-C) exhibited a strong molecule ion at 66.

Nuclear Magnetic Resonance Spectrum. A sample of the photoproduct **4** ($\sim$20 mg) was collected by preparative vpc from a base-treated concentrate. The collection tube was connected with a vacuum system, then immersed in liquid nitrogen to retain the volatile photoproduct, and finally evacuated. The sample was transferred first to a 5-ml flask containing 2 ml of dimethyl sulfoxide and 1 g of potassium *tert*-butoxide (MSA Corporation) and then to an nmr tube (also connected with the vacuum system) containing 1 ml of carbon tetrachloride. The lower portion of the nmr tube was immersed in liquid nitrogen while the tube was sealed off at the top with a torch. The nmr spectrum (Varian A-60, probe temp = 0°) exhibited a slightly split olefinic hydrogen peak at δ 6.10–6.30 (2.0 H), a complex envelope at 1.90–2.17 (3.1 H), and a complex multiplet at 1.45–1.75 (1.1 H).

An nmr spectrum taken after storing the sealed tube for several weeks at room temperature was completely changed. The new spectrum (greater than 95% of the total signal) exhibited a triplet at δ 6.17 (2 H, olefinic), a complex multiplet at 2.6–3.0 (2 H), a complex multiplet at 1.9–2.2 (2 H), a complex envelope in the range 1.0–1.8 (4 H), and a complex multiplet at 0.6–0.9 (2 H, cyclopropyl). The new spectrum was ascribable to the Diels–Alder adduct of bicyclopentene and cyclopentadiene, a compound which was later isolated from the photolysis solution. There were traces of other signals in the olefinic region, but there was no evidence of dicyclopentadiene.

A sample of photoproduct **4** was sealed in an nmr tube as previously described, and the decomposition of the photoproduct was followed by taking a series of spectra over a period of several hours (probe at 38°). The spectrum of cyclopentadiene first appeared, and then the previously described spectrum (Diels–Alder adduct) became discernible.

Ultraviolet Spectrum. A sample of photoproduct **4** was collected from a non-base-treated concentrate by preparative vpc. The peak was cut at its maximum to eliminate traces of cyclopentadiene. The sample was quickly dissolved in cold 95% ethanol and diluted to appropriate concentration. The uv spectrum (taken in cold ethanol within 5 min after collecting sample) exhibited strong end absorption in addition to absorptions at 232 ($\epsilon_{\max}$ 100) and 245 mμ ($\epsilon_{\max}$ 900) tailing out to 290 mμ. The sample was stored at room temperature in a sealed uv cell and spectra were taken pe-

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(15) A retroene mechanism for the thermal conversion of 4 to cyclopentadiene was ruled out by J. E. Baldwin, R. K. Pinschmidt, Jr., and A. H. Andrist, *J. Amer. Chem. Soc.*, 92, 5249 (1970). The recently reported isomerization of 2-methylbicyclo[2.1.0]pent-2-ene to 1-methylcyclopentadiene [J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1567 (1970)] suggests a possible concerted rearrangement mechanism for the parent compound as well, but S. McLean, University of Toronto (personal communication), has recently obtained evidence which leaves such a rearrangement course open to question.

(16) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Amer. Chem. Soc.*, **93**, 6141 (1971).

riodically. After 30 min the spectrum was essentially unchanged; however, after 16 hr a peak appeared at 239 mμ. After 60 hr at room temperature the peak at 239 mμ (cyclopentadiene, λ_{max} 239 mμ (ϵ_{max} 3400)) reached its maximum value.

Pyrolysis. The outlet tube of the vapor fractometer was heated to approximately 150°, and a sample of photoproduct **4** was collected in the usual manner (column at room temperature). The retention time of the reinjected sample corresponded with cyclopentadiene, and there was no photoproduct **4** remaining.

Diimide Reduction of Photoproduct 4. In a 50-ml round-bottomed flask (flushed with nitrogen) were placed 0.8 g (0.005 mol) of disodium azodicarboxylate and an ethanolic solution of $\sim$20 mg of photoproduct **4**. The flask was sealed with a silicon rubber serum cap, and 50 μl of acetic acid was injected. The reaction was stirred for 5 min. Vpc analysis ($^1/_4$ in. $\times$ 2 ml, UCON-Oil LB-550-X, oven at 50°) revealed that photoproduct **4** (retention time 4.25 min) was gone and a new peak (retention time 5.6 min) was present. The reaction medium was degassed at $-78°$ on a vacuum line, and a concentrated solution of the reduction product **8** was obtained by distilling 120 μl into a 0.5-ml container. The reduction product **8** was isolated by preparative vpc (same conditions as above).

The nmr spectrum of reduction product **8** (Varian A-60, in carbon tetrachloride) exhibited a complex envelope at δ 1.7–2.4 (2 H), a complex envelope at 1.1–1.7 (4 H), and another complex envelope at 0.4–0.9 (2 H). The nmr spectrum was identical with the spectrum of authentic bicyclo[2.1.0]pentane.[9b] The ir spectrum of the reduction product **8** was also identical with the spectrum of authentic material. Coinjection of the two samples on vpc (same conditions as above) gave a single peak of retention time = 5.6 min.

Diels–Alder Adduct 9. Solvent was removed from a photolysis solution by rotary evaporation, and the residue was chromatographed on neutral alumina using petroleum ether eluent. Vpc analysis of the first fraction ($^1/_4$ in. $\times$ 2 m, phenyl type silicone oil, oven at 118°) revealed a peak (retention time = 36 min) which was unresolvable from dicyclopentadiene. The peak was collected by preparative vpc (same conditions as before). The mass spectrum (CEC 103-C) exhibited a strong fragment at 66 and a molecular ion at 132. The nmr spectrum revealed that the peak consisted of a mixture of $\sim$20% dicyclopentadiene (identified by comparison with the spectrum of authentic dicyclopentadiene) and 80% of the compound identified by nmr interpretations as the Diels–Alder adduct **9** of cyclopentadiene and bicyclo[2.1.0]pent-2-ene.

Isomerization of Bicyclo[2.1.0]pent-2-ene, Kinetic Study. Bicyclopentene ($\sim$5 mg, collected from a non-base-treated concentrate) was dissolved in 10 ml of *n*-heptane. Cyclohexane ($\sim$5 mg) was added as an internal standard for vpc analysis. Portions of the stock solution (0.5 ml) were transferred to four 1-ml test tubes (6 $\times$ 50) which were then sealed with silicone rubber serum caps. The bottom halves of the 1-ml test tubes were immersed in diglyme inside large test tubes (18 $\times$ 150) which in turn were immersed in constant temperature baths. Temperatures were measured inside the larger test tubes and are corrected. Samples were analyzed by vpc ($^1/_4$ in. $\times$ 2 m, UCON-Oil LB-550-X, oven at 50°) at approximate time intervals for each temperature. Since sharp symmetrical peaks were observed, bicyclopentene concentrations were based on peak heights and were standardized by the internal standard.

Photolysis of Cyclopentadienide. Approximately 200 ml of the cyclopentadiene stock solution was added to the reaction flask, and the system was swept with nitrogen for 20 min while stirring. A loose glass stopper served as a valve. The stopper was removed, and sodium metal strips were cut in small pieces which fell into a brisk nitrogen stream from the reaction flask. An excess of sodium metal was added. The flask was swept with nitrogen for a few minutes with the stopper in place, and then the system was sealed. The reaction medium was stirred for approximately 12 hr, at a slow reflux. When the preparation was complete and immediatey preceding transfer to the photolysis vessel, 50 ml of *tert*-butyl alcohol was added into a brisk nitrogen stream from the reaction flask.

The Pyrex photolysis vessel and quartz immersion well were dried in an oven at 120° and were assembled under a nitrogen flush. The assembled apparatus was flushed with nitrogen for 20 min and then connected to the transfer tube of the reaction flask. Approximately 160 ml of the anion solution was transferred to the photolysis vessel by nitrogen pressure and was maintained under nitrogen until the end of the photolysis.

All photolyses were performed with the Hanovia immersion well photochemical apparatus used above. No filters were used. Samples were taken by syringe during photolysis and were analyzed by vpc for volatile products ($^1/_4$ in. $\times$ 2 m, UCON-Oil LB-550-X, oven at 50°). Solutions were usually photolyzed for 2 hr.

The photolyzed sodium cyclopentadienide solution was poured into a 500-ml Erlenmeyer flask, and approximately 250 ml of ethyl ether was added. The mixture was neutralized with dilute aqueous hydrochloric acid and was poured into a 1-l. separatory funnel. The ether layer was washed with eight 400-ml portions of water to remove *tert*-butyl alcohol and tetrahydrofuran and was dried, first with saturated sodium chloride solution and then over anhydrous sodium sulfate. After the solvent was removed by rotary evaporator, the residue was chromatographed on neutral alumina. Vpc analysis of nonpolar material ($^1/_4$ in. $\times$ 2 m, succinate polyester of diethylene glycol, oven at 74°) revealed equal amounts of two dimeric, colorless photoproducts, representing $\sim$5% of consumed starting material. In addition, smaller amounts of colored hydrocarbons as well as considerable polymeric material was recovered.

Identification of Dimeric Photoproducts. Evidence presented below reveals that the dimeric photoproducts are the *meso*- and *d,l*-3-(3′-cyclopentenyl)cyclopentenes (**2a, b**). Photoproducts (**2a, b**), found in the first fractions from column chromatography of the photolysis mixture were contaminated by dicyclopentadiene (presumed not to be a photoproduct). The two photoproducts could be separated from each other and from the dicyclopentadiene by preparative vpc ($^1/_4$ in. $\times$ 2 m, succinate polyester of diethylene glycol, oven at 74°). Retention times were: **2b**, 8.0 min; **2a**, 8.7 min; dicyclopentadiene, 9.2 min.

The mass spectra (Atlas Ch-4) of **2a** and **2b** are identical, exhibiting a molecular ion at 134 and major fragments at 66 and 67. Nmr spectra of the photoproducts (A-60, in carbon tetrachloride; vinyl δ 5.65 (4 H); methinallylic, 2.68 (2 H); allylic, 2.26 (4 H); and methylene, 1.2–2.0 (4 H)) are identical except for fine splitting in the olefinic region. Isomer **2b** exhibits greater olefinic fine splitting than **2a**.

Catalytic Hydrogenation of Photoproducts 2a, b. In a 250-ml hydrogenation flask containing a magnetic stirrer were placed 100 ml of ethyl alcohol, 50 mg of platinum oxide, and the first fraction from column chromatography of the photolysis mixture. The reaction mixture was treated with 1 atm of hydrogen for 48 hr. The solution was filtered, and solvent was removed by rotary evaporator. The reduction product was collected by preparative vpc ($^1/_4$ in. $\times$ 2 m, phenyl type silicone oil, oven at 100°). The mass spectra of the reduction product (Atlas Ch-4) exhibited a molecular ion at 138, and the fragmentation pattern was identical with that of authentic dicyclopentyl.[16] The ir spectrum of the reduction product (Perkin-Elmer 421 grating spectrophotometer) was identical with the published spectrum of dicyclopentyl[17] and with the ir spectrum of authentic dicyclopentyl. Coinjection of the reduction product with authentic dicyclopentyl on vpc ($^1/_4$ in. $\times$ 2 m, phenyl type silicone oil, oven at 100°) gave a single peak.

Diimide Reduction of Photoproducts 2a, b. In a 125-ml Erlenmeyer flask were placed 1.0 g (0.0060 mol) of disodium azodicarboxylate, 25 ml of ethyl alcohol, and the first fraction from column chromatography of the photolysis mixture (containing photoproducts **2a, b**). One gram (0.02 mol) of acetic acid was added, and the mixture was stirred for 1 hr. The reaction mixture was filtered, and the solvent was removed. Analysis by vpc ($^1/_4$ in. $\times$ 2 m, succinate polyester of diethylene glycol, oven at 74°) revealed three products in the C_{10} region—dicyclopentyl (retention time 11.5 min), the reduction product from dicyclopentadiene (retention time 19 min), and a partial reduction product **3** (retention time 15 min) which could be further reduced to dicyclopentyl. The partial reduction product **3** was isolated by preparative vpc. Its nmr spectrum (vinyl, δ 5.64 (2 H); allylic, 2.2 (3 H); and methine, methylene, 1.0–1.9 (11 H)) and mass spectrum (molecular ion 136) are consistent with the proposed structure, 3-cyclopentylcyclopentene. Identification of the partial reduction product **3** as 3-cyclopentylcyclopentene is confirmed by the fact that photoproducts **2a, b** were later identified as the *meso*- and *d,l*-3-(3′-cyclopentenyl)cyclopentenes. Diimide reduction of the nonpolar material from nonirradiated sodium cyclopentadienide solution gave the dicyclopentadiene reduction product but no dicyclopentyl and no 3-cyclopentylcyclopentene.

Deuteriodiimide Reduction of Photoproducts 2a, b. In a 125-ml Erlenmeyer flask were placed 3.0 g (0.018 mol) of disodium azodi-

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[17] American Petroleum Institute Research Project 44, ir spectrum no. 1088.

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 Perdeuteriocyclopentadienide. Perdeuteriocyclopentadienide 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, azulenium 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 knowledge, 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