

Photochemical Rearrangements of Some Benzo C₉H₁₀ Isomers

R. C. Hahn* and R. P. Johnson¹

Contribution from the Department of Chemistry, Syracuse University, Syracuse, New York 13210. Received August 19, 1975

Abstract: Direct irradiation of benzo[8,9]bicyclo[5.2.0]nona-2,4,8-triene (**2**) gives one electrocyclic ring closure product (**7**; 60%) and three identified products formally derivable from benzocyclobutene ring opening: benzo[2,3]bicyclo[6.1.0]nona-2,4,6-triene (**5**; 17%), benzo[3,4]tetracyclo[6.1.0.0.2⁷.0^{5,9}]-non-3-ene (**8**, 17%), and a *cis*-dihydrobenzindene (**6**; 2.4%). Direct irradiation of **5** gives primarily **8**; sensitization of **2** gives **5** (80%) and **7** (20%); sensitization of **5** gives **6**. Evidence is cited to support the contention that thermal and photochemical reactions of **2** involving cyclobutene ring opening are best accounted for in terms of diradical intermediates.

Recent years have seen widespread interest in syntheses and interconversions of (CH)_n and C_nH_{n+1} hydrocarbon isomers.^{2,3} A myriad of thermally and photochemically induced transformations have been observed on a particular potential energy surface, and have afforded a broad testing ground for the validity and applicability of orbital symmetry concepts.⁴ One of the more widely explored sets of isomers lies on the C₉H₁₀ potential surface,³ which includes such well-known molecules as barbaralane and cyclonona-tetraene. A number of benzannelated C₉H₁₀ isomers also have been prepared and examined;⁵ we reported recently on the photochemistry of one of these, benzo[7,8]bicyclo[4.2.1]nona-2,4,7-triene (**1**).⁷ This highly reactive compound rearranges through the singlet excited state to the



two possible cyclobutenes and to benzobarbaralane (a di- π -methane rearrangement product);⁸ the triplet gives benzobarbaralane as the only monomeric product.

We now report the photochemical rearrangements of another benzannelated C₉H₁₀ isomer, benzo[8,9]bicyclo[5.2.0]nona-2,4,8-triene (**2**). Compounds **1** and **2** are formally related via a [1,5] sigmatropic shift, although this transformation has not been observed in either direction.^{5e} Interestingly, when **2** was first prepared, it was mistakenly identified as **1**.⁹ Hydrocarbon **2** is of interest, from a photochemical point of view, as a bichromophoric¹⁰ molecule; i.e., it contains both benzocyclobutene and cycloheptadiene chromophores. The uv spectrum of **2** (λ_{\max} 247, 266, 272.5 nm) is essentially a composite of the spectra of cyclohepta-



diene (**3**, λ_{\max} 248 nm) and the tetrahydro derivative **4** (λ_{\max} 266, 272.5 nm).^{5a}

One a priori possibility, then, was that photochemical behavior of **2** would be a summation of those of the individual chromophores. Although reports of benzocyclobutene photochemistry are limited,¹¹ the primary mode of reaction seems to be cleavage of the cyclobutene ring to an *o*-xylylene structure. More numerous examples of cycloheptadiene photochemistry almost invariably involve electrocyclic ring closure to bicyclo[3.2.0]heptenes.¹²

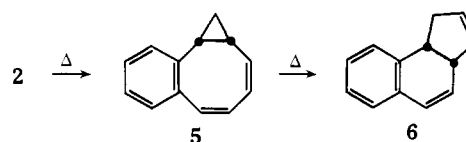
Photochemical processes requiring chromophoric interaction also could occur. Sigmatropic shifts in particular would find driving force in alleviation of the cyclobutene ring

strain; the reported thermal behavior of **2** involves exclusively a formal [1,5]-sigmatropic shift as the primary process.^{5a,e} The ubiquitous di- π -methane reaction also would appear possible, using the C₈-C₉-C₁-C₂-C₃ linkage.⁸

Results and Discussion

Hydrocarbon **2** was conveniently prepared as a mixture (ca. 1:1) with 7-phenylcycloheptatriene by the known reaction of benzyne with cycloheptatriene.^{5a,e,13} Pure **2** was isolated initially through preparative GLC, but this method was not suitable for preparation of large quantities, especially considering the thermal sensitivity of **2**.^{5a,e} It was found most convenient to reflux the benzyne product mixture with 0.6 equiv of maleic anhydride; **2** is essentially unreactive, while the phenylcycloheptatriene is nearly quantitatively removed via adduct formation. Further purification of **2** was effected by chromatography over silica gel. A similar purification using tetracyanoethylene has been reported.^{5e}

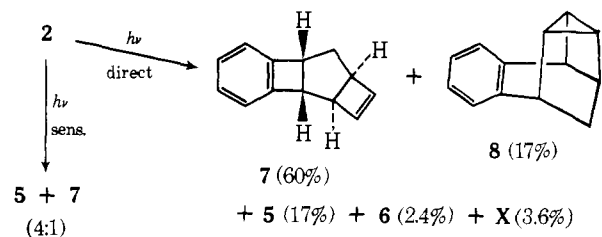
Thermal Rearrangements. Thermolysis of **2** was found independently in this laboratory to cause sequential rearrangement to benzo[2,3]bicyclo[6.1.0]nona-2,4,6-triene (**5**) and *cis*-dihydrobenzindene **6**, in accord with reported re-



sults.^{5a,e} First-order kinetic parameters for the **2** \rightarrow **5** rearrangement also were determined: $k_{147,6} = 5.95 \times 10^{-5} \text{ s}^{-1}$; $t_{1/2} = 194 \text{ min}$, $\Delta G^\ddagger = 33.1 \text{ kcal/mol}$. Other syntheses of **5**^{5c,14} afforded spectral data matching those found; **6** has been identified by hydrogenation to the hexahydro derivative.^{5a,e} This thermal source of **5** and **6** proved to be useful in elucidating some of the photochemistry of **2**.

Photochemical Rearrangements. Direct irradiation of a dilute solution of **2** (Corex filter) rapidly gave a product mixture which contained three major and two minor products in the percentages 60:17:17:3.6:2.4 (VPC analysis). This distribution was essentially constant to ca. 80% conversion, at which time secondary rearrangements began to be noticeable. At ca. 95% conversion, the three major products had ratios of 60:20:13, and some other small peaks began to appear in the chromatogram. High conversions were necessary to facilitate product isolation; one of the photoproducts overlapped partly with starting material on VPC. Photoproducts were isolated by preparative VPC and characterized spectroscopically (vide infra). Overall results are summarized in Scheme I.

Scheme I



Benzophenone sensitized irradiations were somewhat less complex, giving only two primary products **5** and **7** (Scheme I) in a 4:1 ratio. Conversion to products was extremely rapid and was complicated by secondary sensitized transformation of **5** to **6**. The secondary nature of photoproduct **6** was confirmed by analysis of irradiations carried to varying degrees of completion (see Experimental Section). Independent irradiation of pure **5** also was performed (vide infra).

Identification of Photoproducts. The major photoproduct (60%) from direct irradiation of **2** was identified as *anti*-benzo[8,9]tricyclo[5.2.0.0^{2,5}]nona-3,8-diene (**7**) on the basis of spectroscopic data. The mass spectrum indicated isomerism with starting material (mol wt 168). The infrared spectrum showed a band at 1552 cm⁻¹, suggestive of a cyclobutene ring. This was supported by the ¹H NMR spectrum which showed a narrowly split AB quartet ($J_{AB} = 2.8$ Hz) at δ 6.08. Cyclobutene olefinic protons characteristically¹⁵ do not couple with adjacent ring protons and appear as a singlet in symmetrical systems; in **7**, they couple only with each other. This lack of coupling from either olefinic moiety lends a pseudosymmetry to the molecule; the two pairs of methine protons (H_1, H_2 and H_5, H_7) show nearly identical splitting patterns.

The anti stereochemistry also was assigned from the ¹H NMR spectrum. Models indicate that H_1 and H_2 are orthogonal for this configuration (dihedral angle $\sim 90^\circ$) and thus do not couple to each other. Were the cyclobutene ring syn to the benzene (dihedral angle $\sim 0^\circ$), H_1 and H_2 would be expected to couple strongly. The ultraviolet spectrum of **7** supports the presence of a benzocyclobutene chromophore, showing a greatly enhanced ¹L_b benzenoid band (λ_{\max} 259.9 nm (ϵ 1705) 267 (2638), 273.1 (2655)).^{13a}

Thermolysis of **7** (sealed tube, 180 °C) gave dihydrobenzindene (**6**), with a half-life of ca. 880 min. This reaction is assumed to go through nonconcerted ring opening to **2**, which then rearranges relatively rapidly to **6** via **5**. Detection of intermediates was not attempted, however; other pathways could not be ruled out.

Hydrocarbon **5**, obtained as 17% of the products from direct irradiation of **2** and up to 80% from sensitization, was identical with material on hand from thermolysis experiments.

Identification of the third major photoproduct (17%) from direct irradiation proved to be more difficult. The mass spectrum again indicated isomerism with starting material. The ¹H NMR and ir spectra clearly indicated absence of olefinic functionality, but retention of an aromatic ring. The ultraviolet spectrum showed a ¹L_b band at 269 nm with ϵ_{\max} 420; this feature ruled out benzocyclobutenyl ($\epsilon_{\max} \geq 2000$)^{13a,16} and indanyl ($\epsilon_{\max} \geq 1300$)¹⁶ chromophores.

Most distinctive (and useful) in the 100-MHz ¹H NMR spectrum of this compound were a benzylic two-proton multiplet (δ 3.40–3.60) and a unique high-field, one-proton doublet of doublets (δ 0.64, $J = 10.5, 2$ Hz). The splitting pattern of the latter, especially the large (geminal) coupling constant, was taken as indicating a highly shielded meth-

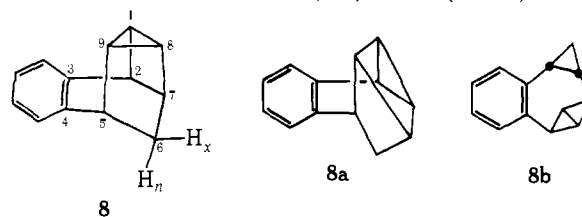
Table I. 100-MHz Spin Decoupling of Benzo[3,4]tetracyclo[6.1.0.0^{2,7}.0^{5,9}]non-3-ene (**8**)^a

Position irradiated	Partial results
δ 3.40–3.60 (H_2, H_5)	Broad d at 2.62 (H_7) collapsed to broad s; quartet of d at 1.99 (H_{6x}) collapsed to d of d, $J = 10.5, 1.6$ Hz
δ 2.52–2.72 (H_7)	Quartet of d at 1.99 (H_{6x}) collapsed to quartet, $J = 10.5, 5.5$ Hz; d of multiplet at 0.64 (H_{6n}) collapsed to broad d, $J = 10.5$ Hz; sextet at 2.36 (H_8) collapsed to t
δ 0.64 (H_{6n})	Quartet of d at 1.99 (H_{6x}) collapsed to broad d of d, $J = 6$ Hz

^a Done in CDCl₃ with a Varian XL-100 instrument (FT mode).

ylene proton. Three other one-proton resonances and a two-proton resonance were readily discerned.

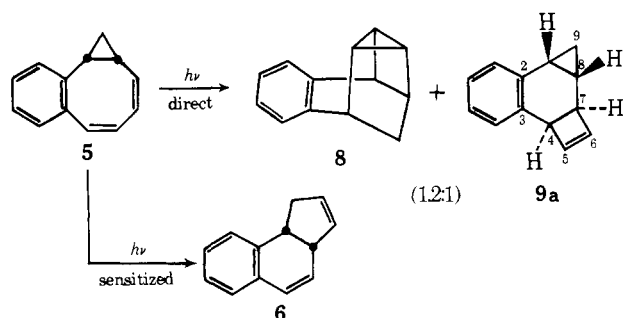
Structural requirements dictate that for an isomer of **2**, loss of two double bonds must coincide with formation of two new rings. Thus, in consideration of possible structures for the photoproduct, a benzannelated tetracyclic isomer was mandated. Within reasonable limitations it was of interest to establish the total number of isomers embodying the structural features described above. Using a computer-assisted structure elucidation program,¹⁷ a complete list of isomers was compiled meeting the following requirements: ortho-disubstituted benzene, two benzylic methine protons, seven other carbons and six other hydrogens, no other double bonds, no triple bonds, no methyl groups, no quaternary carbons, and no bond between the benzylic carbons. Fourteen structures were generated. Of these, seven were eliminated for having indan moieties, two were too symmetrical (only five types of aliphatic protons), two could not be constructed with a Prentice-Hall Brumlik model set. The remaining three structures were **8**, **8a**, and **8b** (below).



Of these, **8** provided the best match between expected and actual ¹H NMR spectra. The unique high-field doublet of doublets (above) was assignable to the endo proton at C-6, shown by a molecular model to be in a region affected by benzenoid anisotropic shielding. The nonbenzo analogue of **8** (a tetracyclononene) has been reported to show a similar ¹H NMR resonance.^{4d} Other proton assignments, consistent with the results of decoupling (double irradiation) experiments, are summarized in Table I.

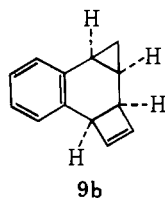
The two minor photoproducts from direct irradiation were collected as a single GLC peak and analyzed as a mixture. The ir and NMR spectra indicated the presence of **6** and one other compound (**X**) in ca. 1:1.5 ratio. Compound **X** remains unidentified because of separation difficulties and lack of material; however, VPC and spectroscopic comparisons clearly ruled out **9a** (see below) as a possibility. Dihydrobenzindene (**6**) isolated from sensitized runs was essentially free of contamination by **X**.

Secondary Rearrangements. Photochemistry of Benzo[2,3]bicyclo[6.1.0]nona-2,4,6-triene (5**).** Direct irradiation of **5** (Corex filter) was found to slowly give tetracycle **8** and one new isomer, identified as **9a** (ratio 1.2:1). This result is in accord with observations from direct irradiation of **2**, in which a slow decrease in the proportion of **5** at high conver-



sion accompanied an increase in the proportion of **8** and formation of other secondary products.

The photoproduct mixture from **5** was resolved by column chromatography and **9a** was characterized spectroscopically. As before, the mass spectrum indicated isomerism with starting material. In addition to an aromatic multiplet, the ^1H NMR spectrum displayed four distinct protons as two AB quartets, the first (δ 6.15 and 6.27, $J_{\text{AB}} = 2.5$ Hz) characteristic of cyclobutene olefinics, and the second (δ 3.54 and 3.74, $J_{\text{AB}} = 4.5$ Hz) assignable as the associated methine protons (H_4 and H_7). A higher field multiplet (δ 0.8–2.14) appeared for the four remaining cyclopropyl protons. The anti stereochemistry (**9a** rather than **9b**) is assignable on the basis of lack of coupling between H_7 and H_8 ; these protons are orthogonal for **9a** (according to models), but should be strongly coupled in **9b**. The infrared spectrum supported the assignment as **9a**, showing absorp-



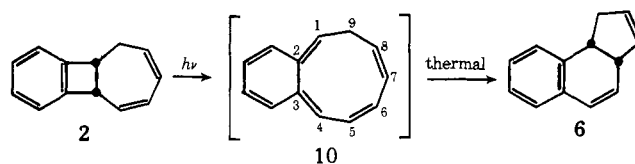
tions at 1565 and 1022 cm^{-1} , characteristic of cyclobutene and cyclopropane moieties, respectively.

Benzophenone-sensitized irradiation of **5** proceeded very rapidly to give **6**, in accord with observations from sensitization of **2**. Additionally, **6** was slowly destroyed by prolonged irradiation with benzophenone.

Rearrangement Mechanisms. Of the four photoproducts identified from direct and sensitized irradiation of **2** (**5**, **6**, **7**, and **8**), only **7** does not arise from cyclobutene ring opening (CRO), and will be discussed separately. Appearance of **7** as the major product from direct irradiation of **2**, as a symmetry-allowed process, is not unexpected. However, formation of **7** from triplet-excited **2**, though minor (20% of photoproducts), contrasts markedly with the total absence of cyclobutenes on sensitization of isomeric benzo[4.2.1]triene (**1**) (see above). This contrast, plus the results of direct irradiation of **2** (in particular, formation of 17% of the symmetry-forbidden **5**), may be taken to indicate that excited state singlet \rightarrow triplet intersystem crossing is more facile for **2** than for **1**; as much as 20% of the photochemistry ensuing from direct irradiation of **2** may occur from the triplet (17% plus 20% of 17%). Another possibility is that formation of **5** (from direct or sensitized irradiation of **2**) proceeds via vibrationally excited ground state(s) of **2**, in accord with the known thermal conversion. If this is the case, then *no* intersystem crossing needs to be postulated for singlet excited **2**. However, singlet excited **5** fails to give detectable amounts of chemically productive vibrationally excited ground state (i.e., no **6**); this makes it less likely, in our view, that such states play a significant role in photoinitiated rearrangements of **2**.

Photochemistry of the benzobicyclo[6.1.0] system **5** clearly involves very little intersystem crossing, as evidenced by the totally different products from direct and sensitized irradiations. Even though the two double bonds in **5** are nearly orthogonal in the ground state, direct irradiation results in electrocyclic closure to **9a**, albeit inefficiently. Precedent for this behavior is found in the photochemistry of 1,3-cyclooctadiene;¹⁸ for the latter, however, cyclobutene formation competes with more efficient *cis*-*trans* isomerization, and is a very minor pathway. For **5**, the increased constraints due to fused benzene and cyclopropane rings minimize any possibility of *cis*-*trans* isomerization.

In CRO reactions of **2**, the relevance of singlet vs. triplet or of orbital symmetry arguments is open to question. Of the three identified CRO products from direct irradiation of **2**, only **6** (6.6% of CRO products) could be claimed as a clear consequence of orbital symmetry influence. One such symmetry-allowed sequence would begin with excited state benzocyclobutene ring opening (disrotatory) to give the fused cyclononatetraene derivative **10** (ground state), fol-



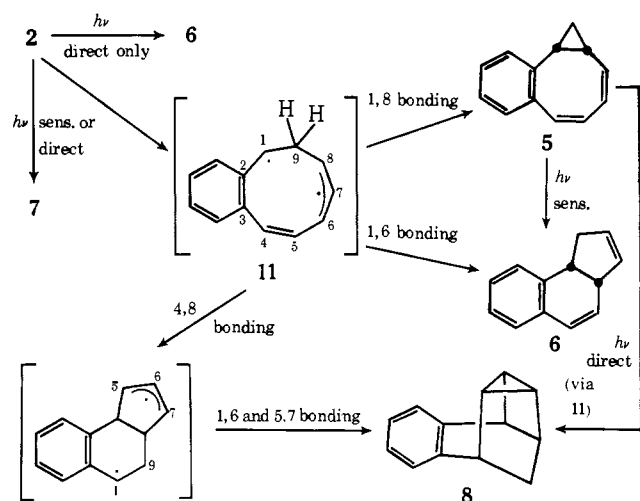
lowed by concerted electrocyclic closure to **6**. Another excited state symmetry-allowed route from **2** to **6** is a suprafacial sigmatropic [1,3] shift.

Orbital symmetry influence appears to be even further diminished in the photochemistry of **5**. Although cyclopropane ring opening (to **10**) or a sigmatropic [1,3] shift would lead to **6** in symmetry-allowed fashion, only sensitization (*not* direct irradiation) of **5** gives detectable amounts of **6**. Thus the evidence regarding the nature of photochemical CRO processes of **2**, as well as cyclopropane ring opening reactions of **5**, weighs heavily against concertedness. For these reasons, plus the strain of having six of the nine-membered ring atoms coplanar in **10** (not necessary in parent cyclononatetraene), plus the potential loss of aromaticity, the existence of **10** as a discrete entity is highly questionable.^{19,20} Excited state ring opening of other benzocyclobutenes has been reported to be nonstereospecific.¹¹ It was concluded that orbital symmetry concepts are inapplicable because $^1\text{L}_b$ benzenoid excitation is not a simple HOMO \rightarrow LUMO transition.¹¹

Conversion of **2** or **5** to **8** on direct irradiation, in preference to conversion to **6**, is noteworthy. It is clear that **8** is a more highly strained species than **6**; thus lack of energy may preclude formation of **8** on thermolysis or sensitization of **2** and **5**. However, the energy available in an excited singlet state of **2** or **5** should be sufficient to populate transition states leading to **5**, **6**, or **8**. Even if a symmetry-allowed excited state pathway should exist for direct conversion of **2** or **5** to **8**, it does not appear reasonable that symmetry allowedness would lower the activation energy for this process sufficiently to make it so much more facile than routes to **5** and **6**. Therefore, we assign minor roles to orbital symmetry and energy effects in the singlet photochemistry of **2** and **5** not involving cyclobutene formation.

For the reasons cited above, it is suggested that ring-opening rearrangements of **2** and **5** proceed predominantly through diradical species such as **11**; straightforward empirical routes to photoproducts can be traced *via* such species (Scheme II). Hypotheses to account for the several modes of behavior noted, however, will be withheld until more definitive evidence is in hand.

Scheme II. Proposed Pathways for Rearrangement of 2 and 5



Experimental Section

Nuclear magnetic resonance spectra were obtained on Varian A-60, T-60A, or XL-100 spectrometers, in either CDCl_3 or CCl_4 . Vapor phase chromatographic analytical and preparative separations were done on a Varian Aerograph Model A-700 instrument, equipped with thermal conductivity detection. Peak areas were determined by cutting and weighing and are uncorrected for response factors. These were found to vary only slightly for the isomers involved in this study. Ultraviolet spectra were obtained on a Cary Model 118 and infrared spectra on a Perkin-Elmer Model 137 Sodium Chloride Spectrophotometer. Mass spectra were run on a Hitachi Perkin-Elmer Model RMU-6E single focusing spectrometer.

Cyclohexane and hexane used in irradiations were spectroqual-ity. Benzophenone was recrystallized before use.

Preparation of Benzo[8,9]bicyclo[5.2.0]nona-2,4,8-triene (2). Benzenediazonium-2-carboxylate hydrochloride,²¹ from 5 g (0.37 mol) of anthranilic acid and 87.5 g (0.75 mol) of isopentyl nitrite, was mixed with dichloroethane (600 ml), propylene oxide (40 ml), and 53 g (0.58 mol) of cycloheptatriene. The mixture was refluxed gently for 4 h, foaming and turning dark. Solvent removal at reduced pressure left a dark oil which was steam distilled (ca. 700 ml of distillate). Separation, drying, solvent removal, and vacuum distillation gave 21.98 g (35%) of product mixture as a yellow oil, bp 68–75 °C (0.4 mm). Analysis by NMR indicated a 52:48 mixture of 2 and 7-phenylcycloheptatriene. In other experiments using the free benzenediazoniumcarboxylate in place of the hydrochloride, similar results were obtained.

The above product mixture, 100 ml of benzene, and 7.65 g (0.6 equiv) of maleic anhydride were refluxed together for 18 h. After cooling and removal of most of the solvent, 200 ml of petroleum ether was added and the mixture was cooled in an ice bath to complete precipitation of the adduct. The adduct was filtered and washed with petroleum ether (3 × 50 ml). Combined organic liquids were concentrated and chromatographed over a silica gel column (2.5 × 20 cm); elution was with 500 ml of petroleum ether. Concentration at reduced pressure and vacuum distillation yielded 9.56 g (15.3% based on anthranilic acid) of ca. 95% pure triene 2, bp 56–58 °C (0.2 mm). Material for photolyses was further purified by chromatography over silica gel, followed by distillation. Spectral data for 2 (NMR, uv) were identical with those reported in the literature.^{5e}

Thermal Rearrangement of 2. Preparative-scale rearrangements were done neat in evacuated, sealed Pyrex tubes at 180 °C. In one experiment, 0.499 g of 2 was thermolyzed for 40 min. Analysis of the resulting mixture by NMR indicated ca. 55% 6, 40% 5, and 5% 2. Chromatography over silica gel (1 × 150 cm) eluted with petroleum ether in 100-ml fractions gave (fractions 18–20) 0.15 g of 5, contaminated with ca. 10% of 2, and (fractions 23–38) 0.25 g of 6. Spectral data for 5 and 6 were identical with those reported.

To study kinetics of the 2 → 5 rearrangement, a solution of 40 mg of 2 in 0.15 ml of $\text{DMSO}-d_6$ in a tightly capped NMR tube was heated in a constant temperature bath at 147.6 ± 0.2 °C (re-

fluxing cyclohexanone). Periodically, NMR spectra of the mixture were taken and percentages of 2, 5, and 6 were determined by integration of appropriate resonances. The results clearly indicated the stepwise transformation 2 → 5 → 6. Linear first-order kinetics were observed for the 2 → 5 rearrangement and the following data calculated: $k_{147.6} = 5.95 \times 10^{-5} \text{ s}^{-1}$, $t_{1/2} = 194 \text{ min}$, $\Delta G^\ddagger = 33.1 \text{ kcal/mol}$. Qualitatively, the second step (5 → 6) was somewhat slower.

Direct Irradiation of 2. A typical experiment is described. In an immersion-well photovessel, equipped with a 450-W Hanovia medium pressure lamp and Corex filter, 155 ml of cyclohexane was stirred and purged with prepurified N_2 for 1 h. Triene 2 (312 mg) was added and purging continued an additional 30 min prior to and during irradiation. Progress of irradiation was monitored by VPC analyses of aliquots (20% Carbowax 20M on Chromosorb W, 6 ft × 0.25 in, 150 °C). Conversion was ca. 50% after 45 min; reaction was terminated after 105 min. Solvent removal at reduced pressure gave an oil which was analyzed by VPC. The chromatogram showed ca. 5% 2 remaining, plus four major product peaks (I–IV) in the ratios 60:20:13:6. Partial overlap of the peak for product II with that of starting material prevented accurate analysis of this compound at low conversions (<60%). Attempts to analyze the product mixture using a variety of other VPC columns or by affinity or reverse-phase (Corasil C18; methanol-water) high-pressure liquid chromatography were less successful.

Preparative chromatography on the Carbowax column yielded the photoproducts (all colorless oils): I (first peak, retention time (rt) 6.5 min), 120 mg collected; II (rt 9.4 min), 40 mg collected; III (rt 11.0 min), 15 mg collected; and IV (rt 13.0 min), 10 mg collected.

Photoproduct I (60%) was identified as benzo[8,9]tricyclo[5.2.0.0^{2,5}]nona-3,8-diene (7): bp 40–45 °C (0.05 mm); ^1H NMR (CCl_4) δ 6.81–7.24 (m, 4 H, aryl), 5.98–6.20 (AB quartet, $J_{AB} = 2.8 \text{ Hz}$, H_3 , H_4), 4.37 (quintet, H_7), 3.54–3.86 (d, $J = 4 \text{ Hz}$, overlapping with quintet, H_1 (d) and H_5 (quintet)), 3.44 (d, $J = 3.5 \text{ Hz}$, H_2), and 1.71–2.02 (m, H_6 's); ir (NaCl) 2990, 2880, 2810, 1598, 1552, 1445, 812, 996, 972, 741, 734, and 694 cm^{-1} ; uv (hexane) λ_{max} (ϵ) 249 nm (sh, 485), 256 (sh, 1000), 259.9 (1705), 267 (2638), and 273.1 (2655); MS m/e (rel%) 168(44), 167(100), $P + 1$ (16); $\text{C}_{13}\text{H}_{12}$ requires 14.

Photoproduct II (20%) was identified as benzo[3,4]tetracyclo[6.1.1.0^{2,7}.0^{5,9}]non-3-ene (8): bp 45–50 °C (0.05 mm); ^1H NMR (100 MHz, CDCl_3) δ 7.0–7.3 (m, 4 H, aryl), 3.40–3.60 (m, H_2 , H_5), 2.52–2.72 (broad d, H_7), 2.36 (sextet, H_8), 1.99 (quartet of d, $J = 10.5$, 5.5, and 1.6 Hz, $\text{H}_{6,x}$), 1.63–1.88 (m, H_1 , H_9), 0.64 (d of m, $J = 10.5 \text{ Hz}$, $\text{H}_{6,y}$); ir (NaCl) 3040, 2940, 2850, 1476, 1455, 949, 934, 898, 878, 808, 793, 774, 758, and 744 cm^{-1} ; uv (hexane) λ_{max} (ϵ) 250 nm (223), 256 (314), 258 (311), 261 (sh), 262.3 (415), 266 (273), and 269.1 (417); MS m/e (rel%) 168 (89), 167 (100), $P + 1$ (13.5); $\text{C}_{13}\text{H}_{12}$ requires 14. Spin decoupling also was done at 60 and 100 MHz (see text).

Photoproduct III (13%) was identified as benzo[2,3]bicyclo[6.1.0]nona-2,4,6-triene (5) by comparison (ir, ^1H NMR, VPC retention time) with material prepared from thermolysis of 2.

Photoproduct IV had the same retention time as that of 6, but the VPC peak proved to be a mixture (ir, ^1H NMR) of 6 and an unidentified compound X in the approximate ratio 1:1.5. The ^1H NMR spectrum of X displayed two olefinic resonances; however, because of the minute quantities and separation difficulties, no further characterization could be made.

The two major photoproducts also could be isolated by column chromatography over 20% AgNO_3 -silica gel. Elution with petroleum ether–2% ethyl ether gave pure 8 followed by pure 7. Silver-catalyzed rearrangement of 8 was not detected under these conditions. Elution with pure ether gave the remainder of the product mixture.

Sensitized Irradiation of 2. In the above described apparatus, with a Pyrex filter, a solution of 280 mg of triene 2 and 825 mg of benzophenone in 155 ml of cyclohexane was purged with N_2 for 1 h previous to and throughout irradiation. Progress of irradiation was monitored by VPC analysis of aliquots (20% DEGS on Chromosorb W, 5 ft × 0.25 in., 130 °C). Reaction was terminated after a total of 6 min. Solvent removal at reduced pressure gave a colorless oil which was chromatographed on a column of neutral alumina (2.5 × 15 cm). Elution with petroleum ether yielded the product mixture as a colorless oil. Analysis by VPC indicated starting

Table II. Benzophenone-Sensitized Irradiation of **2**

Apparent conversion of 2 to products, %	Product distribution, %		
	5	6	7
7.8	61.8	13.4	24.8
20.6	50.0	21.0	28.9
58.5	33.5	30.0	36.5
78.5	24.1	38.4	37.4
95.3	9.5	48.7	41.5

material and three major products **5**, **6**, and **7** in the ratios 41.5:19.5:17.7:21.3. Products were isolated by VPC and characterized as before.

In other similar irradiations, reaction was carefully monitored at short intervals. Very brief irradiations yielded mixtures containing only traces of **6**. Prolonged irradiation led to nearly complete disappearance of **5**. Results are summarized in Table II. Extrapolation to 0% conversion gave a **5**:**7** ratio of 4:1. At high conversions, some destruction of **6** was noted.

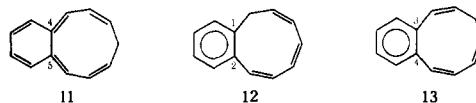
Thermolysis of Benzo[8,9]tricyclo[5.2.0.0^{2,5}]nona-3,8-diene (7). Photoproduct **7** (38 mg) in 0.25 ml of benzene in an evacuated sealed Pyrex tube was heated at 180 °C for 1760 min. Solvent removal left a slightly yellow oil. Analysis by ir and ¹H NMR indicated a mixture of **7** and dihydrobenzindene **6** in the ratio (NMR) 25.3:74.7. From these results, the half-life of **7** at 180 °C was estimated to be ca. 880 min.

Photolysis of Benzo[2,3]bicyclo[6.1.0]nona-2,4,6-triene (5). Direct Irradiation. A solution of 94 mg of **5** in 155 ml of hexane was irradiated as described for **2** (Corex filter). Progress was monitored by VPC analyses of aliquots (20% DEGS on Chromosorb W, 130 °C) and reaction was terminated after 260 min. Concentration at reduced pressure yielded a yellow oil; VPC and ¹H NMR analysis showed essentially complete loss of starting material **5**, with formation of two products in the ratio (from VPC) 1.2:1. The mixture was chromatographed on a column of silica gel-20% AgNO₃ (1 × 10 cm). Elution with petroleum ether (250 ml) yielded 42 mg of the major product, which was identified as tetracycle **8** (ir, NMR, VPC retention time). Continued elution with 20% benzene-petroleum ether (125 ml) yielded the minor product as a yellow oil, which was further purified by VPC (as above) to give ca. 25 mg of pure **9a**: colorless oil; ir (NaCl) 3010, 2870, 1580, 1565, 1492, 1039, 1022, 828, 790, 752, 721, and 697 cm⁻¹; ¹H NMR (CCl₄) δ 6.78-7.32 (m, 4 H, aryl), 6.27 (d, *J* = 2.5 Hz, H₅ or H₆), 6.15 (d, *J* = 2.5 Hz, H₅ or H₆), 3.74 (d, *J* = 4.5 Hz, H₄), 3.54 (d, *J* = 4.5 Hz, H₇), 0.80-2.14 (m, 4 remaining protons); MS *m/e* (rel%) 168 (76), 167 (100), P + 1 (17); C₁₃H₁₂ requires 14.

Sensitized Irradiation of 5. A solution of 100 mg of **5** (92% pure by VPC, containing **2** as major impurity) and 547 mg of benzophenone in 155 ml of cyclohexane was irradiated as described for **2** (Pyrex filter). Progress was monitored by VPC analyses; the run was terminated after 14 min. Evaporation of solvent gave oily white crystals which were extracted with pentane (5 × 5 ml). Concentration of the extracts, followed by chromatography on a column of alumina (pentane elution) and concentration of the eluate, gave an oil which was analyzed by VPC (Carbowax column at 150 °C). The chromatogram showed two major peaks, starting material **5** and one photoproduct in a 20:80 ratio. The photoproduct was isolated by VPC and characterized as **6** by comparison (ir, VPC retention time) with material on hand.

References and Notes

- (1) National Science Foundation Trainee, 1973; Syracuse University Graduate Fellow, 1974-76.
- (2) For a recent review, see L. T. Scott and M. Jones, Jr., *Chem. Rev.*, **72**, 181 (1972).
- (3) See, for example, (a) M. Jones, Jr., and S. D. Reich, *J. Am. Chem. Soc.*, **89**, 3935 (1967); (b) A. G. Anastassiou and R. C. Griffith, *ibid.*, **93**, 3083 (1971); (c) J. A. Berson, R. R. Boettcher, and J. J. Volmer, *ibid.*, **93**, 1540 (1971); (d) S. Masamune and N. Darby, *Acc. Chem. Res.*, **5**, 272 (1972); (e) H. Tsuruta, T. Kumagai, and T. Mukai, *Chem. Lett.*, 933 (1973).
- (4) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970; (b) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *Acc. Chem. Res.*, **5**, 402 (1972); (c) J. A. Berson, *ibid.*, **5**, 406 (1972).
- (5) (a) M. Kato, T. Sawa, and T. Miwa, *Chem. Commun.*, 1635 (1971); (b) T. Tsuji, H. Ishitobi, and H. Tanida, *Bull. Chem. Soc. Jpn.*, **44**, 2447 (1971); (c) A. G. Anastassiou, S. S. Libsch, and R. C. Griffith, *Tetrahedron Lett.*, 3103 (1973); (d) A. G. Anastassiou and R. C. Griffith, *J. Am. Chem. Soc.*, **96**, 611 (1974); (e) L. Lombardo and D. Wege, *Tetrahedron*, **30**, 3945 (1974). For a study of some benzannulated (CH)₁₀'s, see ref 6.
- (6) L. A. Paquette, M. J. Kukla, and J. C. Stowell, *J. Am. Chem. Soc.*, **94**, 4920 (1972).
- (7) (a) R. C. Hahn and R. P. Johnson, *Tetrahedron Lett.*, 2149 (1973); (b) *J. Am. Chem. Soc.*, **97**, 212 (1975).
- (8) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
- (9) I. Tabushi, H. Yamada, Z. Yoshida, and H. Kuroda, *Tetrahedron Lett.*, 1093 (1971).
- (10) (a) F. Scully, J. Grutzner, and H. Morrison, *J. Am. Chem. Soc.*, **95**, 5100 (1973); (b) W. Lippke, W. Ferree, Jr., and H. Morrison, *ibid.*, **96**, 2134 (1974).
- (11) G. Quinkert, M. Fincke, J. Palmowski, and W.-W. Wiersdorff, *Mol. Photochem.*, **1**, 433 (1969).
- (12) (a) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961); (b) O. L. Chapman, D. J. Pasto, A. A. Griswold, and G. W. Borden, *J. Am. Chem. Soc.*, **84**, 1120 (1962).
- (13) (a) L. Lombardo and D. Wege, *Tetrahedron Lett.*, 3981 (1971); (b) P. Crews and J. Beard, *J. Org. Chem.*, **38**, 522 (1973).
- (14) L. B. Anderson, M. J. Broadhurst, and L. A. Paquette, *J. Am. Chem. Soc.*, **95**, 2198 (1973).
- (15) Cf. (a) I. Murata, Y. Sugihara, and N. Ueda, *Tetrahedron Lett.*, 1183 (1973); (b) R. M. Coates and K. Yano, *J. Am. Chem. Soc.*, **95**, 2203 (1973); (c) K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).
- (16) R. C. Hahn, P. H. Howard, S.-M. Kong, G. A. Lorenzo, and N. L. Miller, *J. Am. Chem. Soc.*, **91**, 3558 (1969), and references therein.
- (17) R. E. Carhart, D. H. Smith, H. Brown, and C. Djerassi, *J. Am. Chem. Soc.*, **97**, 5755 (1975). We are indebted to Dr. Smith for introduction to this program and guidance in its use.
- (18) (a) R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 4141 (1962); (b) W. J. Nebe and G. J. Fonken, *ibid.*, **91**, 1249 (1969).
- (19) Photochemistry of the nonbenzo analogue of **5** has been reported; see (a) ref 3d, and (b) A. G. Anastassiou, V. Orfanos, and J. H. Gebrian, *Tetrahedron Lett.*, 4491 (1969). Direct or sensitized irradiation gives cyclononatrienes, reversibly.
- (20) Comparison of the apparent stabilities of four isomeric bicyclo[7.4.0]tridecahexaenes reveals a critical dependence on the position of the six-membered ring. The isomers with [2,3] and [4,5] six-ring fusions (**10** and **11**^{5e}) have double burdens of very high ring strain and lack of aromaticity; no trace of either has been detected. Both isomers with [1,2] and [3,4] six-ring fusions (**12**^{5d} and **13**^{5c}), which require no



more than four coplanar atoms in the nine ring, have been isolated; **13** is eminently stable at room temperature. For this isomer, the only thermally allowed disrotatory ring closure would entail loss of the stabilization associated with aromaticity; this is not true for **12** (or for parent cyclononatriene).

- (21) F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, **48**, 12 (1968).