Photochemical Valence Bond Isomerization of Some Benzo-C_9H_{10} Hydrocarbons*

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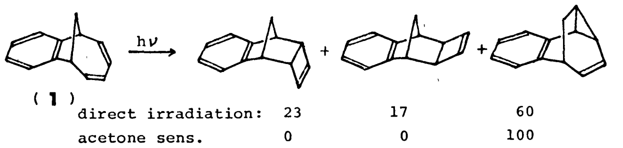
Studies have been carried out on the photochemical valence bond isomerization of some benzobicyclo-C_9H_{10} hydrocarbons, *i. e.*, benzo[8,9]bicyclo[5.2.0]nona-2,4,8-triene (**2**), benzo[2,3]bicyclo[6.1.0]nona-2,4,6-triene (**3**), *cis*-3*a*,9*b*-dihydro-1*H*-benz[*e*]indene (**6**), and benzo[6,7]bicyclo[3.2.2]nona-2,6,8-triene (**10**), with use of a low pressure mercury lamp. From a comparison of photolysis at low temperatures with that at room temperature, the stereochemical courses are discussed in terms of conformations of these compounds.

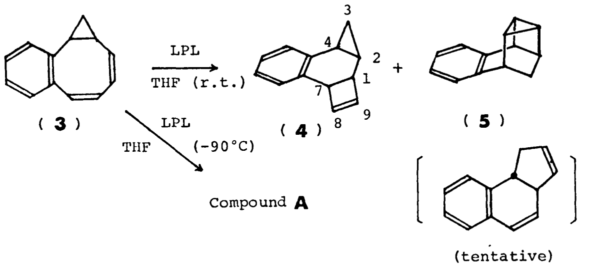
Interest has been taken in the thermal isomerization of benzo-C_9H_{10} hydrocarbons in connection with the valence bond isomerization of parent C_9H_{10}-hydrocarbons,[1] several studies[2] having been carried out. In the photochemical reaction of benzo[7,8]bicyclo[4.2.1]nona-2,4,7-triene (**1**), Hahn and Johnson reported a difference in the product distribution between the direct and sensitized irradiation.[3] Their recent paper on photochemical rearrangements of benzo[2,3]bicyclo[6.1.0]nona-2,4,6-triene (**3**) with use of a medium pressure mercury lamp (MPL)[4] has prompted us to report our independent study* on these reactions and those of other benzo-C_9H_{10} hydrocarbons photoinduced by a low pressure mercury lamp (LPL). Compound **3** was formed by thermal isomerization of **2**,[2a] both **2** and **3** being related to (*Z*,*Z*,*Z*,*Z*)-benzo[2,3]cyclonona-1,3,5,7-tetraene. Photochemical interconversion of these compounds is allowed in view of the orbital symmetry rule.



Scheme 1.

Results and Discussion

Photolysis of Benzo[2,3]bicyclo[6.1.0]nona-2,4,6-triene (3). Photolysis of **3** in tetrahydrofuran using an LPL at room temperature gave, along with some Skellysolve B insoluble polymeric material, a Skellysolve B soluble hydrocarbon mixture consisting of more than 70% *anti*-benzo[5,6]bicyclo[5.2.0.$0^{2,4}$]nona-5,8-diene (**4**) and less than 30% benzotetracyclononene (**5**).[5] The structure of **4** was deduced from its spectral data. The small coupling between H_1 and H_2 in the NMR spectrum is consistent only with the *anti*-structure. Compound **5** was also obtained by UV irradiation of *cis*-3*a*,9*b*-dihydro-1*H*-benz[*e*]indene (**6**) (*vide infra*). The latter compound is very likely to be an intermediate product in the formation of **5** from **3**. The production of **4** and **5** by photolysis of **3** with an MPL was reported by Hahn and Johnson, but their product ratio of **5** to **4** is larger than that we obtained using an LPL. Since it is reasonable to assume that the efficiency of a four pi-electrocyclic reaction is much grater with an LPL than that with an MPL, **4** was considered to be the main product in our experiment.



Scheme 2.

On the other hand, when **3** dissolved in THF-d_8 in a quartz NMR tube was irradiated at −90 °C using the same lamp, an unknown isomer **A**[6] (mass m/e 168 (M^+)) was obtained along with some polymeric material at the expense of **3**. Compound **4** was not detected.

The rigid extended conformation (**3a**) for **3** in its ground state very likely predominates at ambient temperature from the fact that thermal rearrangement occurs moderately only at elevated temperature, 150 °C, probably *via* inversion to the envelope conformer (**3b**), and that the NMR spectrum of **3** shows no temperature dependence in the range from room temperature to −90 °C. The following surmise on the photochemical behavior of **3** is possible from an examination of the molecular model. If the excitation occurs with 2537 Å light, one of the double bonds slightly conjugated to phenyl or another ethylenic group would change the conformation by turning its p-orbitals to nearly right angles to each other,[7] and the p-orbitals would enter into conjugation with either an aromatic or some other olefinic double bond as depicted in **3c** and **3d** with no additional strain. Since **3c** and **3d** are more flexible than **3a** or **3b** at room temperature, fast bonding between the nearest lobes of p-orbitals at C_4 and C_7 occurs in disrotatory motion to give **4**.[8]

On the other hand, **3** would be more firmly fixed in the extended conformation, **3a**, at −90 °C, rearrangement to **4** thus being suppressed and some other slow reaction becoming dominant. In sensitized irradiation at room temperature, **3** gives **6**[4] probably through inversion to **3b** from its triplet state followed by allowed

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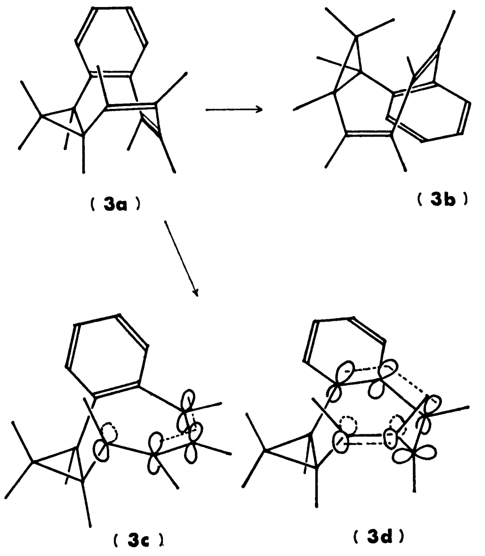
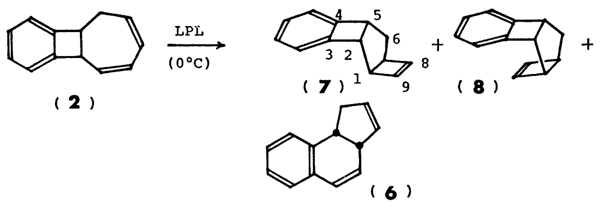
* Parts of this work (on the photolysis of Compounds **3** and **6**) were presented at the 30th Spring Meeting of the Japan Chemical Society, April 1—4, 1974 (Osaka). See the abstracts (1974), p. 1528.



Scheme 3.

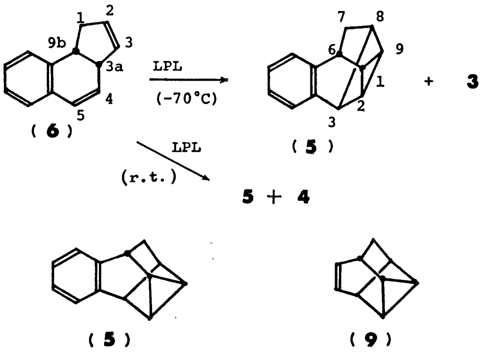
1,3-sigmatropic shift of 1-8 bond to 1-6.

Photolysis of Benzo[8,9]bicyclo[5.2.0]nona-2,4,8-triene (2). Irradiation of **2** in methanol with an LPL for 35 min gave three compounds; **6** (yield 9%), **7** (15%), and **8** (15%). They were separated by GLC, **7** and **8** being identified respectively as *anti*- and *syn*-benzo[3,4]-tricyclo[5.2.0.0^{2,5}]nona-3,8-diene in the following way. The UV spectra of the two compounds [**7** λ_{max}^{EtOH}: 262 (log ε, 3.16), 268 (3.34), 274 (3.31); **8** λ_{max}^{EtOH}; 265 sh (3.13), 270 (3.27), 276 (3.22)] showed a strong benzenoid band, suggesting the presence of benzocyclobutene moiety.[9] Their NMR spectra showed AB type proton signals characteristic of cyclobutene olefinic: δ 6.04 and 5.96 ppm (J=2.6 Hz) in **7** and δ 5.90 and 5.55 ppm (J=2.5 Hz) in **8**. Comparing the spectra with those of bicyclo[3.2.0]hept-6-ene derivatives,[10] and considering the splitting pattern of C_2 protons [**7** δ 3.76, d, $J_{2,5}$=4.0 Hz; $J_{1,2}$=quite small; **8** δ 3.94, d,d $J_{1,2}$= 9.0 Hz, $J_{2,5}$=5.0 Hz], we conclude that the structures of **7** and **8** are respectively of *anti* and *syn* conformation. Hahn and Johnson reported the formation of **3**, **6**, and **5** in addition to the main product (**7**) by photolysis of **2** with an MPL.[4] It is worth while to note that a new electrocyclic reaction product **8** was produced in an amount almost equal to that of **7** in the photolysis with an LPL. Neither **3** nor **4** was detected in the UV irradiation mixture of **2**. Even if compound **3** is formed, showing a high intensity absorption at 258 nm in UV spectrum, it would absorb light of the LPL to undergo change to **4** and others. The presence of **6** and the absence of **4** suggest a possible direct route from **2** to **6** under the present conditions.



Scheme 4.

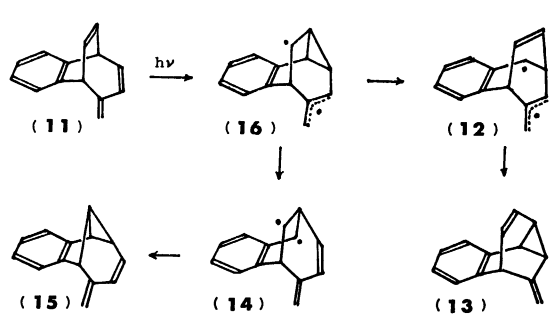
Photolysis of cis-*3*a,*9*b-*Dihydro-1*H-*benz*[e]*indene (6).* In the photochemical isomerization of the parent C_9H_{10}-hydrocarbons, it was reported that *cis*-8,9-dihydroindene and *cis*-bicyclo[6.1.0]nona-2,4,6-triene afford a similar photostationary mixture *via cis-trans* interconversion between (E,Z,Z,Z)- and (Z,Z,Z,Z)-cyclonona-1,3,5,7-tetraene.[1a] Taking this into consideration, we studied the photochemical behavior of **6**. Benzo[4,5]tetracyclo[4.3.0.0^{2,9}.0^{3,8}]non-4-ene(**5**) was formed readily, along with **4**, by irradiation of **6** with an LPL at room temperature. Compound **5** was separated by means of GLC and characterized by UV and NMR spectra. The unusually high field resonance of one of the methylene protons in the NMR spectrum was observed in the case of a similar compound (**9**).[1b] The formation of **3** from **6** has been proved by photolysis at low temperature, a condition which suppresses the conversion of **3** into **4**.



Scheme 5.

Thus compound **6** dissolved in THF in a quartz NMR tube was irradiated with an LPL at −65——70 °C and was partly transformed into **5** along with a small quantity of **3**. The acetophenone sensitized irradiation of **6** proceeded more distinctly, compound **5** being the only product detected.

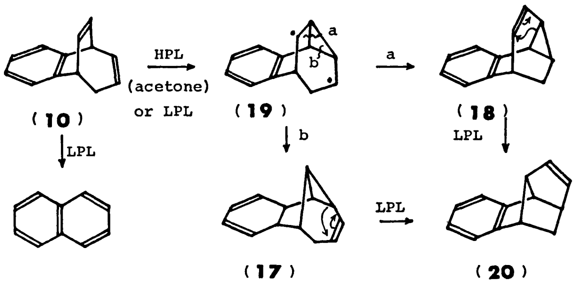
Photolysis of Benzo[6,7]bicyclo[3.2.2]nona-2,6,8-triene (10). Photochemical isomerization of **10** has been studied, since 4-oxo derivative of **10** is photochemically related to 1-oxo derivative of **6**.[11] Sensitized photochemical isomerization of this sort of compound has been extensively studied and found to proceed in two directions through di-pi-methane mechanism.[12] In the case of the 9-*exo*-methylene analogue (**11**) of **10**, two products are formed, of which **13** is formed through stabilized biradical **12**



Scheme 6.

preferably to **15** produced through less stabilized biradical **14**.

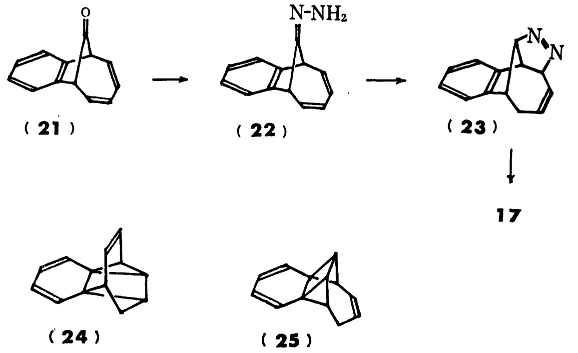
In contrast, photolysis of **10** in acetone[13] using a high pressure mercury lamp (HPL) through a Pyrex filter gave rise to the formation of **17** and **18** in 52 and 9% yields, respectively, accompanied by recovery of **10** (15%). If we assume that the initial bonding occurs between olefinic carbons as observed in the case of benzobicyclo[2.2.2]octatriene,[14] the reaction is governed by the comparative easiness of bond fission at *b* rather than *a* in the biradical intermediate (**19**). From an examination of the molecular model, the bond C_1–C_2 is seen to be more parallel to benzenoid pi-orbitals than the bond C_1–C_8. Thus the fission at *b* predominates over *a* to give **17** as the main product.



Scheme 7.

The difference in behavior of benzobicyclo[2.2.2]-octatriene in direct and sensitized irradiation[14] led us to study direct photolysis of **10**. When irradiation was carried out by use of an LPL at room temperature, **10** in ether was transformed into **17** (18%) and **18** (12%) accompanied by naphthalene (8%)[15] and a new compound (**20**)(11%). Both **17** and **18** isolated in pure form were independently transformed entirely into **20** by photolysis (LPL) in quartz NMR tubes in ether solution; *i.e.*, **17** gave **20** in 52% yield after 12 h irradiation, and **18**, **20** in 4% yield after 15 h irradiation. In acetone using a HPL, both **17** and **18** remained unchanged. Examination of Newman's projection formula of **17** and **18** revealed that in **17**, pi-electron at C_3 position is nearly parallel to the sigma bond at C_2 extended to C_9, while in **18**, the C_6–C_7 olefinic plane bisects the interior angle at C_8 of the three membered ring. It is reasonable to assume that the fission of C_2–C_9 in **17** is easier than that of C_2–C_8 in **18**, if we assume that the difference in ring strains between **17** and **18** is small. From the experiments, it is evident that, in contrast to benzobicyclo[2.2.2]-octatriene, **10** does not undergo the rearrangement involving aromatic-olefinic [$\pi2+\pi2$] intermediates such as **24** and **25**, **20** being a secondary product originating mainly from **17** and partly from **18** on irradiation of **10** using an LPL.

*Characterization of **17**, **18**, and **20**.* Compound **17** was synthesized starting from benzo[7,8]bicyclo-[4.2.1]nona-2,4,7-trien-9-one (**21**)[16] as follows. Its hydrazone (**22**) was treated with potassium *t*-butoxide in DMSO giving its isomeric azo-compound (**23**), which was either pyrolyzed at 180 °C or photolyzed with a HPL (Pyrex filter) to give **17**, each in 70% yields. The compound was identical with a product obtained by photolysis of **10**.



Scheme 8.

Benzobarbaralane (**18**) is one of the products obtained by the thermal rearrangement of **10**,[2b] the physical data being identical with those reported.

The structure of **20** was deduced mainly on the basis of its NMR spectrum and decoupling experiments. The UV spectrum [$\lambda_{\max}^{\text{EtOH}}$: 262 (log ε, 3.14), 268 (3.16), 275 (3.13)] showed the presence of benzocycloalkene moiety of ring size less than 5.[17] Introduction of a methylene group and an ethylenic linkage without conjugation to aromatic ring, and its structural relationship to **17** and **18** make up the structure of **20**.

As expected, the proton coupling constants (Table 1) of **20** were similar to those of norbornane and norbornene,[18] strongly supporting the structure.

TABLE 1. THE PMR CHEMICAL SHIFTS AND THE COUPLING CONSTANTS OF COMPOUND **20** BY MEANS OF THE FIRST-ORDER ANALYSIS OF THE 100 MHz SPECTRA AND ITS DECOUPLING EXPERIMENTS

Chemical shifts (δ):

7.3—6.74 ppm	m	Ar-H	2.74—2.56	m	H_3
6.38	d, d	H_9	2.50—2.32	m	H_1
5.72	d, d, d	H_8	1.38	d, d	H_{2exo}
3.3—3.02	m	H_6, H_7	1.19	d, d	H_{2endo}

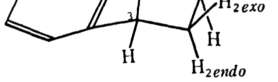
Coupling constants (J):

$J_{2exo,3}=5.0$ Hz $J_{1,9}=3.4$ Hz

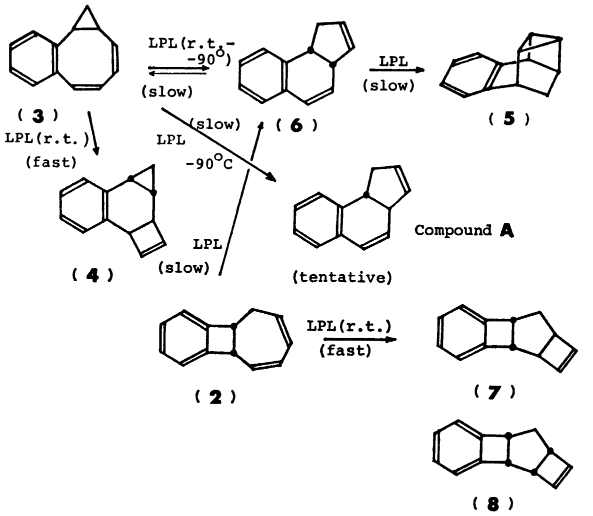
$J_{1,2endo}=4.5$ Hz $J_{7,8}=2.8$ Hz

$J_{8,9}=5.8$ Hz $J_{2exo,2endo}=11.0$ Hz

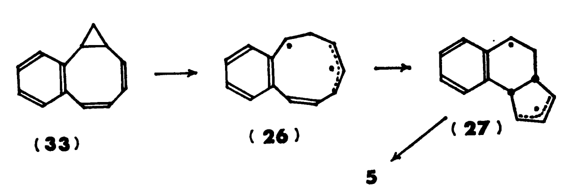
$J_{2endo,3}$, $J_{1,2exo}$, $J_{3,7}$; quite small



The photochemical relationship between compounds **2**—**8** is summarized in Scheme 9. We could not obtain evidence for the transient formation of **26** when **2**, **3** and **6** were photolysed. We consider that the formation of **5** on photolysis of **2** and **3** takes place *via* an intermediate **6** and not *via* a route involving **26** and **27**.



Scheme 9.



Scheme 10.

Experimental

The NMR spectra were obtained on a JEOL Model PS-100 spectrometer, with tetramethylsilane as the internal standard. The chemical shifts are expressed in ppm from TMS. The Mass spectra were measured on a Hitachi RMU-6 mass spectrometer by the indirect injection method at 180 °C. The IR were recorded on a JASCO Model IRE spectrometer, and the UV on a Hitachi Recording Spectrometer, Model EPS-2 or Model 323. VPC analysis was carried out on a Varian Aerograph Model-90P gas chromatograph under the quoted conditions. The NMR measurements at low temperatures were carried out at the University of Alberta by courtesy of Professor Satoru Masamune.

*Photolysis of Benzo[2,3]bicyclo[6.1.0]nona-2,4,6-triene (**3**). Irradiation at Room Temperature*: The triene **3** (14 mg), dissolved in anhydrous THF (1 ml) in a sealed quartz test tube, was externally irradiated with an LPL (200 Watts) for 30 min. The subsequent evaporation of the solvents gave a semi-solid, which was extracted with Skellysolve B. The Skellysolve B soluble oily material (10.5 mg) showed an NMR spectrum mainly composed of **4**, along with some **5**. The GLC separation of **4** was carried out using GLC [10% Apiezone L on Chromosorb WAW 1/4″×6 ft; He flow rate, 40 ml/min; column temperature, 150 °C; retention time, 20 min]. **4** UV, $\lambda_{\max}^{\text{EtOH}}$; 258 (infl.), 270.5, 280. NMR (CCl_4) δ: 6.7—7.2 (4H, m), 6.20, 6.10 (H_8, H_9, AB-type, $J=2.7$ Hz), 3.70, 3.50 (H_1, H_7, AB-type, $J=4.5$ Hz), 1.86 (H_4, d, $J=2.1$, t, $J=4.3$ Hz), 1.43 (H_{3exo}, d, $J=2.9$, t, $J=4.3$ Hz), 1.06 (H_2, d, $J=4.3$, t, $J=2.1$ Hz), 0.22 (H_{3endo}, d, $J=2.9$, t, $J=2.1$ Hz). MS (80 eV), *m/e* (rel. intensity), 168(M^+,63), 167(100), 165(46), 153(73), 152(52), 141(39), 115(55), 83(27). Found: C, 92.88; H, 7.12%. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19%.

Irradiation at −90 °C: Compound **3** (17 mg), dissolved in THF-d_8 (0.3 ml) containing 15% of TMS, was degassed and sealed in a quartz NMR tube. This was then irradiated at −90 °C for 6 h while the reaction was monitored by NMR measurements at −90 °C. The gradual appearance of a sharp singlet at 6.48 ppm in compensation for those of the starting material was noticed. After six hours' irradiation, the peak height at 6.48 ppm became almost the same intensity as the 2H signal at 5.74 ppm of the starting **3**. The NMR spectra of the mixture remained unaltered when taken at several elevated temperatures, *i.e.*, −60, −30, 0 °C, and room temperature. After the evaporation of the solvent, a Skellysolve B insoluble material (4 mg) was filtered out and the soluble part (13 mg) was separated by GLC [10% Apiezone L on Chromosorb WAW, 1/4″×5 ft; He, 38 ml/min; 138 °C]. The materials corresponding to Peak 1 [retention time, 17.9 min; 7.5 mg] and Peak 2 [r.t., 21.1min; 2.6 mg] were collected. The physical data of the former were consistent with those of **3**.[17)] The latter was separated again using GLC[10% Carbowax 20M on Chromosorb WAW 1/8″×6ft; He, 40 ml/min; 160 °C] and gave two peaks in almost equal intensities [r.t., (*i*) 11.8 min; (*ii*) 12.9 min]. From the physical data, it was revealed that the compound corresponding to *i* was an unknown substance, A[6)], while the one corresponding to *ii* was **6**.[17,18)] The physical data of **3** and **6**: **3**; IR $\nu_{\max}^{\text{liq. film}}$: 3050, 3000, 2910, 2840, 1497, 1455, 1448 sh, 1125, 1115, 1030, 985, 945, 895, 850, 830, 790, 782, 760, 724, 700 cm^{-1}. UV $\lambda_{\max}^{\text{EtOH}}$: 259 (log ε; 3.69), 269(3.61). NMR (CCl_4) δ: 7.40—6.80 (4H, m), 6.53 (H_4, d, $J=12$ Hz), 5.99 (H_5, broad d, $J=12$ Hz), 5.71 (H_6, H_7 ,broad s), 2.01 (H_1, broad t, d, $J_{1,8}=J_{1,9exo}=8.8$ Hz, $J_{1,9endo}=6.0$ Hz), 1.57 (H_8, broad t, d, $J_{1,8}=J_{8,9exo}=8.8$ Hz, $J_{8,9endo}=6.0$ Hz), 1.06 (H_{9exo}, t, d, $J_{1,9exo}=J_{8,9exo}=$ 8.8 Hz, $J_{9exo,9endo}=4.0$ Hz), 0.53 (H_{9endo}, t, d, $J_{1,9endo}=$ $J_{8,9endo}=6.0$ Hz, $J_{9exo,9endo}=4.0$ Hz). MS (80 eV), *m/e* (rel. intensity), 168 (M^+, 84), 167(100), 166(22), 165(47), 153 (55), 152(41). Found: C, 92.52; H, 7.27%. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19%. **6**; UV $\lambda_{\max}^{\text{EtOH}}$: 225 sh (log ε; 4.32), 261(3.89), 269.5(3.90), 280 sh (3.66). NMR(CCl_4) δ: 7.08—6.81 (4H, m), 6.21 (H_5, d, d, $J_{4,5}=9.6$ Hz, $J_{5,3a}=2.6$ Hz), 5.93—5.70 (H_2, H_3, m), 5.46 (H_4, $J_{4,5}=$ 9.6 Hz, $J_{4,3a}=2.6$ Hz), 3.71—3.29 (2H, m), 2.86—2.11 (2H, m). MS (80 eV), *m/e* (rel intensity), 168 (M^+, 100), 167(97), 166(26), 165(46), 153(53), 152(32). Found: C, 92.65; H, 7.17%. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19%.

*Photolysis of Benzo[8,9]bicyclo[5.2.0]nona-2,4,8-triene (**2**).* Compound **2** (170 mg), dissolved in methanol (150 ml), was irradiated using an LPL (10 watts) for 35 min under nitrogen with external cooling. After the rough separation of the products by column chromatography on alumina, the hydrocarbon mixture was separated by GLC [10% Apiezone L on Chromosorb WAW 1/4″×5 ft; He 40 ml/min; 150 °C], yielding **7** (15%), **8** (15%), and **6** (9%). Physical data of **7** and **8**: **7**; NMR (CCl_4) δ: 7.25—6.76 (4H, m), 6.04 (1H, d, $J=2.6$ Hz), 5.96 (1H, d, $J=2.6$ Hz), 4.32 (H_5, m), 3.76 (H_2, d, $J=4.0$ Hz), 3.72—3.56 (H_7, m), 3.38 (H_1, d, $J=3.5$ Hz), 2.08—1.60 (H_6, m). **8**; NMR (CCl_4) δ: 7.15—6.60 (4H, m), 5.90 (1H, d, $J=2.5$ Hz), 5.55 (1H, d, $J=2.5$ Hz), 4.32—4.1 (H_5, m), 3.94 (H_2, d, d, $J=9.0$, 5.0 Hz), 3.72—3.48 (H_1, H_7, m), 1.80—1.52 (H_6, m).

*Photolysis of Benzo[2,3]bicyclo[4.3.0]nona-2,4,7-triene (**6**).* Compound **6** (50 mg), dissolved in THF (0.6 ml) in a quartz NMR tube, was degassed and sealed. The tube was then irradiated externally with an LPL (200 watts) while being cooled externally with dry ice–methanol in a quartz Dewar bottle with a quartz window. In the course of 7 hours' irradiation, a characteristic broad doublet at δ 0.61 ppm appeared, and gradually increased in the NMR spectrum. The separation of the products by column chromatography on silicic acid gave a colorless liquid (21 mg), which contained

6, **5**, and **3** in a ratio of *ca.* 6 : 3 : 1, as estimated by means of the NMR spectrum. The GLC separation of the liquid was carried out as follows: 10% Apiezone L on Chromosorb WAW 1/4″×6 ft; He, 40 ml/min; 147 °C: Retention times; **5**, 22 min; **3**, 24 min; **6**, 28 min. **5**; NMR (CCl_4) δ: 7.2—6.8 (4H, m), 3.44 (2H, m), 2.56 (1H, m), 2.88 (1H, m), 2.05—1.6 (3H, m), 0.62 (1H, d, J=10 Hz).

Similarly, **6** (20—70 mg), dissolved in THF (80 ml), was irradiated using an LPL (10 watts) at room temperature for 1 h under nitrogen; this resulted in **5** and **4**, instead of **5** and **3**. The NMR analysis of the products revealed that it contained **5** and **4** in a ratio of *ca.* 3 : 1.

Photolysis of Benzo[6,7]bicyclo[3.2.2]nona-2,6,8-triene ***(10)***.

Irradiation Using a HPL (Ushio High Pressure Mercury Lamp, UM-425, 450 Watts) in Acetone: Compound **10** (300 mg), dissolved in acetone (350 ml), was irradiated using a HPL through a Pyrex filter under nitrogen for 70 min. After a usual work up, the product was roughly chromatographed on silicic acid (hexane), giving a colorless liquid (228 mg). The GLC separation of the liquid, performed on 10% Apiezone L on Chromosorb WAW at 141 °C, gave three peaks, which led us to estimate the yields as follows; **10** (15%), **17** (52%), and **18** (9%). The tetracyclic compound, **17**, was identical with the sample synthetically obtained below. **18**; IR $\nu_{max}^{liq.\ film}$: 3020, 2916, 2840, 1629, 1495, 1462, 1040, 1025, 1000, 962, 945, 868, 835, 810, 781, 767, 740, 707 cm^{-1}. NMR (CCl_4) δ: 7.3—6.8 (4H, m), 5.88—5.4 (2H, finely-splitted m), 3.20 (1H, b), 2.52 (1H, t, J=8Hz), 2.3—1.9 (2H, m), 1.44 (1H, t, J=2Hz). MS (80 eV) *m/e* (rel intensity), 168(M$^+$, 100), 167(90), 165(29), 153(48), 152(27).

Irradiation Using an LPL at 0 °C: Compound **10** (188 mg), dissolved in ether (230 ml), was irradiated using an LPL (10 watts, immersion type) for 4.5 h under nitrogen while the reaction was monitored with TLC. After the evaporation of the solvent, the residue was chromatographed on silicic acid (hexane), and the hydrocarbon fractions were collected. The GLC analysis [5% Apiezone L, 1/4″×6 ft; He, 50 ml/min; 141 °C] revealed that it contained five species, estimated to be as follows: Retention times (yield); (a) 3.2 min (naphthalene, 8%), (b) 5.7 min (**20**, 11%), (c) 8.1 min (**10**, 18%), (d) 9.4 min (**17**, 18%), (e) 12 min (**18**, 12%). They were separated in pure forms and characterized. **20**; IR $\nu_{max}^{liq.\ film}$: 3060, 2970, 2865 1572, 1328, 1265, 958, 915, 866, 726, 729 cm^{-1}. NMR: Table 1. MS (80 eV), *m/e* (rel intensity); 168 (M$^+$, 88), 167 (100), 165 (28), 153 (38), 152 (23).

The Direct Irradiation of ***17*** *and* ***18*** *Using an LPL*: Compound **17**, (20 mg), dissolved in anhydrous ether (0.5 ml) in a quartz NMR tube, was irradiated using an LPL (10 Watts) for 12 h at 0—5 °C. The NMR and GLC analysis of the products showed that they were composed of **20** and **17** in a ratio of 48 : 52. The same experiment using **18** (20 mg) instead of **17** was also carried out (15 hs' irradiation). The products were **20** and **18** in a ratio of 4 : 96.

Synthesis of ***17***. *Preparation of the Hydrazone* ***(22)***: The **21** ketone (180 mg) and 100% hydrazine hydrate (0.4 ml), dissolved in absolute ether (7 ml), were stirred under reflux for 20 h. The solvent was then evaporated *in vacuo*, and the residual liquid, dissolved in benzene, was dried with anhydrous sodium sulfate. The subsequent evaporation of the solvent gave a crude hydrazone (220 mg). **22**; IR $\nu_{max}^{liq.\ film}$: 3360, 3200, 3020, 2940 cm^{-1}, (no νC=O). NMR ($CDCl_3$) δ: 7.22, 7.19 (4H, Ar-H), 6.4—5.5 (4H, m), 4.56 (1H, d, J=8 Hz), 4.08 (1H, d, J=8 Hz), 6.0—4.0 (very broad, N-H).

9,10-Diazabenzo[2,3]tricyclo[6.3.0.0^{4,11}]undeca-2,6,9-triene ***(23)***: To the hydrazone (**22**), dissolved in anhydrous DMSO (1.5 ml), was added, drop by drop, a solution of potassium *t*-butoxide (1.5 g) in DMSO (3.8 ml) over a period of 95 min. After the mixture had then been stirred further for 19 h at room temperature, it was poured into water and extracted with dichloromethane. The combined organic extracts were washed with water, dried (anhydrous Na_2SO_4), and concentrated to dryness. The residue was chromatographed on silicic acid, using hexane–ether (10 : 1 v/v) as the solvent. The crude crystalline product (138 mg) was purified by sublimation. **23**; 100 mg (52%), mp 80—81 °C. UV λ_{max}^{EtOH}: 261.5 (log ε, 2.90), 268.5 (3.08), 275.5 (3.09), 335(2.53). IR $\nu_{max}^{CCl_4}$: 3040, 2960, 1537, 1485, 1465 cm^{-1}. NMR (CCl_4) δ: 7.2—6.84 (4H, m), 5.58 (H_{11}, t, J=8Hz), 5.68—5.16 (H_6,H_7,H_8, m), 3.77—3.56 (H_4, m), 3.31 (H_1, bt, J=8Hz), 2.38—1.80 (H_5, 2H, m). Found: C, 79.71; H, 6.25; N, 13.81%. Calcd for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.28%.

Preparation of ***17***: *Photolysis of the Azo Compound* ***(23)***. The azo compound, **23** (12 mg), dissolved in anhydrous ether (1.5 ml), was irradiated for one hour with a HPL through a Pyrex filter at room temperature. Silicic acid chromatography of the products gave pure **17** (7 mg; 69%).

Thermal Decomposition of ***23***. Compound **23** (30 mg), dissolved in diethylene glycol (1 ml), was heated at 180 °C for 4 h. The reaction mixture was then poured into water and extracted with ether. After being washed and dried, the combined organic layer was concentrated and chromatographed on silicic acid (hexane–ether 1: 1 v/v) to give **17** (18 mg; 70%), along with recovered **23** (7 mg). **17**; IR $\nu_{max}^{liq.\ film}$: 3025, 2910, 2840, 1483, 1462, 1182, 1142, 1027, 998, 943, 912, 880, 843, 808, 772, 745, 718 cm^{-1}. UV λ_{max}^{EtOH}: 266.5 sh (log ε, 2.95), 272(3.07), 279.5(3.03). NMR (CCl_4) δ: 7.2—6.7 (4H, m), 5.7—5.3 (H_3, H_4, m), 3.50 (H_6, d, t, $J_{1,6}$=6.0 Hz, $J_{6,5exo}$=$J_{6,5endo}$=3.2 Hz), 2.74—2.32 (H_{5exo}, m), 2.50 (H_9, d, d, $J_{1,9}$=6.0, $J_{2,9}$=7.5 Hz), 2.12 (H_1, q, $J_{1,9}$=$J_{1,6}$=6.0, $J_{1,2}$=7.5 Hz), 1.87 (H_{5endo}, d,d,d, $J_{5endo,5exo}$=16.5 Hz, $J_{4,5endo}$=5.5 Hz, $J_{6,5endo}$=2.7 Hz), 1.52 (H_2, broad t, $J_{2,9}$=$J_{1,2}$=7.5 Hz). MS (80 eV), *m/e* (rel. intensity), 168 (M$^+$, 91), 167(100), 165(49), 153(77), 152(66), 141(21), 115(47). Found: C, 92.81; H, 7.29%. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19%.

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5) It has been reported that Compounds **4** and **5** were formed in a ratio of 1.0 : 1.2 when Compound **3** was irradiated using an MPL.[4]

6) Owing to its limiting amount, the structure of the unknown substance, **A**, has not yet been limited. This compound was thermally stable and showed a fragmentation pattern in its mass spectrum very similar to that of **6**. The UV spectrum of this compound exhibited strong absorptions at 247 and 255 nm. Its NMR spectrum showed a sharp aromatic proton peak at 7.01, olefinic at 6.38 and 5.96 ppm and aliphatic at 3.6—2.1 ppm in a ratio near 4 : 2 : 2 : 4. The catalytic hydrogenation of **A** gave 2,3-dihydro-1*H*-benz[*e*]indene and a substance whose UV spectrum was similar to that of *cis*- or *trans*-2,3,3*a*,4,5,9*b*-hexahydro-1*H*-benz[*e*]indene. Therefore we tentatively identified this compound, **A**, as *trans*-3*a*,9*b*-dihydro-1*H*-benz[*e*]indene.

7) When Compound **3** was irradiated with an LPL at room temperature in the presence of O_2, a mixture of dialdehydes was formed by the cleavage of one of the double bonds. The spectral data of the product: IR $\nu_{\max}^{\text{liq. film}}$: 2840, 2750, 1700(vs), 1680(vs), 1620, 1600 cm^{-1}. UV $\lambda_{\max}^{\text{EtOH}}$: 288. NMR ($CCl_4$) δ: 8.64 (d,d, J=2.5 Hz, 6 Hz), 9.72 (d, J=8 Hz).

Another explanation is possible involving the isomerization of one of the *cis* double bond to *trans*, followed by thermal conrotatory ring closure to a cyclobutene, as is often observed in medium-sized cyclic polyenes. However we consider this as an unlikely possibility because we could not detect in the NMR spectra either a *trans* compound isomeric to **3**, taken at −90 °C just after the irradiation of **3** at the same temperature, or **4**, taken at room temperature after the solution had been allowed to warm up.

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