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The Photorearrangement of Benzonorbornadiene

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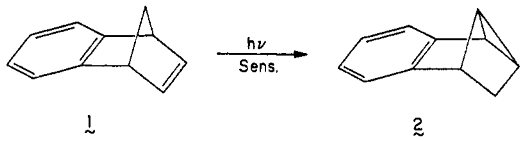
Abstract: The triplet sensitized rearrangement of benzonorbornadiene (1,4-dihydro-1,4-methanonaphthalene) has been studied in detail. Through labeling experiments, evidence is obtained for an intermediate diradical which resembles a partially closed quadricyclane ring. The quantum yield for the reaction is 0.5 with the T_1 state of benzonorbornadiene estimated to be 70 kcal. No fluorescence was detected from benzonorbornadiene and evidence is presented which points to a facile rearrangement during direct irradiation which differs from the triplet-state reaction.

The photochemistry of the bicyclo[2.2.1]hepta-2,5-diene ring has been explored extensively. The hydrocarbon has been studied in solution[2] and in the vapor phase,[3] and recently 7-oxo derivatives[4] and 7-aza derivatives[5] have been investigated. The primary photoprocess in solution is isomerization to the tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane ring (quadricyclane). The details of this isomerization, however, are poorly understood.

For instance, the isomerization is effected by direct irradiation[2a,4,6] or by sensitization.[2b,6d,7] The quantum yield has not been reported in any of these cases and the excited states involved (*i.e.*, the triplet, first excited singlet, vibrationally excited ground state, or some combination thereof) have not been assigned.[8] The ring closure is often depicted as a concerted process although there is no experimental evidence on the point and different excited states could have different pathways.

The work on benzonorbornadiene was initiated to study the effect of incorporating one of the bicycloheptadiene double bonds in an aromatic ring. *A priori*, the primary products could be a quadricyclane, methylnaphthalenes,[9] or benzyne and cyclopentadiene if reactions analogous to norbornadiene take place. Also, based on absorption spectra and by analogy to barrelene and benzobarrelene,[10] benzonorbornadiene should have E_{S_1} lower than and E_{T_1} higher than, norbornadiene. This should enhance intersystem crossing[11] and increase the triplet concentration on direct irradiation of benzonorbornadiene relative to norbornadiene.

When the rearrangement of benzonorbornadiene **1** gave **2** instead of the expected products,[13] the mechanism of the rearrangement was investigated further.



Results

Prolonged periods of direct irradiation did not appear to give any **2**, while acetophenone sensitization gave good conversion. The need for a triplet sensitizer was also established for the diacetoxy derivative,[13] and three mechanisms were postulated to explain the results (Scheme I).

Precedence can be found for each. Intermediate **3** resembles the proposed intermediate for hydride reduc-

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[2] (a) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); (b) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

[3] B. C. Roquitte, *ibid.*, **85**, 3700 (1963).

[4] (a) E. Payo, L. Cortès, J. Mantècon, C. Rivas, and G. de Pinto, *Tetrahedron Lett.*, 2415 (1967); (b) H. Prinzbach, M. Arguelles, and E. Druckrey, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1039 (1966).

[5] H. Prinzbach, R. Fuchs, and R. Kitzing, *ibid.*, **7**, 67 (1968).

[6] (a) S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **80**, 1950 (1958); (b) H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963); (c) D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Lett.*, 2779 (1965); (d) H. Prinzbach and J. Rivier, *ibid.*, 3713 (1967); (e) H. Tanida, Y. Hata, Y. Matsui, and I. Tanaka, *J. Org. Chem.*, 30, 2259 (1965); (f) J. R. Edman, *ibid.*, **32**, 2920 (1967); (g) H. Prinzbach and J. Rivier, *Angew. Chem. Intern. Ed. Engl.*, **6**, 1068 (1967); (h) H. Prinzbach, M. Arguelles, P. Vogel, and W. Eberbach, *ibid.*, **6**, 1070 (1967).

[7] (a) P. R. Story and S. R. Fahrenholtz, *J. Am. Chem. Soc.*, **86**, 527 (1964); (b) P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **86**, 4211 (1964).

[8] Roquitte[3] concluded from studying the direct irradiation of norbornadiene in the vapor phase and in ether solution that cyclopentadiene and acetylene ($\Phi \approx 0.45$ in vapor and $\Phi = 0.12$ in ether) probably are formed from a higher vibrational level of the first excited singlet state while the origin of toluene ($\Phi = 0.042$ in both media) is unknown. No quadricyclane was detected. It seems reasonable to assume that quadricyclane forms in the vapor phase but because of excess vibrational energy, which is lost in solution, isomerizes back to norbornadiene. The lack of quadricyclane formation in ether is puzzling.[2]

[9] S. J. Cristol and R. Caple [*J. Org. Chem.*, **31**, 585 (1966)] find α- and β-methylnaphthalene among the thermolysis products of benzonorbornadiene.

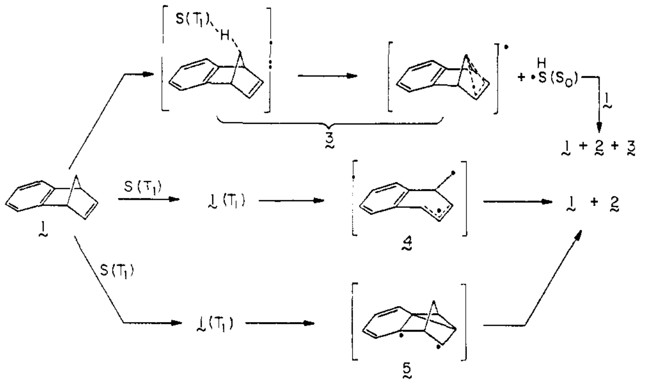
[10] R. S. H. Liu, private communication.

[11] The energy gap between S_1 and T_1 is important in determining the rate of intersystem crossing.[12]

[12] (a) R. E. Kellogg, *J. Chem. Phys.*, **44**, 411 (1966); (b) R. G. Bennett and P. J. McCartin, *ibid.*, **44**, 1969 (1966).

[13] J. R. Edman, *J. Am. Chem. Soc.*, **88**, 3454 (1966).

Scheme I



tion of 7-halonorbornadienes. This reaction gives a good yield of tricyclo[4.1.0.0^{3,7}]-4-heptene.[14] Intermediate 4 is analogous to the proposed structure initially formed in the rearrangement of norbornadiene to toluene.[3] Structure 5 could be representative of the norbornadiene to quadricyclane rearrangement. A common feature of all routes is the possibility of forming more than one product, including starting material, which will necessarily lead to a quantum yield of less than one.

The irradiation experiments are summarized in Table I.

Table I. Irradiation of Benzonorbornadiene

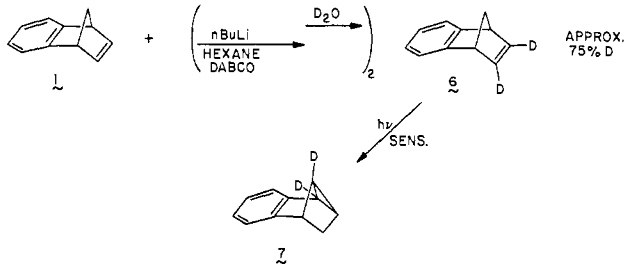
Sensitizer	T_1, kcal	Result	Φ^a
None[b]		−	
Xanthone	74.2[c]	+	
Acetophenone	73.6	+	0.51, 0.47
Benzophenone	68.5	+	0.037
Triphenylene[d]	66.6	+	
Fluorenone	51 (53.3)	−	
Anthracene[e]	42.6, T_2 (74.4)	+	
9,10-Dichloroanthracene[e]	40.2, T_2 (?)	+	
9,10-Dibromoanthracene[e]	40.2, T_2 (?)	+	

[a] The isomerization of myrcene was used for an actinometer: R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, **89**, 4936 (1967). [b] Run in a quartz apparatus with 2537-Å light. [c] Xanthone is a good sensitizer and qualitatively appeared similar to acetophenone. [d] Very poor sensitizer. Product peak on glpc just detectable. [e] Energy transfer from T_2: R. S. H. Liu and J. R. Edman, *J. Am. Chem. Soc.*, **90**, 213 (1968).

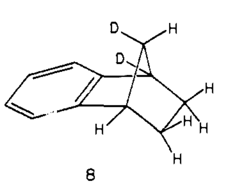
The direct irradiation experiment was performed under conditions[15] where an identical quantity of the same concentration norbornadiene was quantitatively converted to quadricyclane. The photorearrangement of benzonorbornadiene to 2 does not take place, therefore, from the S_1 state. On the basis of the sensitized experiments it is concluded that the rearrangement occurs from the T_1 state and that the rate of intersystem crossing in benzonorbornadiene is quite slow. Intermediate 3 is highly unlikely based on the fact that triphenylene sensitizes the rearrangement and an abstraction reaction has never been demonstrated for triphenylene.[16]

The quantum yield of 0.5 for acetophenone is consistent with either intermediate 4 or 5. The labeled compound 6 was synthesized and rearranged to distinguish between them (Scheme II). Compound 6 is described in the literature.[17] However the current synthesis is more reliable.[18]

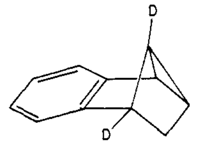
Scheme II



Although it is difficult to prove the structure of compound 7 unambiguously, the evidence is convincing. Photoproducts 2 or 7 can be reduced to benzonorbornene by hydrogen with a palladium-on-charcoal catalyst. When 7 is reduced with hydrogen, the benzonorbornene obtained clearly has a deuterium at one of the benzylic positions as shown by integration of the pmr spectrum. A comparison of the pmr spectrum of this benzonorbornene with that of published spectra[19] and the spectrum of an authentic sample established 8 as the structure of the reduced compound. This result does not eliminate 9 as the precursor of 8, but it does eliminate intermediate 4 from further consideration.[20]



8



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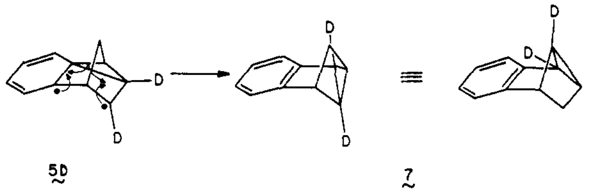
The product from a labeled intermediate such as 5D, however, would be 7 and not 9 (Scheme III). Furthermore, it is difficult to conceive of a reasonable mecha-

Scheme III



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[14] P. R. Story, *J. Am. Chem. Soc.*, **83**, 3348 (1961). A similar reaction occurs with 7-halobenzonorbornadienes: S. J. Cristol and G. W. Nachtigall, *ibid.*, **90**, 7133 (1968).

[15] Rayonet photochemical reactor from Southern N.E. Ultraviolet Co. equipped with 16 G8T5 bulbs.

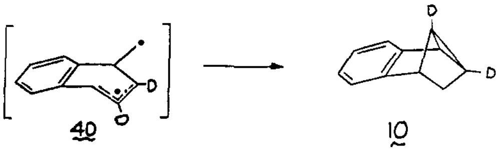
[16] R. R. Saures and A. Shurpik, [*J. Org. Chem.*, **33**, 799 (1968)] observe a similar rearrangement in the bicyclo[3.2.1]heptadiene system. Significantly, they did not report any abstraction of the allylic protons in the presence of ketonic sensitizers.

[17] T. Goto, A. Matematsu, Y. Hata, R. Muneyuki, H. Tanida, and K. Tori, *Tetrahedron*, **22**, 2213 (1966).

[18] We thank Professor A. Streitwieser, Jr., for drawing the procedure of C. G. Screttas and J. F. Eastham [*J. Am. Chem. Soc.*, **87**, 3276 (1965)] to our attention.

[19] (a) K. Tori, Y. Hata, R. Muneyuki, Y. Takano, and T. Tsuji, *Can. J. Chem.*, **42**, 926 (1964); (b) K. Tori, K. Anono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, **9** (1966).

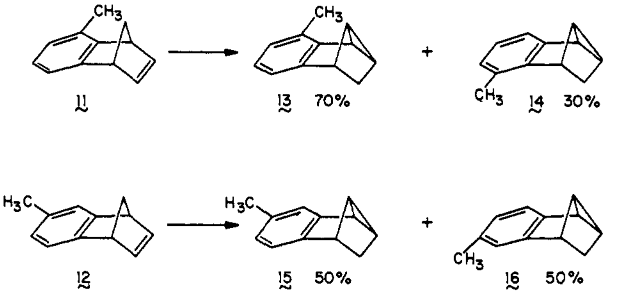
[20] Deuterated 4 would give 10. Reduction of 10 would give a benzonorbornene with no deuterium at the benzylic positions.



nism which would convert **6** exclusively to **9**. Assignment of the pmr spectrum of **2** is more consistent with **7** than with **9**.[21]

Evidence for an intermediate involving the benzene ring carbons was obtained by rearranging the monomethyl compounds **11** and **12** (Scheme IV). Structures **13** and **14** were tentatively assigned by analogy to the pmr spectrum of the aromatic region of **2**.[21] The downfield methyl group was assigned to **13**. Regardless of the accuracy of the assignment, the *ortho* methyl group appears to have a directive effect on the rearrangement while the *meta* group does not.

Scheme IV



The direct irradiation of benzonorbornadiene was also investigated further and was found to be concentration dependent. Irradiation of $1.3 \times 10^{-3}\,M$ solutions of **1** in a quartz fluorometric cell gave the results shown in (Figure 1). The end product, depicted by curve d, was stable for 24 hr at the irradiation conditions and gave the same retention time on silicone oil and silicone gum nitrile glpc columns as benzonorbornadiene. The transformation from the intermediate, represented by curves b and c, to the end product is photochemical and not simply thermal. A solution displaying uv curves a and b is stable for at least 3 days in the dark at room temperature as judged by the steady intensity of the uv absorptions. The apparent lack of rearrangement in more concentrated solutions (10%) can best be explained by self-quenching. One would expect that the intensity of fluorescence from **1** should also be concentration dependent if this explanation is correct. Unfortunately, under conditions which gave a good fluorescence spectrum of benzene, no emission from benzonorbornadiene could be detected. Using $\Phi_f = 0.053$[22] for benzene, the quantum yield of fluorescence for benzonorbornadiene in solution is less than 0.001.

Discussion

The rearrangement of benzonorbornadiene to tetracyclo[$5.4.0.0^{2,4}0^{3,6}$]undeca-1(7),8,10-triene proceeds *via* the triplet state. The reaction is not observed during direct irradiation because of the poor intersystem crossing from $S_1 \rightarrow T_1$. The lack of intersystem crossing was unexpected. As noted earlier, the energy gap in benzonorbornadiene between S_1 and T_1 should favor intersystem crossing relative to norbornadiene. An estimate of E_{T_1} for benzonorbornadiene can be made by bracketing using the quantum yields for acetophenone and benzophenone. This method gives a value of about 70 kcal for benzonorbornadiene and 69 kcal for norbornadiene. The energies of the S_1 states of these molecules are not known and are difficult to determine exactly from the absorption spectra. However, S_1 for norbornadiene is certainly higher than S_1 for benzonorbornadiene, and based on energy considerations only, one would not expect norbornadiene to intersystem cross more efficiently than benzonorbornadiene.

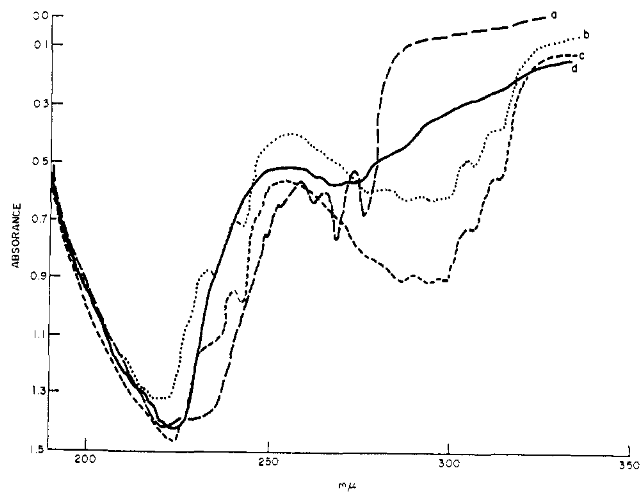
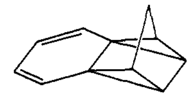


Figure 1. a, Uv absorption of benzonorbornadiene ($1.3 \times 10^{-3}\,M$ in hexane); b, after 30 min irradiation in Srinivasan Griffin reactor, air temperature 30° (sample diluted approximately 5:1 to obtain spectrum, $2.6 \times 10^{-4}\,M$ in hexane; assuming same molecular weight as starting material); c, 60 min irradiation ($2.6 \times 10^{-4}\,M$); d, 135 min irradiation ($2.6 \times 10^{-4}\,M$), assuming same molecular weight as starting material.

Ziegler and Hammond[23] recently have found that analogous to benzonorbornadiene, 7-oxobenzonorbornadiene intersystem crosses very poorly and possibly displays different primary photochemistry in the S_1 and and T_1 states. Direct irradiation gives benz[*f*]oxepin[23] while dimer and mostly polymer are produced with a triplet sensitizer.[24]

The many examples of quadricyclane formation from bicyclo[2.2.1]heptadienes tempt one to draw structure **17** as an intermediate on the path from **1** to **2**.[25] However, energy considerations and direct irradiation results suggest diradical **5** is a better intermediate.



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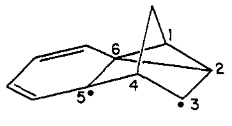

5

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[21] J. R. Edman and G. S. Reddy, unpublished results.

[22] W. R. Dawson and M. W. Windsor, *J. Phys. Chem.*, **72**, 3251 (1968).

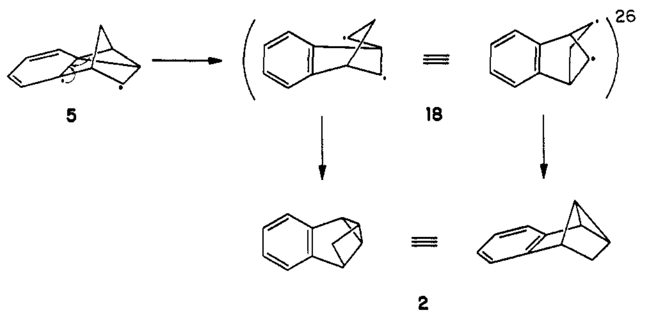
[23] G. R. Ziegler and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 513 (1968).

[24] G. R. Ziegler, *J. Am. Chem. Soc.*, **91**, 446 (1969).

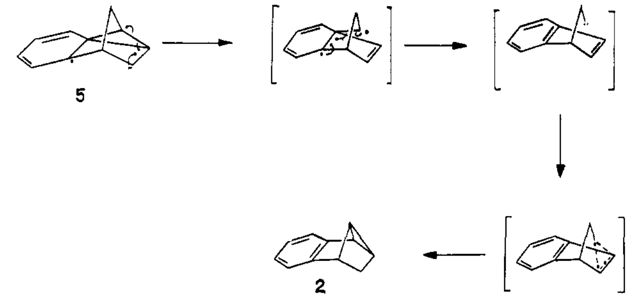
[25] Ziegler and Hammond[23] propose such an intermediate in the rearrangement of 7-oxobenzonorbornadiene to benz[*f*]oxepin. A referee of our communication and numerous individuals in private conversations have suggested the same intermediate. It is also in accord with the divinylmethane mechanisms recently proposed by H. E. Zimmerman, R. W. Brinkley, R. S. Givens, and M. A. Sherwin, *ibid.*, **89**, 3932 (1967).

Structure **5** represents an energy minimum on the path from **1** to **17**. Four possibilities available to **5** are bonding across C_3–C_5 to give **17**; breaking bond C_1–C_6 followed by ring closure to give **2** (Scheme V);[26] breaking bond C_2–C_6 to give starting material **1**; or breaking bond C_1–C_2. The latter possibility could lead to **2** *via* a carbene intermediate (Scheme VI). The various reactions could take place within the triplet manifold or **5** might first intersystem cross to the singlet.

Scheme V

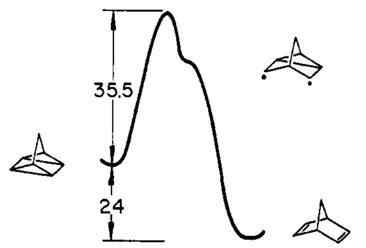


Scheme VI



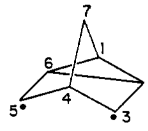
The major factor in deciding the fate of **5** is the activation energy required for the various processes and the available energy in **5**. The ring closure is an activated process while the bond-breaking steps should require little if any activation energy. The total energy available for the conversion of **1** to **2** is about 70 kcal (E_{T_1}). Turner, *et al.*,[27] have recently calculated a need for 59–60 kcal for converting norbornadiene to quadricyclane. These calculations depend on whether the following energy diagram (Scheme VII) is valid for both the excited states and thermal reactions of norbornadiene. In a rigid molecule, this assumption seems good, since there can be very little distortion of the excited-state geometries relative to the ground-state geometries. The major difference would be in the lifetime of the diradical intermediate and this should not affect the gross features of the energy profile. The loss of aromaticity in going from **1** to **5** will make this a much more energy-demanding process than the corresponding conversion of norbornadiene. While the conversion of **17** to **1** will require less activation energy relative to quadricyclane–norbornadiene, the difference between the ground-state energies of **1** and **17** could well be enough to boost the energy required for the over-all conversion of **1** → **17** to greater than 70 kcal. As a result, the triplet state of benzonorbornadiene has sufficient energy to form the diradical **5** but then lacks the additional energy needed to ring close to **17**. Instead, bonds C_1–C_6 or C_2–C_6 break in a thermal-type reaction.[28]

Scheme VII



Unlike the isomerization of the simple hydrocarbon where only C_2–C_6 breaks, the quantum yield of 0.5 suggests that C_2–C_6 and C_1–C_6 break with equal probability.[29]

In the hydrocarbon, represented by **19** (presumably the 7-oxo and 7-aza derivatives are comparable), the T_1 state has sufficient energy to ring close, and quadricyclane or products derived therefrom are isolated.[30] The inability of the benzo derivatives to ring close explains the extensive polymer formation when a triplet sensitizer is used with 7-oxobenzonorbornadiene. The diradical **20**, lacking sufficient energy to ring close, can either isomerize to an unstable tricyclic ether **21**, which polymerizes, or serve as an initiator.



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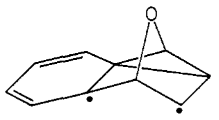

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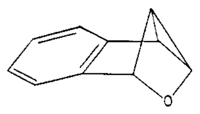

21

The S_1 state of benzonorbornadiene, in contrast to norbornadiene, leads to products different from those derived from T_1. This can be explained by postulating an initial concerted isomerization of the S_1 state of **1** to **17**. Norbornadiene, by analogy, while giving the same

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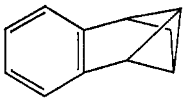
(26) In practice, the conversion of **5** to **2** may be concerted. The pairs of compounds depicted by **18** and **2** are D and L isomers. Throughout the paper, **5** and **2** are meant to represent racemic mixtures. As drawn, **5** could only lead to



the mirror image of the structure depicted.

(27) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Am. Chem. Soc.*, 90, 4315 (1968).

(28) It is conceivable but unlikely that sufficient energy for ring closure is present but a combination of rate factors virtually excludes the process.

(29) Assuming each triplet of benzonorbornadiene forms diradical **5**.

(30) This mechanism is consistent with a quantum yield of 0.9 as reported by Murov and Hammond[31] if the rate of ring closure is favorable relative to bond breaking. Traces of rearranged product due to breakage of C_1–C_6 could go undetected because of experimental difficulties. The quantum yield of 0.26, reported by Liu and Edman,[32] is consistent with the rate constant for C_1–C_6 bond breakage being very slow relative to breakage of C_2–C_6 and ring closure. If the mechanism proposed for this reaction, with **19** as an intermediate with a finite lifetime, is substantially correct, it seems quite reasonable that breakage of C_2–C_6 to give starting material will compete effectively with ring closure.

(31) S. Murov and G. S. Hammond, *J. Phys. Chem.*, 72, 3797 (1968).

(32) See Table I, footnote *e*.

product from both states, may do so by two different mechanisms, a concerted one from S_1 and a stepwise one from T_1. A detailed analysis of the direct irradiation of benzonorbornadiene must await further study although it is worth noting the uv spectrum of the final product (curve d, Figure 1) resembles that of benzocycloheptatriene.[33,34]

Experimental Section

All the quantum yield studies employed a merry-go-round apparatus immersed in a constant-temperature bath maintained at room temperature. A 450-W Hanovia high-pressure lamp was used with filters as indicated. Gas chromatographic analysis of both norbornadiene and benzonorbornadiene was done on a 0.25 in. × 3 ft column packed with 20% Dow 200 on 60–80 mesh Gaschrom R. The inlet and column must be at room temperature to minimize isomerization during separation.

Benzonorbornadiene was prepared by the method of Wittig and Knaus[35] using *o*-bromofluorobenzene. Pure samples for actinometry were obtained by preparative gas chromatograph using a $^3/_8$ in. × 3 ft column packed with 10% silicone Gum Nitrile XE on 60–80 Gaschrom R. The material was distilled *in vacuo* prior to use.

Methylnorbornadienes.[36] **Dideuteriobenzonorbornadiene 6.** Benzonorbornadiene, 2 g, triethylenediamine (DABCO) sublimed from barium oxide, 0.4 g, and 4 ml of *n*-hexane were stirred under nitrogen at room temperature. Butyllithium, 0.9 g, in hexane was added dropwise. A white precipitate formed and the mixture was refluxed for 24 hr. The initial white precipitate slowly disappeared to give a clear solution, and a second precipitate appeared and eventually the entire solution jelled. The mixture was cooled and excess deuterium oxide was added with stirring. The hexane layer was separated, any remaining solids were filtered off, and the water layer was extracted with two 4-ml portions of hexane. The combined hexane layers were dried over magnesium sulfate, and the hexane was distilled. A 45% recovery of crude benzonorbornadiene was obtained by vacuum distillation of the residue. This material contained about 0.9 atom of deuterium on the basis of integration of the pmr spectrum. A second run gave material which was about 75% deuterated at the olefinic positions. The material was purified by preparative glpc on a 3-ft silicon nitrile column.

Photorearrangement of Benzonorbornadiene. Benzonorbornadiene, 14.2 g (0.1 mole), acetophenone, 12 g (0.1 mole), and ether, 500 ml, were placed in a cylindrical Pyrex vessel and degassed with a stream of nitrogen for 20 min. The flask was placed in a photoreactor[15] equipped with 16 F8T5 BLB lamps, fitted with a magnetic stirrer and condenser, and irradiated under nitrogen until the conversion to product as determined by glpc was complete. The ether was distilled at atmospheric pressure. A careful distillation at reduced pressure first gave the acetophenone and then the photoproduct. Some higher boilers remained in the flask. A pure sample was obtained by preparative gas chromatography on a Dow 200 column: bp 220° (DTA); n^{27}D 1.5742.

Anal. Calcd for $C_{11}H_{10}$: C, 93.04; H, 7.96; mol wt, 142. Found: C, 92.52; H, 7.12; mol wt, 142 (mass spectrum).

8(11)-Methyltetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene. A solution of deoxygenated ether, 80 ml, *o*-methylbenzonorbornadiene,[36] 2.37 ml, and acetophenone, 1.8 ml, was irradiated for 24 hr under nitrogen with 16 F8T5 BLB bulbs.[15] The ether was distilled at atmospheric pressure. The residue was distilled at approximately 180° (0.03 mm) to give a mixture containing acetophenone, product, and impurities. The 70–30 mixture of isomers was purified by preparative glpc on a $^3/_8$ in. × 5 ft silicon nitrile column, n^{25}D 1.5700.

Anal. Calcd for $C_{12}H_{12}$: C, 92.38; H, 7.75. Found: C, 92.44; H, 7.96.

9(10)-Methyltetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene 15 and 16. The experimental and work-up conditions are identical with those for the 8(11)-methyl mixture, n^{25}D 1.5683.

Anal. Calcd for $C_{12}H_{12}$: C, 92.38; H, 7.75. Found: C, 92.65; H, 7.68.

Reduction of Tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-trienes. Deuterioacetonitrile, 0.4 ml, containing tetracyclo[5.4.0.0^{2,4}.0^{3,6}]-undeca-1(7),8,10-triene, 40 mg, was placed in a small vial equipped with a micromagnetic stirrer. The vial was fitted with a serum cap and two syringe needles. The vial was flushed with nitrogen and ~20 mg of 10% Pd/C was added. The vial was flushed with deuterium or hydrogen and the solution was stirred vigorously. The disappearance of **2** or **3** and the appearance of benzonorbornene were followed by glpc on a Dow 200 column. The reduction was usually complete after 40 min at room temperature. The solutions were then filtered and their pmr spectra determined without further purification.

Quantum Yield for Benzonorbornadiene Rearrangement. Sample tubes containing 0.35 *M* benzonorbornadiene and 0.35 *M* acetophenone in hexane and actinometry tubes containing 0.2 *M* myrcene and 0.35 *M* acetophenone in hexane were degassed with three freeze–thaw cycles. The tubes were placed in the merry-go-round apparatus and irradiated using Corning A-54 filters to ensure uniformity of light transmission. The benzonorbornadiene tubes were removed after 152 and 190 min (40–50% conversion). The myrcene tubes were removed after 1500 min (~30% conversion). A value of 0.023 was taken as the quantum yield for the myrcene reaction.[37] Similar runs were made using benzophenone in place of acetophenone. The remaining sensitizers cited in Table I were checked qualitatively at concentrations such that only the sensitizers absorbed light. The analyses were made on the Dow 200 column at 140°.

Quantum Yield of Norbornadiene Rearrangement. A stock solution of freshly distilled norbornadiene in distilled, spectrograde hexane was prepared immediately before use. Sample tubes containing 0.4 *M* norbornadiene and 0.4 *M* acetophenone in hexane and 0.4 *M* norbornadiene and 0.375 *M* benzophenone in hexane were degassed with three freeze–thaw cycles and sealed. The actinometer tubes contained 0.4 *M* myrcene and 0.4 *M* acetophenone in hexane and 0.4 *M* myrcene and 0.375 *M* benzophenone in hexane. The norbornadiene–benzophenone tubes were removed after 34 and 39 min, the norbornadiene–acetophenone tubes after 80 and 109 min. The actinometer tubes were removed after 1430 min.

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[33] G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

[34] Identical results were obtained with the diacetoxy derivative.[13]

[35] G. Wittig and E. Knaus, *Ber.*, **91**, 895 (1958).

[36] Generously supplied by Dr. Francis M. Logullo, Textile Fibers Department, Du Pont Co. See F. M. Logullo, Ph.D. Thesis, pp 110–111, Case Institute of Technology, 1965.

[37] See Table I, footnote *a*.