Photochemical Reorganization Reactions of *o*-Divinylbenzene, 3,4-Benzotropilidene, 1,2-Benzotropilidene, and 1-Phenyl-1,3-butadiene[1]

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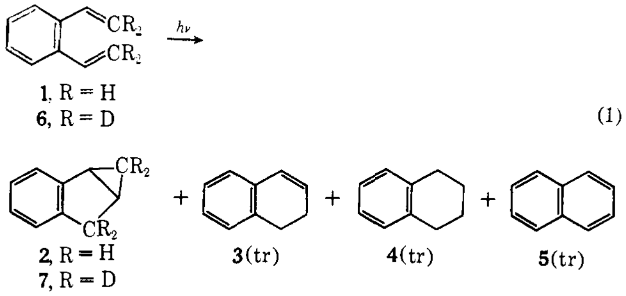
Abstract: The photochemical reorganizations of the title compounds are described. *o*-Divinylbenzene produces benzobicyclo[3.1.0]hex-2-ene by a mechanism involving carbon skeletal rearrangements and not hydrogen migration, as demonstrated by deuterium labeling experiments. The progenitor of this product is shown not to be 2,3-dihydronaphthalene although this intermediate is also apparently formed in the photolysis. Both 3,4-benzotropilidene and 1,2-benzotropilidene produce benzonorcaradiene by a 1,7-sigmatropic hydrogen migration as shown by studying appropriately deuterated compounds. In addition 1,2-benzotropilidene produces, as a primary product, a small amount of 2,3-benzobicyclo[3.2.0]hepta-2,6-diene by an electrocyclic ring closure. *trans*-1-Phenyl-1,3-butadiene, upon irradiation, produces initially a mixture of the cis and trans isomers but prolonged irradiation gives 3-phenylcyclobutene. The inability to sensitize any of the above reactions (except cis–trans isomerization) suggests that they are occurring *via* singlet excited states.

The usual photochemical reactions of 1,3,5-hexatrienes are the formation of 1,3-cyclohexadienes, bicyclo[3.1.0]hexenes, and occasionally 3-vinylcyclobutenes.[7] In contrast, 1,5-hexadienes frequently rearrange to bicyclo[2.1.1]hexanes upon irradiation.[8] In this paper we present the photochemistry of several hexatrienes with one double bond of reduced bond order, by virtue of its inclusion in an aromatic ring. Our initial motivation for such a study was the hope that the benzo moiety might render the hexatriene unit like a 1,5-hexadiene. Thus, we had hoped that *o*-divinylbenzene (**1**) might yield benzobicyclo[2.1.1]hex-2-ene upon irradiation.

Results

Irradiation (medium pressure mercury arc, Pyrex filter) of dilute ether or pentane solutions of **1**, prepared by the method of Wittig,[9a] afforded, in about 13% yield, benzobicyclo[3.1.0]hex-2ene (**2**).[2] In addition there were traces of three other compounds whose vlpc retention times matched those of 1,2-dihydronaphthalene (**3**), tetralin (**4**), and naphthalene (**5**; eq 1). These compounds were shown not to be arising from the photoproduct **2** by appropriate control experiments. It was further demonstrated that no benzobicyclo[2.1.1]hex-2-ene[5] was formed from **1** (<1% of the amount of **2** would have been detectable). The structure of **2** was proven by spectral comparison with the authentic material synthesized by the Simmons–Smith reaction of methylene iodide with indene as reported by Goodman and Eastman.[10]



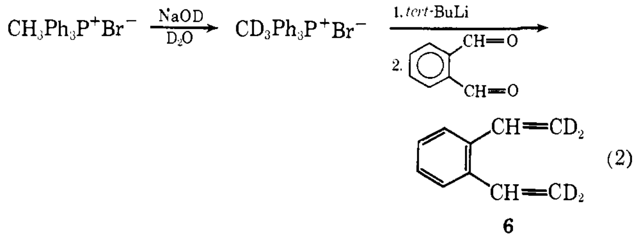
1, R = H
6, R = D

(1)

2, R = H
7, R = D

3(tr) **4**(tr) **5**(tr)

The mechanistic aspects of this novel rearrangement were probed by employing *o*-divinylbenzene-d_4 (**6**) containing (93% of) four terminal methylene deuterons. The preparation of **6** was by the Wittig reaction[9a] of dideuteriomethylenetriphenylphosphorane with *o*-phthalicdicarboxaldehyde; eq 2 shows the synthetic sequence. Upon photolysis, **6** afforded **7**, with intact (*ca.* ± 5%) dideuteriomethylene groups. The analysis of **7** was by nmr spectroscopy with the proton assignments of **2** being made as follows (see Figure 1 in ref 2 for the nmr spectrum). The multiplet, of relative area 2, at τ 7.0 ppm is assigned to the benzylic hydrogens,



(2)

6

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[1] From the Ph.D. Thesis of G. W. Gruber, Case Western Reserve University, Cleveland, Ohio, 1970. Portions of this work have appeared in preliminary communications.[2-5]

[2] M. Pomerantz, *J. Amer. Chem. Soc.*, **89**, 694 (1967); also see J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 696 (1967).

[3] M. Pomerantz and G. W. Gruber, *ibid.*, **89**, 6798 (1967).

[4] M. Pomerantz and G. W. Gruber, *ibid.*, **89**, 6799 (1967).

[5] M. Pomerantz, *ibid.*, **88**, 5349 (1966).

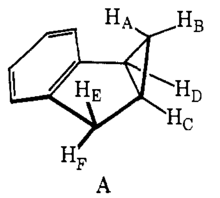
[6] (a) Alfred P. Sloan Foundation Research Fellow; author to whom correspondence should be sent at the Belfer Graduate School of Science, Yeshiva University, New York, N. Y. 10033; (b) Texaco Corporation Fellow, 1968–1969.

[7] For a review of hexatriene photochemistry see: G. J. Fonken in "Organic Photochemistry," Vol. 1, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 222. Also see: J. Meinwald and P. H. Mazzocchi, *J. Amer. Chem. Soc.*, **88**, 2850 (1966), and K. R. Huffman, M. Loy, W. A. Henderson, Jr., and E. F. Ullman, *J. Org. Chem.*, **33**, 3469 (1968).

[8] See: J. S. Swenton, *J. Chem. Educ.*, **46**, 7 (1969).

[9] (a) G. Wittig, H. Eggers, and P. Duffner, *Justus Liebigs Ann. Chem.*, **619**, 10 (1958); (b) A. M. Kan, G. R. Proctor, and L. Rees, *J. Chem. Soc.*, 990 (1966).

[10] A. L. Goodman and P. H. Eastman, *J. Amer. Chem. Soc.*, **86**, 908 (1964); A. L. Goodman, Ph.D. Thesis, Stanford University, Stanford, Calif., 1963.

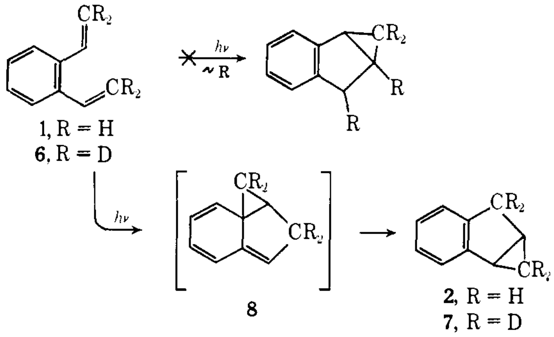


A

H_E and H_F (A) since, by employing spin decoupling, it was observed that these protons are coupled to only one other hydrogen. This hydrogen, H_C, appears as a multiplet at τ 8.3. Of the remaining nonaromatic hydrogens the lowest field multiplet at τ 7.8 must be due to the benzylic hydrogen H_D, which leaves the sextet (actually a double triplet) and the quartet at τ 9.1 and 10.0, respectively, assignable to the cyclopropylmethylene group. The distinction between H_A and H_B can, in addition, be made in the following way. The τ 9.1 absorption shows one coupling constant of the order of 7–8 Hz whereas the higher field quartet shows couplings only of 3–4 Hz. This indicates, since cis vicinal cyclopropane coupling constants are larger than the corresponding trans coupling constants,[11] that the lower field multiplet is due to H_B and hence the higher field quartet is due to H_A.[12]

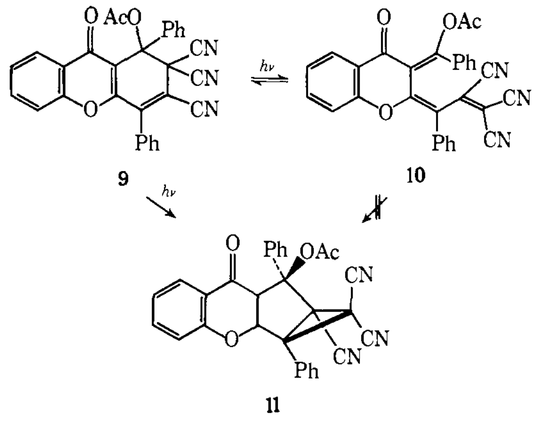
The labeling pattern in **7** therefore precludes a hydrogen shift mechanism and is compatible with the intermediate formation of **8** (see Scheme I). Driving force

Scheme I



for conversion of **8** to **7** is provided by rearomatization and, probably, some loss of strain energy.

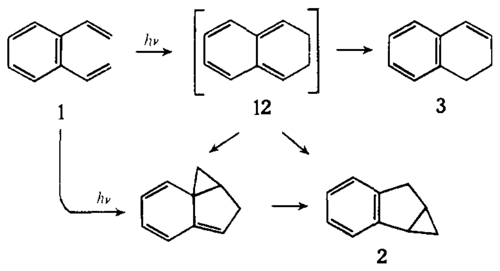
There are many examples of the photochemical formation of bicyclo[3.1.0]hexenes from 1,3,5-hexatrienes. In most cases it has merely been assumed that the corresponding 1,3-cyclohexadienes were not involved, despite the fact that cyclohexadiene formation is a common, nearly general, photoreaction of hexatrienes.[7,16] In at least one case, however, a 1,3-cyclohexadine has been shown to be the precursor of a bicyclo[3.1.0]hexane. Ullman and coworkers[17] demonstrated that **9**, rather than **10**, is the progenitor of **11** (eq 3).



(3)

Since 1,2-dihydronaphthalene (**3**) was present in the mixture resulting from irradiation of **1**, it was thought that 2,3-dihydronaphthalene (**12**) might be its precursor by a hydrogen shift or catalysis mechanism. This further suggests that **12** might be an intermediate in the formation of benzobicyclo[3.1.0]hex-2-ene (**2**; see Scheme II). If this were the case, it might be possible to trap **12** with a dienophile. To this end, **1** with perfluoro-2-butyne in ether at −55° was irradiated. The products were naphthalene (39%), benzobicyclo[3.1.0]hex-2-ene (**2**; 10%), and only a trace of 1,2-dihydronaphthalene (**3**). When the above experiment was repeated, without added dienophile, the results were unchanged. Thus it appears that at −55°, if 2,3-dihydronophthalene is formed, much or all of it is rapidly oxidized to naphthalene. Similar photoaromatizations occur with *cis*-stilbene[18,19] and 1,4-diphenyl-1,3-butadiene.[20]

Scheme II



In hopes of forming an addition or rearrangement product indicative of a 2,3-dihydronaphthalene precursor, a sample of **1** was irradiated in methanol. Under these conditions, along with about 17% of **2**, there was produced 15% of 1,2-dihydronaphthalene and 14% of α-methoxytetralin. It appears, then, that 2,3-dihydronaphthalene (**12**) was again formed in the irradiation of **1**. Apparently in aprotic solvents, around room temperature, processes leading to nonvolatile products predominate. Dehydrogenation apparently occurs at low temperature while rearrangement and addition occur in methanol. The remarkable feature of these reactions is the relatively constant (10–17%) formation of benzobicyclo[3.1.0]hex-2-ene (**2**). This suggests that the genesis of **2** is independent of the various reactions of 2,3-dihydronaphthalene (see Scheme III).

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(11) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1966, p 695.

(12) A Johnson–Bovey calculation,[13] using the nmr spectrum reported for bicyclo[3.1.0]hex-2-ene,[14,15] supports the above assignments.

(13) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(14) G. Wittig and F. Wingler, *Chem. Ber.*, **97**, 2146 (1964).

(15) J. Meinwald and P. H. Mazzocchi, *J. Amer. Chem. Soc.*, **88**, 2850 (1966).

(16) See: W. G. Dauben and J. H. Smith, *J. Org. Chem.*, **32**, 3244 (1967).

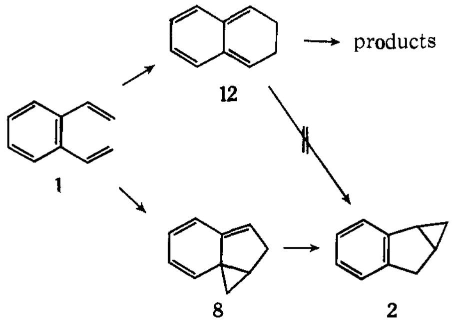
(17) E. F. Ullman, W. A. Henderson, Jr., and K. R. Huffman, *Tetrahedron Lett.*, 935 (1967).

(18) F. L. Mallory C. S. Wood, and T. J. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964).

(19) W. R. Moore, D. D. Morgan, and F. R. Stermitz, *ibid.*, **85**, 829 (1963).

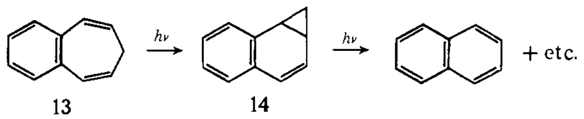
(20) G. J. Fonken, *Chem. Ind. (London)*, 1327 (1962).

Scheme III



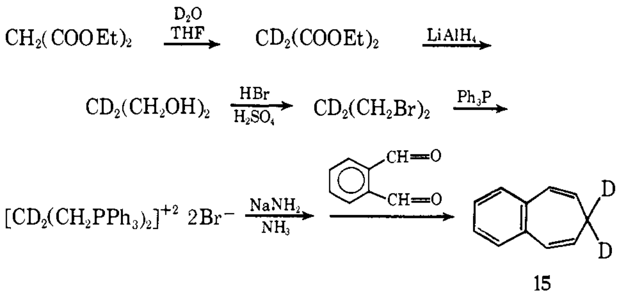
Since Nenitzescu and coworkers had reported the preparation and trapping of 2,3-dihydronaphthalene by debromination of 1,4-dibromotetralin[21] we chose to further examine the chemistry of **12** generated in this manner. When we repeated this reaction without employing a dienophile, the product mixture consisted mainly of naphthalene (**5**) with traces of 1,2-dihydronaphthalene (**3**) and tetralin (**4**). Since we knew that **12** was being formed in these reactions we repeated the above reaction but this time we irradiated the mixture during the course of the reaction. The products were the same as when we did not irradiate; no benzobicyclo[3.1.0]hex-2-ene (**2**) could be detected. This result means either that **12** does not produce **2** photochemically or that under the reaction conditions **12** is not absorbing the light. A distinction between these two possibilities was made by repeating the above reaction, this time with added *o*-divinylbenzene (**1**), such that reaction mixture which was being irradiated consisted of 1,4-dibromotetralin, magnesium, and **1** in ether. Analysis of the products indicated, as in the earlier experiments, naphthalene (**5**), 1,2-dihydronaphthalene (**3**), and tetralin (**4**) and, in addition, benzobicyclo[3.1.0]hex-2-ene (**2**) was also a product. Thus, under conditions where **12** is produced, no **2** is observed and yet under the same conditions **1** gives **2**. 2,3-Dihydronaphthalene (**12**), therefore, cannot be the precursor of **2**.

Since *o*-divinylbenzene almost certainly reacts by way of the spiro compound **8**, we felt that by imposing conformational constraint upon the *o*-divinylbenzene moiety we might alter the course of the rearrangement and thus gain additional insight into this reaction. Thus when we irradiated 3,4-benzotropilidene (**13**),[9] the products were benzonorcaradiene (**14**) along with smaller amounts of naphthalene and additional minor products. Benzonorcaradiene (**14**) was identified by spectral comparison with an authentic sample prepared by the method of Doering[22] and the naphthalene by comparison of its spectra with those of the authentic compound. It could readily be shown that the naphthalene and additional components were arising by further photolysis of **14**.[23] The methylene thus produced was trapped with cyclohexene to produce norcarane.[24]



The mechanistic aspects of this rearrangement (**13** → **14**) were examined by studying the reorganization of 7,7-dideuterio-3,4-benzotropilidene (**15**). The synthesis of **15** was accomplished as follows (Scheme IV): base-catalyzed exchange of malonic ester with D_2O gave dideuteriomalonic ester in good yield. Reduction with $LiAlH_4$ gave 2,2-dideuterio-1,3-propanediol in rather poor yield. Conversion to the dibromide was by the standard precedure[25] and formation of the bisphosphonium salt using triphenylphosphine was by the method of Wittig.[9a] The dideuteriobis(ylide) was prepared using sodium amide in liquid ammonia and then treated with *o*-phthalic dicarboxaldehyde to produce the desired product, **15**. It should be pointed out that, in our hands, this reaction often did not give product (either **13** or **15**) and when it did the yields were poor.

Scheme IV



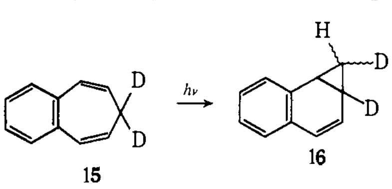
$$CH_2(COOEt)_2 \xrightarrow[THF]{D_2O} CD_2(COOEt)_2 \xrightarrow{LiAlH_4}$$

$$CD_2(CH_2OH)_2 \xrightarrow[H_2SO_4]{HBr} CD_2(CH_2Br)_2 \xrightarrow{Ph_3P}$$

$$[CD_2(CH_2PPh_3)_2]^{+2}\ 2Br^- \xrightarrow[NH_3]{NaNH_2}$$

The nmr spectrum of **15** showed the benzylic vinyl protons as a sharp doublet at τ 3.5 (J = 10.5 Hz) and the other vinyl hydrogens as a broadened doublet at τ 4.4. There was a small peak due to protium in the 7 position which, when integrated, indicated 80–83% of 2-deuterons at that position. The nmr spectrum of the undeuterated material, **13**, showed, in addition to the aromatic absorption at τ 2.9, a doublet at 3.5, a double triplet at 4.4, and a triplet (H_7; J = 6.6 Hz) at 7.55. Also, the long-range H_2–H_7 coupling constant was observed to be 0.6 Hz.

When **15** was irradiated it rearranged to **16**, with one allylic cyclopropyl deuteron and one deuterium atom distributed approximately 50:50 between the exo and endo cyclopropylmethylene hydrogens (eq 4).



(4)

The location of the deuterium atoms in **16** was accomplished by nmr spectroscopy based on the assignments made by Vogel.[26] We have confirmed these assignments both by spin decoupling and by the ob-

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(21) I. G. Dinulescu, M. Avram, and C. D. Nenitzescu, *Chem. Ber.*, **93**, 1795 (1960).

(22) W. von E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).

(23) For the details of the photochemistry of **14** see: G. W. Gruber and M. Pomerantz, *J. Amer. Chem. Soc.*, **91**, 4004 (1969). Also see: D. M. Madigan and J. S. Swenton, *ibid.*, **92**, 7513 (1970).

(24) For analogous photolytic methylene extrusion reactions see, *e.g.*: D. B. Richardson, L. R. Darrett, J. M. Martin, Jr., W. E. Putnam, S. C. Slaymaker, and I. Dvoretsky, *ibid.*, **87**, 2763 (1965).

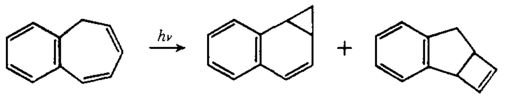
(25) O. Kamm and C. S. Marvel in "Organic Syntheses," Collect. Vol. 1, 2nd ed, H. Gillman and A. H. Blatt, Ed., Wiley, New York, N. Y., 1967, p 30.

(26) E. Vogel, D. Wendish, and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, **3**, 442 (1964).

servation that one of the cyclopropyl CH$_2$ protons shows a coupling constant of 8.5 Hz with the vicinal protons (the other coupling constants for the vicinal cyclopropyl hydrogens being 3–4 Hz). This indicated that that proton must be cis to the other cyclopropyl hydrogens and is therefore exo.[11] In addition the upfield absorptions of **14** are very similar to those of **2** (cyclopropyl CH$_2$) and are absent in 7,7-dideuteriobenzonorcaradiene.[27] The nmr assignments are therefore as follows: τ 2.9, aromatic hydrogens; 3.8, vinyl hydrogens (doublet, J = 2.5 Hz); 7.7, cyclopropyl benzylic hydrogen (multiplet); 8.2, cyclopropyl allylic hydrogen (multiplet); 8.6, exo cyclopropylmethylene hydrogen (double triplet, J = 3 and 8.5 Hz); 10.4 endo cyclopropylmethylene hydrogen (slightly broadened quartet, $J \approx$ 3–5 Hz).

These results (**15** → **16**) clearly indicate that the photochemical reorganization of **13** involves hydrogen migration.

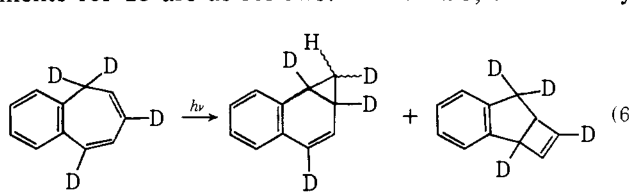
As the next step in the study of these photochemically induced rearrangements, we examined 1,2-benzotropilidene (**17**).[27] Under the photolysis conditions already discussed **17** also rearranged to **14** in excellent yield (*ca.* 65–95%) and to 2,3-benzobicyclo[3.2.0]hepta-2,6-diene (**18**) in *ca.* 0.5% yield (eq 5). Identification of **18** was by comparision with an authentic sample prepared by the benzophenone-sensitized photocycloaddition of maleic anhydride to indene[28] followed by Pb(OAc)$_4$ oxidative bisdecarboxylation.[29] Very recently an independent synthesis of **18** has been reported.[30]



(5)

17 14 18

The mechanism of the photochemical reorganization of **17** was studied by employing 3,5,7,7-tetradeuterio-1,2-benzotropilidene (**19**) which was prepared by base-catalyzed exchange of **17** or rearrangement–exchange of **13**.[27] The products obtained from **19** upon irradiation were the tetradeuteriobenzonorcaradiene (**20**), which contained one deuteron distributed approximately 50:50 in the endo and exo cyclopropylmethylene positions and the tetradeuteriobenzobicyclo[3.2.0]heptadiene (**21**) (eq 6). The labeling patterns were determined by nmr spectroscopy. The nmr spectral assignments for **18** are as follows:[28,30] τ 2.95, aromatic hydrogens (singlet, 4 H); 3.70, vinyl hydrogen (doublet, J = 2.4 Hz, 1 H); 3.92, vinyl hydrogen (doublet, J = 2.4 Hz, 1 H); 5.68, benzylic cyclobutene hydrogen (broad doublet, J = *ca.* 3 Hz, 1 H); 6.30, allylic cyclobutene hydrogen (multiplet, 1 H), and 6.90 and 6.98 benzylic methylene hydrogens (multiplet and apparent singlet respectively, 2 H). Thus, the nmr spectrum of **21** showed, in addition to the aromatic hydrogens, two broad singlets at τ 3.7 and 6.3.



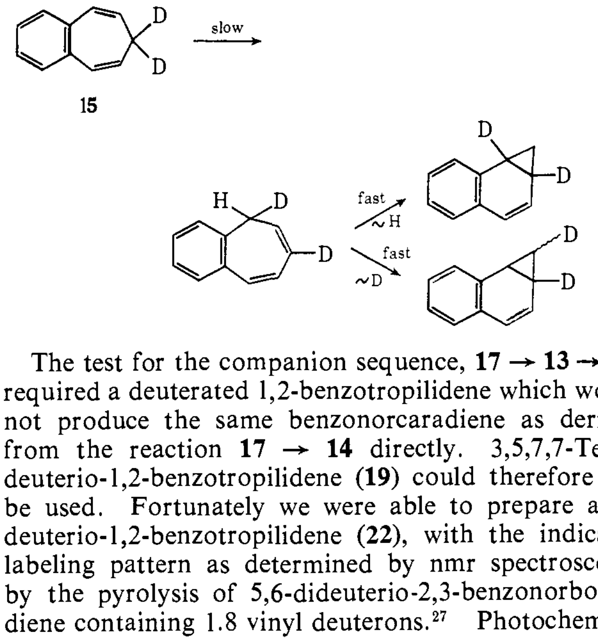
(6)

19 20 21

From these results it is clearly apparent that the benzonorcaradiene is being formed by hydrogen migration, whereas **21** is merely the result of an electrocyclic reaction of a butadiene.[31]

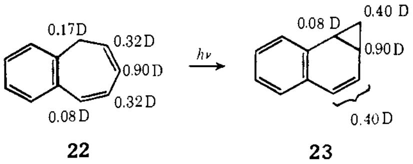
There are two additional mechanistic possibilities for the photorearrangements of the benzotropilidenes which we are able to rule out. The first is that there might be a photostationary state set up between 3,4-benzotropilidene (**13**) and 1,2-benzotropilidene (**17**) and that only one of these isomers is rearranging to benzonoracaradiene. This was easily eliminated by irradiating each to partial completion and demonstrating, by nmr spectroscopy (**13** has a triplet for the methylene hydrogens at τ 7.55 and **17** has a doublet at 7.02), that there was none of the other formed.

The second possibility is that **13** could be rearranging slowly to **17**, and this, in an efficient, high quantum yield reaction, would produce the product **14**. This sequence, along with the companion mechanism of **17** slowly producing **13**, which in turn would rapidly produce benzonorcaradiene, was ruled out in the following way. If the sequence were **13** → **17** → **14** then 7,7-dideuterio-3,4-benzotropilidene (**15**) would be expected to produce at least some benzonorcaradiene containing benzylic deuterium (assuming the first step is a 1,3-hydrogen migration; eq 7). This was not observed.



(7)

The test for the companion sequence, **17** → **13** → **14**, required a deuterated 1,2-benzotropilidene which would not produce the same benzonorcaradiene as derived from the reaction **17** → **14** directly. 3,5,7,7-Tetradeuterio-1,2-benzotropilidene (**19**) could therefore not be used. Fortunately we were able to prepare a dideuterio-1,2-benzotropilidene (**22**), with the indicated labeling pattern as determined by nmr spectroscopy, by the pyrolysis of 5,6-dideuterio-2,3-benzonorbornadiene containing 1.8 vinyl deuterons.[27] Photochemical reorganization of **22** produced the dideuteriobenzonorcaradiene **23** (eq 8). A different labeling pattern



(8)

22 23

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[27] M. Pomerantz and G. W. Gruber, *J. Org. Chem.*, **33**, 4501 (1968).

[28] W. Metzner, H. Partale, and C. H. Krauch, *Chem. Ber.*, **100**, 3160 (1967).

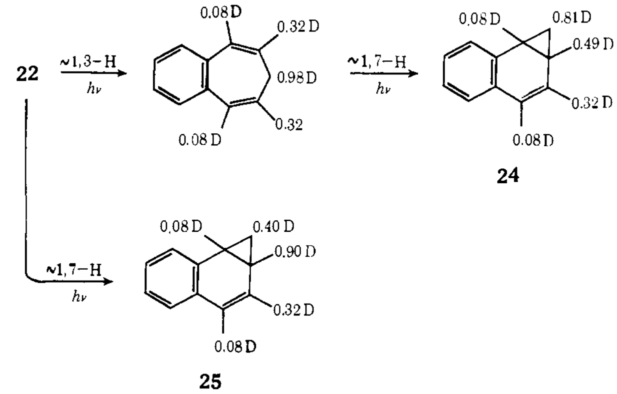
[29] C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chem. Acta*, **41**, 1191 (1958).

[30] W. Metzner and K. Morgenstern, *Angew. Chem., Int. Ed. Engl.*, **7**, 379 (1968); D. Wendish and W. Metzner, *Chem. Ber.*, **101**, 4106 (1968).

[31] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

would have been expected for the product **24**, had there been a 1,3-hydrogen migration to give a 3,4-benzotropilidene, followed by rearrangement to the benzonorcaradiene. Thus, the labeling in **23** agrees completely with the predicted pattern (**25**) (Scheme V), for formation of benzonorcaradiene from **22** by 1,7-sigmatropic migration of hydrogen. Thus neither **13** nor **17** is involved in the rearrangement of the other to benzonorcaradiene (**14**).

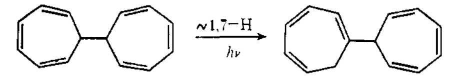
Scheme V



In addition to the compounds already discussed we reexamined the photochemistry of *trans*-1-phenyl-1,3-butadiene.[5] The previous report[32] indicated that a photostationary state containing the cis and trans isomers was produced. We, however, found that prolonged irradiation gave some 3-phenylcyclobutene by an electrocyclic ring closure. The thermal instability of 3-phenylcyclobutene[33] precluded its detection in the earlier study. Thus, phenylbutadiene and 1,3,5-hexatriene[1] are similar in that they both produce, among the products, a cyclobutene.

We have also examined the reactive states by attempting to sensitize these photoreorganizations.

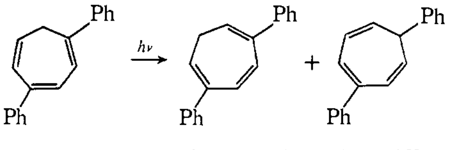
Givens[34] recently demonstrated that ditropyl **26** undergoes 1,7-sigmatropic rearrangement upon direct irradiation, but under conditions of sensitization by benzophenone (E_t = 69 kcal/mol) no rearrangement occurred. Givens did demonstrate, however, that the triplet energy of benzophenone was transferred to ditropyl. This was accomplished by quenching the photoreduction of benzophenone in benzhydrol[35] with ditropyl. Presumably the lowest triplet levels of the present arene dienes are no higher that those of ditropyl. From this it follows that benzophenone should be capable of transferring energy to **1**, **13**, **17**, and 1-phenyl-1,3-butadiene. Under conditions where benzophenone absorbed most of the incident light, 1,2- and 3,4-benzotropilidene do not undergo an observable reaction which cannot be ascribed to direct absorption. Under similar conditions *o*-divinylbenzene (**1**) is destroyed but **2** is not produced. Also, when **1** is sensitized in methanol neither α-methoxytetralin nor other volatile products were formed. Sensitization of *trans*-1-phenyl-1,3-butadiene merely leads to a different photostationary state and does not produce 3-phenylcyclobutene, the product of the direct isomerization. Thus the sensitization studies suggest singlet mechanism for all of the above rearrangements.

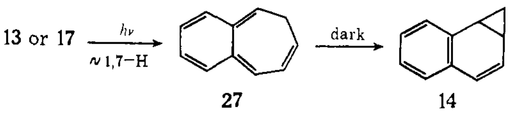


26

Discussion

The photochemistry of 1,2- and 3,4-benzotropilidene is probably best discussed by comparision with related compounds. The sigmatropic shifts of hydrogen observed in these systems are general, and reversible in the tropilidene series.[36] For example, 1,4-diphenyltropilidene, a reasonable model for both 1,2- and 3,4-benzotropilidene, shifts hydrogen 1,7 to form both the 2,5 isomer and the 3,7 isomer.[37] The difference between these products and 2,3-benzotropilidene (**27**, derived from 1,7 hydrogen shift in 1,2- or 3,4-benzotropilidene) is that the latter is unstable with respect to 2,3-benzonorcaradiene (**14**).[26,38]





There is an alternative mechanism which deserves mention. Rather than a 1,7-sigmatropic shift with π bond reorganization we could envision a 1,2-hydrogen migration with concurrent three-membered ring formation.[39] This reaction must be either a ${}_{\pi}2_a + {}_{\sigma}2_a$ or ${}_{\pi}2_s + {}_{\sigma}2_s$ cycloaddition.[31] In either case (assuming both do not occur to the same extent) a definite stereochemistry would be predicted for the deuterium which migrates. One would also anticipate that the antarafacial–antarafacial pathway should be favored.[40] The observation that the products of rearrangement of the deuterated benzotropilidenes contain 50% of a deuteron exo and 50% endo in the cyclopropylmethylene group in **16** and **20** indicates either the 1,7-hydrogen migration is operative or ring flipping is equilibrating these two positions.[26] We anticipated that running the reactions at low temperatures and working them up also in the cold would allow us to detect possible stereospecific deuterium migrations in **15** and **19**. Irradiation of **15** at *ca.* −60° and work-up at temperatures below −20° afforded benzonor-

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(32) O. Grummitt and E. I. Becker, *J. Amer. Chem. Soc.*, **73**, 3479 (1951).

(33) M. Pomerantz and P. H. Hartman, *Tetrahedron Lett.*, 991 (1968).

(34) R. S. Givens, *ibid.*, 663 (1969).

(35) For a discussion of this reaction see: L. M. Stephenson and G. S. Hammond, *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969).

(36) For a review see: G. B. Gill, *Quart. Rev., Chem. Soc.*, **11**, 338 (1968).

(37) T. Mukai, H. Kubota, and T. Toda, *Tetrahedron Lett.*, 3581 (1967).

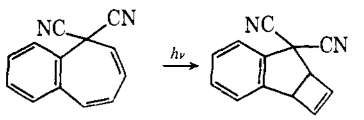
(38) For a related experiment see: T. Toda, M. Nitta, and T. Mukai, *ibid.*, 4401 (1969); G. Maier, *Angew. Chem., Int. Ed. Engl.*, **6**, 402 (1967).

(39) G. W. Griffin, A. F. Marcantonio, H. Kristensson, R. C. Pettersen, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965); H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, **90**, 3749 (1968).

(40) See: J. S. Swenton, A. R. Crumrine, and T. J. Walker, *ibid.*, **92**, 1406 (1970), and H. E. Zimmerman and G. A. Epling, *ibid.*, **92**, 1411 (1970), for a related rearrangement. In this case it is a triplet state reaction involving a phenyl migration (actually it could be envisioned as a di-π-methane rearrangement) with formation of a three-membered ring. The stereochemical result shows the predominant pathway to be the equivalent of ${}_{\pi}2_a + {}_{\sigma}2_a$ cycloaddition.

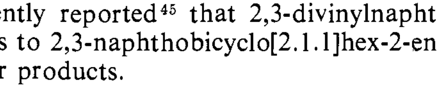
caradiene with 50% exo and 50% endo deuterium. Irradiation of **19** at *ca.* −65° and work-up below −25° again gave a benzonorcaradiene with deuterium equally distributed between the cyclopropylmethylene hydrogens. Analysis was, once again, by nmr spectroscopy. Thus, the failure to observe stereospecific deuterium migration suggests that the mechanism for the conversion of the benzotropilidenes to benzonorcaradiene involves a 1,7-sigmatropic hydrogen shift to produce the valence tautomer of the product and this rapidly, in a thermal reaction, tautomerizes to the observed product.

Ciganek has reported[41] that 7,7-dicyano-1,2-benzotropilidene rearranges to 4,4-dicyano-2,3-benzobicyclo-[3.2.0]hepta-2,6-diene. Of course in this case hydrogen shift is not possible and cyano is a poor migrating group.[41] In tropilidene hydrogen shift is a degenerate reaction, and it is this fact which allows the formation of bicyclo[3.2.0]hepta-2,6-diene.[42] Similarly, with 1,2-benzotropilidene, hydrogen shift occurs greater than 100 times faster then electrocyclization (*vida supra*). The quantum yield for loss of 1,2-benzotropilidene was measured by Pomerantz and Schumann[43] who obtained a value of *ca.* 0.1. From this it follows that the quantum yield for formation of benzobicyclo[3.2.0]hepta-2,-6-diene is less than *ca.* 0.001. This may be compared to the formation of 1,2-dimethylcyclobutene from 2,3-dimethylbutadiene which occurs with a quantum yield of 0.12.[44] The difference might be the result of conformational constraints which inhibit attainment of the proper geometry for reaction.



This should be compared to the similar acyclic system *trans*-1-phenyl-1,3-butadiene which does close to a 3-phenylcyclobutene.[5] Here too the conformational effects are different than in **17**. The alternative, of course, is that where the 1,7-hydrogen migration can occur readily it does so almost exclusively. Now that 2,3-dihydronaphthalene has been implicated in the photochemistry of *o*-divinylbenzene, the system resembles the parent hexatriene.[7]

In conclusion, it is gratifying to know that the original premise for this study has been confirmed. Meinwald recently reported[45] that 2,3-divinylnaphthalene[46] rearranges to 2,3-naphthobicyclo[2.1.1]hex-2-ene, along with other products.



Experimental Section

General. Melting and boiling points are uncorrected. Vapor phase chromatography (vlpc) was done with thermal conductivity detector instruments with 0.25-in. columns or flame ionization detector instruments with 0.125-in. columns. The columns used were the following: (A) 6 ft × 0.25 in. column packed with 20% TCEP on 60–80 mesh Chromosorb P; (B) 12 ft × 0.25 in. column packed with 20% Carbowax 20M on 60–80 mesh Chromosorb P; (C) 5 ft × 0.25 in. column packed with 15% Carbowax 20M on 60–80 mesh Chromosorb P; (D) 10 ft × 0.25 in. column packed with 10% fluorosilicone (FS 1265) on 45–60 mesh Chromosorb P; (E) 7 ft × 0.25 in. column packed with 10% Carbowax 1500 on 45–60 mesh Chromosorb P; (F) 3 m × 0.25 in. column packed with 15% Carbowax 20M on 60–80 mesh Chromosorb P; (G) 2 m × 0.25 in. column packed with 5% SE-30 on 45–60 mesh Chromosorb P; (H) 6 ft × 0.125 in. column packed with 5% SE-30 on DMCS 60–80 mesh Chromosorb W; (I) 6 ft × 0.125 in. column packed with 30% Carbowax 20M on 60–80 mesh Chromosorb P; (J) 6 ft × 0.125 in. column packed with 20% TCEP on 60–80 mesh Chromosorb P; (K) 7 ft × 0.25 in. column packed with Carbowax 20 M on 60–80 mesh Chromosorb P.

Relative yields based upon vlpc integrals are not corrected for differences in the thermal conductivities of the components. Nuclear magnetic resonance spectra were obtained with either a Varian Model A-60A or an A-60 high resolution spectrometer, with tetramethylsilane as internal standard. The samples were 5–25% solutions in carbon tetrachloride, except where otherwise noted. Infrared spectra were obtained with a Perkin-Elmer 237 Infracord spectrometer. Mass spectra were determined using a Varian M-66 mass spectrometer and ultraviolet spectra were obtained with a Cary 15 spectrometer.

General Method of Irradiating Arene Dienes. A G.E. mercury lamp (H 100-A4/T or H 400A33-1) with an immersion well and a Pyrex filter was used. Photolyses were accomplished at about 25° except where otherwise noted.

Irradiation of *o*-Divinylbenzene (1). *o*-Divinylbenzene (1.2 g) in 1200 ml of pentane was outgassed with nitrogen and irradiated for 4 hr with a 400-W lamp. Vlpc (column A) revealed 57% of *o*-divinylbenzene, 40% of benzobicyclo[3.1.0]hex-2-ene (**2**), and <3% (total) of three minor products whose vlpc retention times matched 1,2-dihydronaphthalene, tetralin, and naphthalene. Extended irradiation produced a maximum yield of **2** of 13% of theoretical. No vlpc peak was evident at the retention time of authentic benzobicyclo[3.1.0]hex-2-ene.

Irradiation of Benzobicyclo[3.1.0]hex-2-ene (2). A 100-μl sample of **2** in 80 ml of ether was outgassed with nitrogen for 5 min, irradiated for 4 hr with a 400-W lamp, and concentrated to *ca.* 0.2 ml by rotary evaporation. By vlpc analysis (column B) the sample was identical with starting material.

Trideuteriomethyltriphenylphosphonium Bromide. To 30 g of methyltriphenylphosphonium bromide was added 40 ml of D_2O and 100 μl of 1 *M* NaOD in D_2O. After heating at 50° for 2 hr the water was removed by distillation at reduced pressure and the residue dried at reduced pressure. The above procedure was repeated twice using 30 ml of D_2O each time and finally the solid was pulverized and dried in a vacuum desiccator over P_2O_5; yield, 28.6 g. Nmr analysis showed only a trace of protium in the methyl group.

***o*-Divinylbenzene-d_4 (6).** Into a 250-ml three-necked flask equipped with a stirrer, condenser with drying tube, N_2 inlet, and a rubber septum was put 43 ml of 2 *M* *tert*-butyllithium (86 mmol) in pentane. An additional 20 ml of pentane was added, the mixture was cooled in ice, and then 30 ml of ether was added followed by 28.5 g (79.3 mmol) of trideuteriomethyltriphenylphosphonium bromide and finally an additional 10 ml of ether. After refluxing the mixture for 1 hr, 5.4 g of *o*-phthalicdicarboxaldehyde (40 mmol) in 90 ml of ether was added slowly, and the mixture was refluxed 3 hr. The solution was filtered, and the ether was removed under vacuum. The product was distilled through a microdistilling head and everything boiling below 80° was collected; yield, 90 μl (*ca.* 80 mg; 1.5%). Vlpc (column C) showed **6** to be *ca.* 95% pure. Nmr absorptions at τ 4.80 and 4.52 had decreased compared to **1** and gave a deuterium content of 93%. [Nmr of *o*-divinylbenzene (*1*) showed τ 4.80 (dd, 2, J = 11 and 2 Hz, $\mathrm{H(Ar)C{=}C(}H_t\mathrm{)H}$), 4.52 (dd, 2, J = 2 and 18 Hz, $\mathrm{H(Ar)C{=}C(}H_c\mathrm{)H}$), 3.07 (dd, 2, J = 18 and 11 Hz, $\mathrm{Ar(}H\mathrm{)C{=}CH_2}$), 2.79 (m, 4, aromatic).]

Irradiation of *o*-Divinylbenzene-d_4 (6). *o*-Divinylbenzene-d_4 (**6**) (90 μl) in 60 ml of distilled pentane was irradiated with a 100-W lamp for 15.5 hr. The pentane was distilled through a 4-in. Vigreux column, and the residue was purified by vlpc (column F). Nmr analysis showed that the benzobicyclo[3.1.0]hex-2-ene (**7**) had the starting deuterium in the methylene positions (±5%).

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(41) E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1454, 1458 (1967).

(42) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

(43) M. Pomerantz and W. C. Schumann, unpublished observation.

(44) R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 4141 (1962).

(45) J. Meinwald, Abstracts, 21st National Symposium on Organic Chemistry, Salt Lake City, Utah, June 15–19, 1969, p 67.

(46) The 2,3-naphthalene bond is, of course, of considerably reduced bond order compared to the benzene bonds and thus it is not surprising that this molecule resembles 1,5-hexadiene more closely than *o*-divinylbenzene.

Attempted Reaction of *o*-Divinylbenzene (1) with Hexafluoro-2-butyne. A sample of *o*-divinylbenzene (20 mg) was combined with 10 ml of ether and *ca.* 1 g of hexafluoro-2-butyne. The above solution was irradiated for 5 hr, concentrated by rotary evaporation, and analyzed by vlpc. Preparative vlpc (column B) afforded samples of naphthalene (39% of theoretical), benzobicyclo[3.1.0]hex-2-ene (10%), and only a trace of 1,2-dihydronaphthalene. The naphthalene was identified by its low-voltage mass spectrum (*m/e* 128) and by comparison of its nmr spectrum with that of authentic naphthalene. The methanoindene (2) was identified by comparison of its nmr spectrum with that of an authentic sample.

Irradiation of *o*-Divinylbenzene (1) at −50°. A sample of **1** (25 μl) in 55 ml of ether was irradiated for 2 hr at −50°, concentrated to *ca.* 100 μl by rotary evaporation, and analyzed by vlpc (column A). Based upon the amount of **1** consumed, the yield of naphthalene was 39% of theoretical and the yield of benzobicyclo[3.1.0]hexane was 10% of theoretical. These products were identified as above.

Irradiation of *o*-Divinylbenzene (1) in Methanol. A sample of **1** (150 mg) was diluted in 250 ml of methanol and irradiated for 40 min with a 450-W Hanovia lamp (679A-36) using a Pyrex filter. Vlpc (column I, internal standard) indicated 15% of 1,2-dihydronaphthalene, 17% of benzobicyclo[3.1.0]hex-2-ene, and 14% of α-methoxytetralin. The 1,2-dihydronaphthalene and methanoindene were collected by preparative vlpc (column K) and identified by comparison of their nmr spectra with those of authentic samples. The α-methoxytetralin was identified by its vlpc retention time, the observation that it could not be separated (column I) from authentic material, and its characteristic methoxyl signal in the nmr spectrum of the crude reaction mixtures.

Reaction of 1,4-Dibromotetralin with Magnesium. In a 50-ml, round-bottomed flask equipped with a reflux condenser and a magnetic stirrer was placed 0.3 g of magnesium turnings, 25 ml of anhydrous ether, and 3 g of 1,4-dibromotetralin. This mixture was refluxed for 0.5 hr, cooled, filtered, and concentrated. Analysis by vlpc (column D) showed mostly naphthalene and traces of tetralin and 1,2-dihydronaphthalene.

Reaction of 1,4-Dibromotetralin with Magnesium in the Presence of Uv Light. 1,4-Dibromotetralin (3 g), magnesium (0.3 g), and 55 ml of ether were heated to reflux and irradiated with a 400-W lamp for 2 hr. The mixture was then cooled, filtered, and concentrated. Vlpc analysis (column D) indicated naphthalene and traces of 1,2-dihydronaphthalene and tetralin. No vlpc peak was evident at the retention time of benzobicyclo[3.1.0]hex-2-ene.

Reaction of 1,4-Dibromotetralin with Magnesium in the Presence of *o*-Divinylbenzene and Ultraviolet Light. 1,4-Dibromotetralin (3 g), magnesium (0.3 g), and 50 mg of *o*-divinylbenzene were combined in 100 ml of dry ether and heated to reflux while irradiating with a 400-W lamp for 2 hr. The mixture was then cooled, filtered, and concentrated. Analysis by vlpc (column D) showed benzobicyclo[3.1.0]hex-2-ene, 1,2-dihydronaphthalene, and tetralin, in addition to naphthalene.

Irradiation of 3,4-Benzotropilidene (13). A 50-mg sample of **13** was dissolved in 55 ml of ether and irradiated with a 100-W lamp for 70 min. The solution was then concentrated by rotary evaporation. Vlpc (column B) of the concentrated solution afforded a product which was identified by its nmr spectrum as 2,3-benzonorcaradiene. The details of the nmr spectrum are given in the text.

Irradiation of 2,3-Benzonorcaradiene (14) in Cyclohexene. A sample of **14** (100 mg) was combined with 0.4 ml of cyclohexene in a 0.25-in. i.d. Pyrex tube, suspended on the outside of a Pyrex immersion well, cooled with a stream of water, and irradiated for 26 hr with a 400-W lamp. Preparative vlpc (column E) afforded a compound which had an infrared spectrum identical with that of authentic norcarane.[47]

Ethyl Malonate-d_2. A mixture of ethyl malonate (150 g, 0.94 mol), deuterium oxide (130 g), dry tetrahydrofuran (300 ml), and a catalytic amount of potassium hydroxide was refluxed with stirring for 16 hr. After removal of the tetrahydrofuran by distillation through a 1-ft Vigreux column, the aqueous and organic layers were separated. The aqueous layer was extracted with three 75-ml portions of ether; the combined organic fractions were dried with magnesium sulfate and distilled through a 6-in. Vigreux column. The yield of ethyl malonate-d_2 was 136 g (90% of theoretical), bp 105–106° (42 mm). Analysis by nmr indicated 80–83% of two deuterons.

2,2-Dideuterio-1,3-propanediol. In a 2-l., three-necked flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, and an addition funnel were placed lithium aluminum hydride (47 g, 1.27 mol) and 1 l. of ether. The flask was cooled in ice and ethyl malonate-d_2 (136 g, 0.84 mol) was added at a rate sufficient to maintain a gentle reflux. After the addition was complete (90 min), the mixture was stirred for 15 min at room temperature and then quenched with 75 ml of saturated ammonium chloride. The mixture was filtered with Celite, the filtrate was washed with 1200 ml of ether, and the combined ether fractions were dried with magnesium sulfate. After removal of the solvent, the residue was distilled. Eleven grams (17% of theoretical) of the diol was collected at 85° (3 mm).[48] Analysis by nmr indicated 82% of two deuterons.

2,2-Dideuterio-1,3-dibromopropane.[25] In a 100-ml, round-bottomed three-necked flask equipped with a 50-ml addition funnel, a reflux condenser, and a magnetic stirrer were placed 1.31 g of 95% sulfuric acid, 44 g of 48% hydrobromic acid, and 8 g (0.10 mol) of 2,2-dideuterio-1,3-propanediol. To the above solution was added 21 g of 95% sulfuric acid. The mixture was then refluxed for 2 hr, after which the volatile material was allowed to distill. The distillate was collected at 115–117° and separated into two phases upon condensation. The material was extracted with two 100-ml portions of ether. The ether fractions were combined and washed with 8 ml of 50% sulfuric acid and 10 ml of saturated sodium carbonate solution, and dried with calcium chloride. Evaporation of the ether afforded 17.5 g (86% of theoretical) of 2,2-dideuterio-1,3-dibromopropane. Analysis by nmr indicated 82% of two deuterons.

2,2-Dideuteriotrimethylenebis(triphenylphosphonium) Dibromide. Triphenylphosphine (76 g, 0.29 mol) was placed in a 500-ml three-necked round-bottomed flask equipped with a mechanical stirrer and a reflux condenser. 2,2-Dideuterio-1,3-dibromopropane (24.5 g, 0.12 mol) was added and the slurry was heated to 200° over a 90-min period. At 80° the slurry melted and at 140° a precipitate formed. The mixture was heated at 200° for 30 min, cooled, and dissolved in 300 ml of chloroform. The chloroform solution was refluxed with charcoal for 30 min, filtered, and concentrated to 135 ml. To this was added 120 ml of acetone, after which the solution was refrigerated overnight. The white solid which formed was separated from the solution by filtration and dissolved in 100 ml of absolute ethanol. Ether was added until crystallization started; the mixture was then placed in a freezer for 8 hr, and filtered. The solid was dried at 100° (7–40 mm) for 40 hr, and further dried at 130° (0.2 mm) for 12 hr. The yield of fluffy white material was 56 g (64% of theoretical), mp > 335°.

7,7-Dideuterio-3,4-benzotropilidene (15). **15** was prepared by the method of Wittig,[9a] using 30 g (41 mmol) of 2,2-dideuteriotrimethylenebis(triphenylphosphonium) dibromide, 1.8 g (82 g-atoms) of cut sodium, and 5.5 g (41 mmol) of *o*-phthalicdicarboxaldehyde. The yield of purified **15** was 0.36 g (6% of theoretical). In several additional runs, no 3,4-benzotropilidene was formed.

Irradiation of 7,7-Dideuterio-3,4-benzotropilidene (15). A sample (100 mg) of **15**, containing 1.66 deuterons per molecule, in 55 ml of ether was irradiated for 70 min with a 100-W lamp. Flash evaporation and preparative vlpc (column B) afforded a sample of benzonorcaradiene from which the following nmr spectrum was obtained: τ 10.4, 0.59 H; 8.6, 0.59 H; 8.2, 0.17 H; 7.7, 1 H; two vinyl hydrogens as a doublet at 3.8 and 4 aromatic hydrogens at 2.9 ppm.

Low-Temperature Irradiation of 7,7-Dideuterio-3,4-benzotropilidene (15). A sample of **15** (20 mg) was diluted in 55 ml of propane and irradiated for 10 min at −55 to −78° with a 400-W lamp. The cold temperature was maintained by circulating methanol through a Dry Ice–acetone bath. After the irradiation period the sample was concentrated by distillation at −75° (1 mm), diluted to *ca.* 2 ml with cold carbon disulfide, and concentrated to *ca.* 50 μl by high vacuum distillation at −20°. The remaining material was transferred to an nmr tube, care being taken to keep the material cold at all times. An nmr spectrum showed τ 10.4 ppm, 0.59 H, and 8.6 ppm, 0.59 H.

Irradiation of 1,2-Benzotropilidene (17). A sample of **17** (200 mg) was combined with 55 ml of ether and irradiated for 35 min with a 400-W lamp. The products were purified by preparative vlpc (column B) and identified by comparison of their retention times and nmr spectra with those of authentic material. The prod-

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(47) A sample of norcarane was graciously provided by Dr. Robert Honour and Professor Lester Friedman.

(48) Additional diol can be obtained from the aqueous portion if desired.

ucts were 2,3-benzonorcaradiene (92%), recovered **17** (5%), benzobicyclo[3.2.0]hepta-2,6-diene (*ca.* 0.5%), and less than 3% of naphthalene and 1- and 2-methylnaphthalenes.

2,3-Benzobicyclo[3.2.0]hepta-2,6-diene (18). Indene (20 g), maleic anhydride (10 g), and benzophenone (2 g) were combined with 200 ml of acetone in a photolysis well. The above mixture was outgassed with nitrogen, cooled to −78° with cold, circulating methyl alcohol, and irradiated with a 400-W lamp for 5.5 hr,[28] after which the solution was concentrated by rotary evaporation and 50 ml of ether was added. This solution was stirred for 30 min with a saturated potassium carbonate solution, the aqueous and organic fractions were separated, and the aqueous fraction was acidified with 18% hydrochloric acid. The acidified solution was extracted with three 100-ml portions of ether; the combined ether solutions were dried with magnesium sulfate and concentrated by rotary evaporation, to afford 1 g (7% of theoretical) of 2,3-benzobicyclo[3.2.0]hept-2-ene-6,7-dicarboxylic acid.

The above acid (0.91 g, 3.9 mmol) was dissolved in 40 ml of distilled pyridine and 1.8 g (4 mmol) of lead tetraacetate was added.[29] This mixture was refluxed for 30 min, cooled, and concentrated by vacuum distillation (25 mm). To the residue was added enough 10% hydrochloric acid to make the pH 3. The mixture was then extracted with three 100-ml portions of ether. The combined ether extract was washed with three 30-ml portions of saturated potassium carbonate solution and with two 50-ml portions of water. The ether solution was then dried with magnesium sulfate and concentrated by rotary evaporation to *ca.* 2 ml. Vlpc analysis (column B) demonstrated that the retention time of this sample matched that of **18** from the photolysis of **17**. The nmr spectrum of this material and that of **18** are identical. The nmr spectrum of **18** is described in the text and it agrees with that reported by Metzner.[30]

Photolysis of 3,5,7,7-Tetradeuterio-1,2-benzotropilidene (19). A sample of **19**[27] (100 mg) was combined with 55 ml of ether and irradiated for 20 min with a 400-W lamp. Vlpc (column B) showed the major component had the retention time of benzonorcaradiene. This product was purified by preparative vlpc (column B). Its nmr spectrum consisted of, in addition to four aromatic hydrogens, a singlet at τ 3.8 ppm, 1 H, and broad singlets at 8.6 and 10.4 ppm, 0.5 H each.

3,3,5,7-Tetradeuterio-2,3-benzobicyclo[3.2.0]hepta-2,6-diene (21). A sample of 3,5,7,7-tetradeuterio-1,2-benzotropilidene (600 mg)[27] in 300 ml of ether was irradiated for 30 min with a 400-W lamp and concentrated by rotary evaporation. **21** was collected by preparative vlpc along with 1,4,6,7-tetradeuterio-2,3-benzonorcaradiene. Several such runs provided sufficient material for an nmr spectrum of **21** which consisted of four aromatic hydrogens at τ 2.95 ppm, a vinyl singlet at 3.92 ppm, 1 H, and a singlet at 6.30 ppm, 1 **H**.

Partial Irradiation of 3,4-Benzotropilidene (13). **13** (12 µl) in 2 ml of ether was placed in a tube and irradiated with a 100-W lamp for 10 min. The ether was blown off with nitrogen, and the residue was taken up in CCl_4. The nmr spectrum indicated 32% reaction and no 1,2-benzotropilidiene (±3%). Vlpc (column H) of the starting material showed *ca.* 2% of **17** as did the vlpc of the product.

Partial Irradiation of 1,2-Benzotropilidene (17). A 50-mg sample of **17** was diluted in 55 ml of ether and irradiated with a 100-W lamp for 10 min. The sample was then concentrated by flash evaporation, diluted with 2 ml of carbon tetrachloride, and again concentrated, this time to *ca.* 50 µl. This material was transferred to an nmr tube. Its nmr spectrum revealed 30% of benzonorcaradiene and 70% of 1,2-benzotropilidene. No transition was evident at τ 7.55 ppm and from this it was concluded that no 3,4-benzotropilidene was produced in the reaction.

Photolysis of 1,2-Benzotropilidene-d_2 (22). A sample of **22**[27] (40 mg) was diluted in 55 ml of ether and irradiated for 30 min with a 100-W lamp. The solution was concentrated to *ca.* 100 µl by flash evaporation, diluted to *ca.* 2 ml with carbon tetrachloride, concentrated again, further diluted to 2 ml with carbon tetrachloride, and finally concentrated to 0.05 ml in a stream of nitrogen. The nmr spectrum of this solution displayed the following transitions: τ 10.4 ppm, 0.8 H; 8.6, 0.8 H; 8.2, 0.10 H; 7.7, 0.92 H; 3.8, 1.6 H; and 2.9 ppm, 3.8 H, indicative of deuterated benzonorcaradiene **23**.

Low-Temperature Photolysis of 3,5,7,7-Tetradeuterio-1,2-benzotropilidene (19). A sample (50 mg) of **19** was diluted in 55 ml of dimethyl ether and irradiated with a 100-W lamp at −65° for 33 min. The solution was then concentrated to *ca.* 0.1 ml by vacuum distillation at −78°, and 2 ml of cold carbon disulfide was added and distilled at −25° to *ca.* 0.05 ml. The cold solution was transferred to an nmr tube and its nmr spectrum was obtained at −55°. The ratio of exo to endo of cyclopropylmethylene hydrogens was 1:1 as determined by integration of the transitions at τ 8.6 and 10.4 ppm.

Irradiation of *trans*-1-Phenyl-1,3-butadiene. *trans*-1-Phenyl-1,3-butadiene (1.8 g) (containing a small amount of diphenylamine inhibitor) in 60 ml of ether was irradiated with a 100-W lamp. After 17.5 hr the ratio of 3-phenylcyclobutene:*cis*-1-phenyl-1,3-butadiene:*trans*-1-phenyl-1,3-butadiene (vlpc; column G at 80°) was 1:13.6:5.5, after 26.5 hr it was 1:4.9:1.9, after 41.5 hr 1:1.2:0.56, and after 58 hr there were only small amounts of the butadienes. The cyclobutene peak did not increase in size nearly as rapidly as the butadiene peaks disappeared. The ether was removed under vacuum, and the residue was distilled at 0.2 mm. Everything that would distill with a pot temperature of 65° was collected; yield, *ca.* 0.1 g (6% yield; 75–80% pure). Purification of 3-phenylcyclobutene was by vlpc (column G at 70°); nmr τ 7.55 (dd, 1, J = 15.3 and 2.2 Hz, H_4 cis to Ph), 6.85 (dd, 1, J = 15.3 and 5.0 Hz, H_4 trans to Ph), 5.80 (dd, 1, J = 2.2 and 5.0 Hz, PhC*H*), 3.48 (s, 2, vinyl), and 2.46 (s, 5, aromatic). Catalytic hydrogenation (PtO_2), 1 mol of H_2 uptake, produced phenylcyclobutane,[49] and thermal rearrangement[50] produced *trans*-1-phenyl-1,3-butadiene.

Sensitization. All reactions were accomplished with a Rayonet photochemical reactor with a merry-go-round[51] using 16 3500-Å lamps, except with 1-phenylbutadiene, where 3000-Å lamps were used. The general procedure was to place the sample, sensitizer, and 25 ml of ether in a 25-ml Pyrex test tube, seal the tube with a serum cap, and outgas the solution for 5–10 min prior to irradiation. Analyses were by vlpc using the samples irradiated.

Table I

Compound	% light by sen[a]	Time, min	Comments and results
17	>98[b,c]	36	No reaction
	0	36	59% **14**, 41% unreacted
15	>95[b,c]	22	No reaction
	0	22	61% **14**, 39% unreacted
1	>98[b,c]	36	All **1** destroyed, no **2** formed
	0	36	4% **2**
trans-1-Phenyl-1,3-butadiene	>75[c,d]	65	67% trans, 33% cis
	0	65	86% trans, 14% cis
	>75	*e*	40% trans, 58% cis, 2% 3-phenylcyclobutene
	0	*e*	30% trans, 59% cis, 11% 3-phenylcyclobutene

[a] Approximate per cent of light absorbed by sensitizer. [b] 16 3500-Å lamps. [c] Benzophenone. [d] 16 3000-Å lamps. [e] 7.3 hr.

Sensitized Irradiation of *o*-Divinylbenzene (1) in Methanol. A solution composed of *o*-divinylbenzene (**1**, 40 mg) and 1-methylnaphthalene (*ca.* 50 mg, internal standard) in 120 ml of anhydrous methanol was divided into two 60-ml portions. To one of these was added 100 mg of benzophenone. Both were outgassed with nitrogen for 10 min and then irradiated for 20 min with a 450-W Hanovia lamp (679A-36) through a Pyrex filter. Vlpc analysis (columns I and J) showed for the unsensitized reaction: *o*-divinylbenzene (**1**), 20%, 1,2-dihydronaphthalene (**3**), 9%, benzobicyclo[3.1.0]hex-2-ene (**2**), 10%, and α-methoxytetralin, 10%, all relative to the 1-methylnaphthalene internal standard with no yield implied. The sensitized reaction showed *o*-divinylbenzene (**1**), <3%, with less than 3% combined of 1,2-dihydronaphthalene (**3**) and **2**, and less than 1% of α-methoxytetralin, all once again relative to the internal standard.

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