Photochemistry of Cycloalkenes. VIII. 2-Phenyl-2-norbornene and 2-Phenyl-2-bornene[1a,b]

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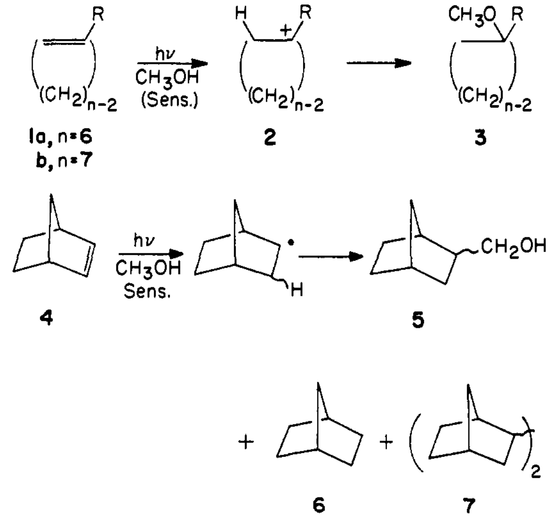
Abstract: The photochemical behavior of 2-phenyl-2-norbornene (**8**) was found to be substantially different from that of the unsubstituted analog 2-norbornene (**4**). In contrast to **4**, which on sensitized irradiation in methanol solution rapidly affords a mixture of the radical type products **5**–**7**, the phenyl derivative **8** was found to be photostable under these conditions. However, direct irradiation of **8** in methanol solution afforded a mixture of the ether **11a** and the endo (**9**) and exo (**10**) isomers of 2-phenylnorbornane. Labeling studies with methanol-*O-d* showed that each of these products was formed in an ionic process involving exo-side protonation at C-3. Similar ionic photochemical behavior was exhibited by the homolog 2-phenyl-2-bornene (**17**), which on irradiation in methanol solution afforded a mixture of 2-*endo*- (**18**) and 2-*exo*-phenylbornane (**19**), 1-phenylcamphene (**20**), and the ethers **21** and **22**. Sensitization of **8** with triplet acetophenone or fluorene afforded no significant photoproducts, and the fluorescence of **8** was found to be quenched by methanol. The photochemical behavior of **8** and **17** is therefore interpreted in terms of a reactive singlet excited state displaying charge-transfer character and is compared with the photochemical behavior reported for other styryl systems.

Recent studies have shown that transfer of triplet energy to cyclohexenes and -heptenes in protic media usually results in protonation of the olefin followed by a variety of subsequent reactions which emanate from the resulting carbocation intermediate (*cf.* **2**).[2,3] In the case of the parent olefins cyclohexene and -heptene themselves, xylene-sensitized irradiation in methanolic solution affords the methyl ethers **3a** and **3b** (R = H) in 51–62% yield.[2b] Although general for six- and seven-membered ring systems, photoprotonation has been found to be highly dependent on ring size, with more conformationally rigid olefins such as cyclopentenes and norbornenes showing instead solely radical behavior.[2b,4] Thus, for example, xylene-sensitized irradiation of 2-norbornene (**4**) in methanol solution affords a mixture of the adducts **5** and reduction products **6** and **7** with no detectable ionic behavior.[2b,4]

In a study of substituent effects, it was found that 1-phenylcyclohexene and -heptene (**1a** and **1b**, R = C_6H_5) show mixed photochemical behavior, affording both radical products analogous to **5** and **6** and the ionic products **3a** and **3b** (R = C_6H_5) on sensitized irradiation.[2b,5] However, extension of the study to 2-phenyl-2-norbornene (**8**) has now revealed that this olefin displays photochemical behavior markedly different from that of either its unsubstituted analog **4** or the larger ring analogs **1a** and **1b** (R = C_6H_5). It is this unexpected photochemical behavior of **8** and its bornyl homolog **17** to which the present discussion is directed.



Results

I. 2-Phenyl-2-norbornene (8). A. Photoproducts. On irradiation in methanolic solution **8** underwent rapid disappearance. The reaction mixture was separated by gas chromatography into two principal components in addition to recovered starting material. Isolation of the first component afforded a colorless liquid which was ultimately identified as an unresolved mixture of 2-*endo*- (**9**) and 2-*exo*-phenylnorbornane (**10**). The presence of two isomers was revealed by the nmr spectrum, which displayed two bands arising from benzylic protons at τ 6.82 and 7.32 with relative areas of 2.6:1. From the chemical shifts it was concluded that these originate from an exo and an endo benzylic proton, respectively, and hence represent the 2-endo and 2-exo isomers **9** and **10**, respectively.[6] This was confirmed by direct comparison with the spectra of authentic specimens of each isomer.

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[1] (a) Part VII: P. J. Kropp, *J. Org. Chem.*, **35**, 2435 (1970); (b) presented in part before the Photochemistry Symposium of the Organic Chemistry Division of the American Chemical Society, 155th National Meeting, San Francisco, Calif., April 1968, Abstract P-86; (c) Alfred P. Sloan Research Fellow; University of North Carolina.

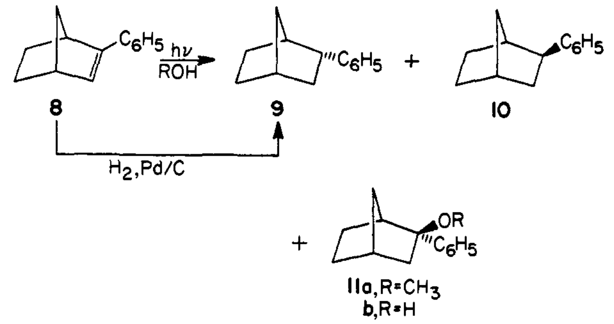
[2] (a) P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, **89**, 5199 (1967); (b) P. J. Kropp, *ibid.*, **91**, 5783 (1969); (c) *Pure Appl. Chem.*, **24**, 585 (1970).

[3] See J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969), and references cited therein.

[4] R. R. Sauers, W. Schinski, and M. M. Mason, *Tetrahedron Lett.*, 4763 (1967).

[5] (a) In this case identical behavior could also be elicited by direct irradiation of the styryl chromophore. See also (b) S. Fujita, T. Nômi, and H. Nozaki, *Tetrahedron Lett.*, 3557 (1969); (c) M. Tada and H. Shinozaki, *Bull. Chem. Soc. Jap.*, **43**, 1270 (1970); (d) H. M. Rosenberg and M. P. Servé, *J. Org. Chem.*, **37**, 141 (1972).

[6] See D. C. Kleinfelter, T. E. Dye, J. E. Mallory, and E. S. Trent, *ibid.*, **32**, 1734 (1967).

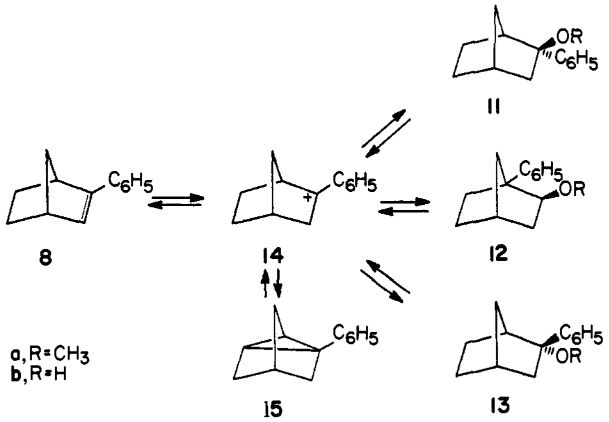


The previously unreported 2-endo isomer **9** was prepared by catalytic hydrogenation of 2-phenyl-2-norbornene (**8**).[7] The nmr spectrum of the resulting product exhibited a complex multiplet at τ 6.82, arising from the benzylic proton H_{2x}, and a triplet of poorly resolved quartets at τ 8.04 (J = 12.5 Hz), presumably arising from the adjacent proton H_{3x}. By contrast, the nmr spectrum of a sample of the 2-exo isomer **10**, prepared by aluminum chloride catalyzed addition of benzene to 2-norbornene,[8] displayed a triplet at τ 7.32 (J = 7 Hz) attributable to the benzylic proton H_{2n}.[9] Identification of the photoproducts as **9** and **10** was corroborated by the fact that nmr and infrared spectra of the photomixture were identical with the superposition of those of **9** and **10** and could be duplicated by obtaining the spectra of a 2.6:1 mixture of **9** and **10**.

Isolation of the second gas-chromatographic component afforded a colorless oil which was readily characterized as a methyl ether by the presence of a three-proton singlet at τ 7.37 in the nmr spectrum and a broad band centered at 9.26 μ in the infrared spectrum. It thus appeared that addition of methanol to 2-phenyl-2-norbornene (**8**) had occurred, and this was supported by the appearance of a parent ion at *m*/*e* 202 in the mass spectrum.

A priori, ionic addition of methanol to **8** might be expected to afford one or more of the ethers **11a–13a**, as shown in Scheme I. However, since the photoether exhibited no nmr bands attributable to either a benzylic proton or a proton adjacent to a methoxyl group, a structure such as that of the 1-phenyl-2-norbornyl derivative **12a**[10] was clearly precluded. Instead, a structure such as that of one of the previously unknown ethers **11a** or **13a** was suggested, in which the phenyl and methoxyl substituents are attached to the same carbon atom. The correct assignment was readily established as **11a** by direct comparison of the photoether with a specimen of **11a** prepared independently from the readily available alcohol **13b**[11] using the general procedure previously reported.[12] The assignment was further supported by the finding that (a) repetition of the irradiation procedure under aqueous conditions afforded the alcohol **11b**[12] as the photoproduct and (b) independent synthesis of the alternative ethers **12a** and **13a** by methylation of the corresponding alcohols **12b** and **13b** revealed that neither had been formed in detectable quantity in the photoprocess.

Scheme I



With the photoproducts **9**, **10**, and **11a** identified, it could be shown that they were formed in yields of 13, 5, and 47%, respectively, in a typical run. Control runs revealed that each product is reasonably photostable under the reaction conditions and is not a precursor of one of its companion photoproducts.

B. Labeling Studies. From the above data it might be concluded that 2-phenyl-2-norbornene (**8**) undergoes photoreaction in methanol *via* two competing pathways: an ionic process leading to the ether **11a** and a radical process affording the norbornanes **9** and **10**. The latter mode of reaction would be completely consistent with the behavior noted previously for the parent 2-norbornene (**4**) and its 2-methyl derivative,[2b] but the former process would be completely unprecedented for such a highly constrained olefin. In order to learn more about this totally unexpected behavior, several labeling studies were undertaken.

Irradiation of 2-phenyl-2-norbornene (**8**) in methf anol-*O-d* again afforded the ether **11a** and a mixture o- the hydrocarbons **9** and **10**. As shown in Table I, mass spectral analysis revealed that, as expected from an ionic mechanism, formation of the photoether **11a** was accompanied by substantial incorporation of deuterium. Likewise, the unreacted starting material displayed the presence of some deuteration, as has been observed previously for other olefins which exhibit ionic photobehavior.[2] Surprisingly, however, **9** and **10** *were also formed with substantial deuterium incorporation.* This suggests that both types of product arise *via* an initial protonation of **8** to form the 2-phenyl-2-norbornyl

Table I. Deuterium Analyses of Materials Recovered from Irradiation of 2-Phenyl-2-norbornene (**8**) in Methanol-*O-d*

	8	**9** and **10**	**11a**
d_0	86	6	7
d_1	14	77	87
d_2	0	17	6

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[7] Subsequently, F. A. Carey and H. S. Tremper, *J. Org. Chem.*, **34**, 4 (1969), and F. R. Jensen and B. E. Smart, *J. Amer. Chem. Soc.*, **91**, 5686 (1969), have reported the preparation of **9** in a similar manner.

[8] L. Schmerling, U. S. Patent 2,480,267 (1949); *Chem. Abstr.*, **44**, 1136 (1950).

[9] The low-field position of the H_{3x} band in the spectrum of **9** is consistent with the report that a 2-*endo*-phenyl substituent causes an inductive deshielding of H_{3x} by approximately 0.2 ppm.[6] The H_{3x} band for 10 appears above τ 8.2 and is overlapped by the other methylene protons. This is also expected, since a 2-*exo*-phenyl group exerts a *shielding* effect on H_{3x}.[6]

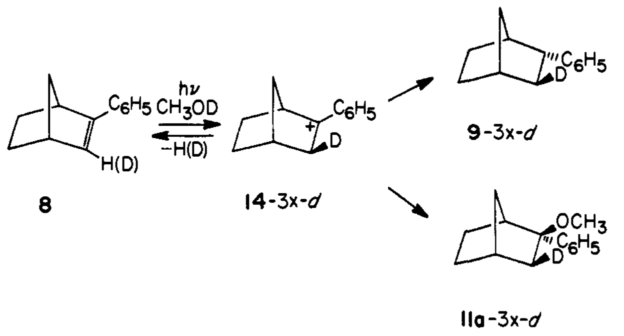
[10] H. A. Bruson, U. S. Patent 2,411,516 (1946).

[11] D. C. Kleinfelter and P. v. R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

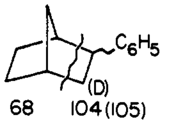
[12] H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Amer. Chem. Soc.*, **86**, 1246 (1964).

cation **14**,[13] which, as outlined in Scheme II, in turn undergoes three competing reactions: (a) nucleophilic capture by solvent to afford the ether **11a**, (b) hydride abstraction to afford the hydrocarbons **9** and **10**, and (c) deprotonation (or dedeuteration) to regenerate the starting olefin **8**.

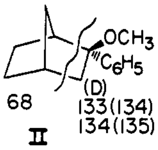
Scheme II



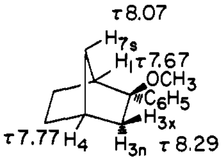
If photoprotonation of **8** involves a simple addition to the styryl chromophore without any concomitant skeletal rearrangement or scrambling as shown in Scheme II, the resulting photoproducts **9–11** should bear deuteration at C-3. Moreover, if protonation occurs from the exo side, as is the normal fashion for norbornenes,[14] the deuterium substituent should be in the 3-exo position. These predictions could be verified by examination of the nmr and mass spectra of **9** and **11a**.[15] The principal fragmentation pattern in the mass spectra of **9** and **10** is one affording fragments at *m/e* 68 and 104, which almost undoubtedly corresponds to a retro-Diels–Alder type of splitting as represented by I. A shift in the *m/e* 104 band in the deuterated photoproduct to 105 without an accompanying shift of the *m/e* 68 band indicated the presence of deuterium substitution at C-2 or -3. This was confirmed by the nmr spectrum of the deuterated photoproduct, which displayed a sharpening of the benzylic proton band of **9** at τ 6.82 and an almost complete loss of the H_{3x} band at τ 8.04. Thus the photoproduct is **9**-3x-*d*.[15]



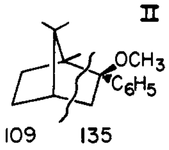
I



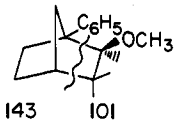
II



III



IV



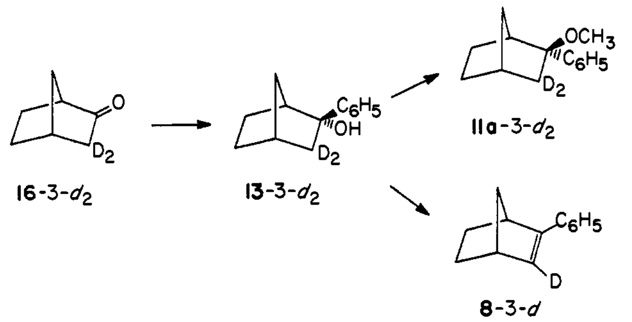
V

The mass spectrum of the photoether **11a** displayed a set of bands at *m/e* 68 and at 133 and 134 that is similarly attributable to a retro-Diels–Alder fragmentation as shown in II; in the deuterated photoproduct the latter two bands were shifted to 134 and 135, as expected with deuteration at C-3. Confirmation of C-3 as the site for deuteration was possible from a study of the nmr spectra of the photoproducts. The spectrum of the ether **11a** displays two one-proton multiplets at τ 7.67 and 7.77, a one-proton doublet at τ 8.07 (J = 9.1 Hz), and one two-proton band at τ 8.29. The corresponding spectrum of the deuterated photoether was very similar except for a marked attenuation of the two-proton band at τ 8.29 which indicated that deuteration had occurred specifically at one or both of the two positions giving rise to that band. It thus became necessary to assign the origin of that band.

The broad bands at τ 7.67 and 7.77 are easily assigned to the two bridgehead positions. By default, the two protons resonating at τ 8.29 must be located at secondary positions. Moreover, since they do not show the usual geminal splitting of 12–13 Hz,[16] they are most likely attached to the same carbon atom, with the lack of geminal splitting being attributable to a fortuitous identity of their chemical shifts. They might thus be the two methylene protons at C-2, -5, -6, or -7. However, the band at τ 8.07, which shows a principal splitting of 9.1 Hz, is probably one of the pair of H_7 methylene protons since the geminal coupling of the C-7 bridge protons of norbornanes is usually 8.5–9.5 Hz, substantially smaller than that for the other methylene pairs.[16,17] The band at τ 8.29 is thus due to the protons at C-3, -5, or -6, and only those at C-3 would be in sufficient proximity to the phenyl and methoxyl groups to experience the unusually strong deshielding effects which are placing these two protons so far downfield. The identifiable bands in the spectrum of **11a** are thus as summarized by III and the deuterated photoproduct is assigned the structure **11a**-3x-*d*.[18]

The C-3 assignment for the position of deuteration was corroborated by an independent preparation of **11a**-*3*-d_2 starting with 2-norbornanone-*3*-d_2[19] as outlined in Scheme III and the Experimental Section. In the spectrum of the resulting deuterated ether the intensity of the τ 8.29 band was greatly reduced, but the

Scheme III



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[13] Spectroscopic studies of the 2-phenyl-2-norbornyl cation support the classical structure **14** for this ion; see P. v. R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Amer. Chem. Soc.*, **85**, 479 (1963); D. G. Farnum and G. Mehta, *ibid.*, **91**, 3256 (1969); and G. A. Olah, J. R. DeMember, C. Y. Liu, and A. M. White, *ibid.*, **91**, 3958 (1969).

[14] See, for example, (a) S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *ibid.*, **84**, 3918 (1962); (b) H. Kwart and J. L. Nyce, *ibid.*, **86**, 2601 (1964); (c) A. Factor and T. G. Traylor, *J. Org. Chem.*, **33**, 2607 (1968).

[15] The low yield of the minor photoproduct **10**, combined with the fact that it could be obtained only as the minor component of a mixture with the endo isomer **9**, precluded an unambiguous assignment of the stereochemistry of deuteration in that case.

[16] P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

[17] The band at τ 8.07 probably arises from H_{7s} since a 7-hydrogen syn to a 2-*exo*-OR substituent is substantially deshielded relative to its anti partner; see D. C. Kleinfelter, *J. Org. Chem.*, **32**, 3526 (1967).

[18] Since H_{3x} and H_{3n} have almost identical chemical shifts, the exo stereochemistry for deuteration can be assigned only by analogy to **9** and to ground-state chemistry.[14]

[19] D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, 31, 115 (1966). See also J. P. Schaefer, M. J. Dagani, and D. S. Weinberg, *J. Amer. Chem. Soc.*, **89**, 6938 (1967).

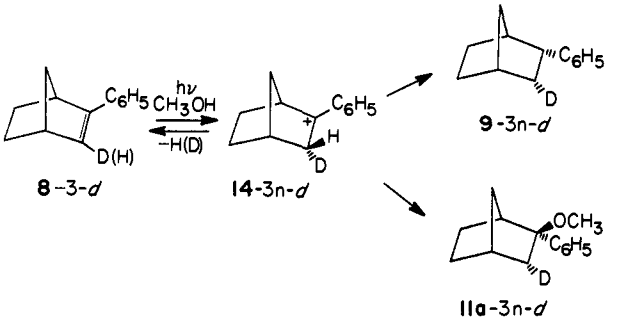
Table II. Deuterium Analyses of Materials Recovered from Irradiation of 2-Phenyl-2-norbornene-*3-d* (**8**-*3-d*) in Methanol

	Starting	Recovered		
	8	**8**	**9** and **10**	**11a**
d_0	17	54	32	34
d_1	83	45	67	65
d_2	0	1	1	1

remainder of the spectrum was almost identical with that of an undeuterated specimen of **11a**. Thus the band at τ 8.29 arises from the H_3 methylene protons and photoprotonation has been shown to occur specifically at C-3.

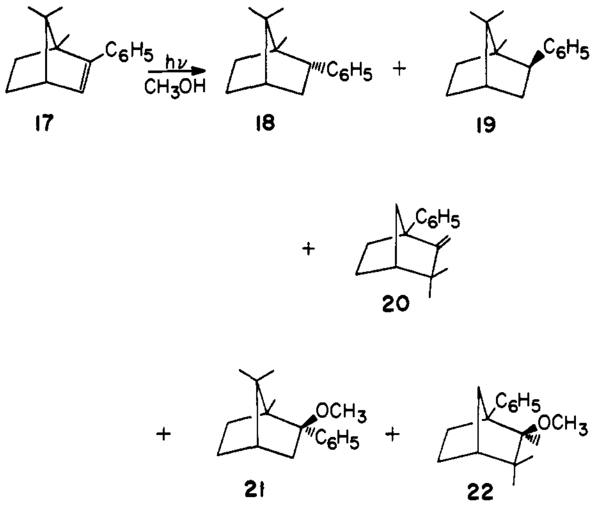
Dehydration of the alcohol **13**-*3*-d_2 used in the preparation of **11a**-*3*-d_2 afforded the olefin **8**-*3-d*, which on irradiation in methanol again provided deuterated specimens of **9** and **11a** as shown in Table II. Since in this case the deuterium atom is already present at C-3, protonation should afford the 3-endo deuterated derivatives of **9** and **11a** as depicted in Scheme IV. In accordance with this the base peak of the mass spectrum of the mixture of norbornane photoproducts **9** and **10** again displayed a prominent shift from *m/e* 104 to 105. The nmr spectrum displayed the usual bands at τ 6.82 and 8.04 corresponding to H_{2x} and H_{3x} of **9**, respectively, but the coupling patterns of each were significantly simplified, as expected for the presence of deuteration at H_{3n}.[15] Likewise, the nmr spectrum of the deuterated photoether was similar to that of an undeuterated specimen of **11a** except for an attenuation in the integral of the H_3 band at τ 8.29 to the level that would be predicted from the mass spectral isotopic analysis listed in Table II assuming that all deuterium incorporation had occurred at C-3.

Scheme IV



C. **Acid-Catalyzed Addition of Methanol.** In contrast to the photoprotonation of **8** in methanol, which lead specifically to a single adduct (**11a**) in addition to the photoreduction products **9** and **10**, acid-catalyzed protonation in 1.8 × 10^{-3} *M* acidic methanol lead to an ether fraction which exhibited a single peak on gas chromatographic analysis but was shown by analysis of the nmr spectrum to consist of a complex mixture which included the ethers **11a**–**12a** and, presumably, also **13a**;[20] there was no detectable formation of either of the reduction products **9** or **10**. Thus, the acid-catalyzed and light-initiated protonations of **8** lead to substantially different results; this precludes the possibility that the light-initiated protonation involves simply the formation of trace quantities of acidic photoproducts followed by acid-catalyzed protonation of **8** in the ground state.[21]

II. **2-Phenyl-2-bornene (17).** The cis introduction of the elements of methanol in the formation of **11a** and of the two hydrogen substituents in the formation of **9**, along with the selective formation of ether **11a** to the exclusion of **12a** or **13a**, raises the question of whether these two photoproducts are formed *via* two concerted four- or five-centered reaction pathways. However, evidence strongly supporting the proposed intermediacy of the 2-phenyl-2-norbornyl cation **14** was afforded by the photochemical behavior of the bornyl analog **17**.[22] On irradiation in methanolic solution, **17** was found to undergo rapid conversion to a mixture of three hydrocarbons (**18**–**20**) and two methyl ethers (**21** and **22**), which in a typical run were formed in yields of 11, 2, 20, 20, and 5%, respectively.[23]



The first hydrocarbon photoproduct was easily identified as 2-*endo*-phenylbornane (**18**) by the similarity of the nmr spectrum with that reported for the 2-*p*-anisyl analog[24] and by an independent preparation from **17** by sodium–liquid ammonia reduction.[24] However, the nmr spectrum of the photoproduct indicated the presence of an impurity, not present in the spectrum of the sodium–ammonia reduction product, which displayed bands at τ 9.25, 9.18, and 7.15. Since these chemical shifts correspond well with those expected for the methyl and benzylic proton resonances of 2-*exo*-phenylbornane (**19**),[24] it is concluded that the 2-exo isomer is formed as a minor photoproduct.

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(20) (a) Comparison of the nmr spectrum of the mixture of ethers with the spectra of authentic specimens of **11a**–**13a** revealed the presence of a number of bands corresponding specifically to those from the spectra of **11a** and **12a**; on the other hand, because of the nature of the spectrum of **13a**, no positive verification of the presence of **13a** in the mixture could be made. However, the presence of **11a** and **12a** under equilibrating conditions suggests the presence of **13a** as well. (b) See M.-H. Rei and H. C. Brown, *J. Amer. Chem. Soc.*, **88**, 5335 (1966).

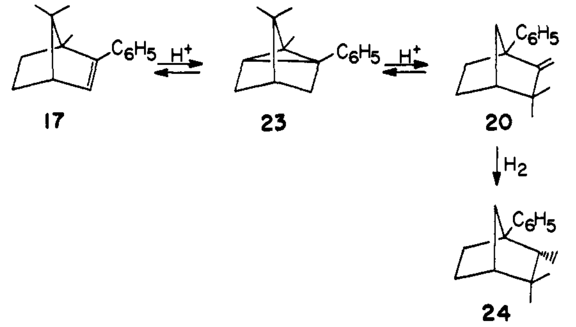
(21) Another conceivable product from the cation **14** is 1-phenylnortricyclene (**15**). Although trace quantities of a material having a gas chromatographic retention time identical with the homolog 2-phenyltricyclene (**23**) were observed on irradiation of 2-phenyl-2-bornene (**17**) (see below), there was no detectable formation of **15** on irradiation of 2-phenyl-2-norbornene (**8**). Control studies showed that **15** is photolabile but does not afford any of the products **9**–**11a** on irradiation in methanol. The photochemistry of **15** will be reported separately.

(22) D. Bernstein, *Chem. Ber.*, **99**, 1742 (1966).

(23) Two additional photoproducts having gas chromatographic retention times similar to that of ether **21** were formed in yields of about 5% each but were not identified because they could not be obtained pure due to overlapping with ether **21** on a number of columns.

(24) (a) T. J. Flautt and W. F. Erman, *J. Amer. Chem. Soc.*, **85**, 3212 (1963); (b) W. F. Erman and T. J. Flautt, *J. Org. Chem.*, **27**, 1526 (1962).

The third hydrocarbon fraction was readily characterized as 1-phenylcamphene (**20**)[25] by the similarity of the nmr spectrum with that previously reported.[25c] The assignment was confirmed through an independent synthesis of **20** by acid-catalyzed rearrangement of **17**. Treatment of a methanolic solution of **17** with 0.1% sulfuric acid at 25° for 68 hr afforded a 20.5:4.2:1.0 mixture of three isomeric hydrocarbons which did not change in composition on longer treatment. The major components were identical with 1-phenylcamphene (**20**) and 2-phenyl-2-bornene (**17**), respectively, whereas the minor component was tentatively identified as 2-phenyltricyclene (**23**) in view of the lack of any resonances attributable to an olefinic proton in the nmr spectrum. In 1% methanolic sulfuric acid the three hydrocarbons **20**, **17**, and **23** were again formed but the ratio shifted to 4.9:1.0:1.9.[26] Catalytic hydrogenation of 1-phenylcamphene (**20**) afforded a dihydro derivative which appeared epimerically pure by gas chromatographic and nmr analysis and is assumed to be the endo epimer **24**.[24] Careful comparison of the gas chromatographic behavior of **24** with that of the crude photoproduct revealed that no detectable amount had been generated by irradiation of **17**.



The two methyl ether photoproducts are tentatively assigned the bornyl and camphenyl structures **21** and **22**, respectively. These assignments are based principally on the high resolution mass spectra, which displayed prominent bands corresponding to the retro-Diels–Alder cleavage patterns IV and V. The structure **21** for the principal photoether was confirmed through an independent synthesis involving methylation of the corresponding alcohol, obtained by addition of phenylmagnesium bromide to camphor.[27]

III. Sensitization and Fluorescence Quenching Studies. In an effort to determine the multiplicity of the reactive excited species involved in the photoprotonation of norbornenes **8** and **17**, sensitization and fluorescence quenching studies were initiated. When a methanolic solution containing **8** and acetophenone was irradiated through a Pyrex filter, there was a slow disappearance of **8** accompanied by the formation of trace quantities of a mixture of the two phenylnorbornanes **9** and **10** as the only observed products; there was no detectable formation of the ether **11a**. Repetition of the experiment in the presence of methanol-*O-d* afforded a mixture of **9** and **10** which contained only minor amounts of deuterium (82% d_0 and 18% d_1), in contrast to the extensive incorporation of deuterium into **9** and **10** which occurred on direct irradiation of **8** in methanol-*O-d*. When the experiment was repeated using fluorene as the photosensitizer there was no reaction by **8**. Although the triplet excitation energy of **8** is not known, that of β-methylstyrene is reported to be 61.8 kcal/mol,[28] and it is thus reasonable to assume efficient transfer of energy from the acetophenone or fluorene triplet (73.6 and 68 kcal/mol, respectively) under these conditions. Moreover, the presence of **8** quenched the photoreduction of acetophenone in methanol and flash photolysis studies showed that **8** quenched the triplet excited state of acetophenone. However, although transfer of triplet energy apparently occurs, the excited state of **8** that is thereby generated does not undergo photoprotonation.[29] Thus the reactive intermediate leading to photoprotonation of **8** on direct irradiation is either a singlet or a higher lying triplet excited state. Evidence supporting the involvement of a singlet, rather than triplet, species was obtained by the finding that the fluorescence of **8** is substantially quenched on going from ether to methanol as solvent (see Table III).

Table III. Fluorescence Quenching Studies[a]

Olefin	Solvent	Fluorescence λ_{max}, nm	Fluorescence ϵ^b	Absorption λ_{max}, nm	Absorption ϵ
1b (R = C_6H_5)	Ether	313	100	246	8,100
	Methanol	315	92	246	8,000
8	Ether	311	100	262	10,100
	Methanol	318.5	39	262	10,200

[a] Excitation wavelength 255 nm. [b] Relative.

The photoprotonation of the norbornenes **8** and **17** on direct irradiation is paralleled by 1-phenylcyclohexene and -heptene (**1a** and **1b**, R = C_6H_5).[2b,5] However, these olefins undergo photoprotonation on sensitized irradiation as well,[2b] and the photoprotonation of the cyclohexene isomer **1a** (R = C_6H_5) is reported to be quenched by 1,3-cyclohexadiene.[5d] Moreover, as summarized in Table III, extension of our fluorescence quenching studies showed that the fluorescence of the cycloheptene isomer **1b** (R = C_6H_5) is not significantly quenched in methanol solution. Thus the photoprotonation of **1a** and **1b** apparently involves a triplet excited state on either direct or sensitized irradiation, in contrast to the behavior of the phenylnorbornenes **8** and **17**, which undergo photoprotonation only through a singlet excited species.

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[25] (a) S. S. Nametkin, A. S. Kichkina, and D. N. Kursanov, *J. Russ. Phys.-Chem. Soc.*, **61**, 1065 (1929); *Chem. Abstr.*, **24**, 841 (1930); (b) D. Bernstein, *Justus Liebigs Ann. Chem.*, 710, 98 (1967); (c) D. C Kleinfelter, R. W. Aaron, T. J. Gerteisen, J. M. Miller, Jr., and T. B. Bennett, Jr., *J. Org. Chem.*, **32**, 3521 (1967).

[26] At this higher concentration an unidentified methyl ether was also obtained, as well as trace amounts of two additional products. These materials were also formed in trace amounts in 0.1% sulfuric acid.

[27] The exo structure was assigned to the alcohol, and hence to the ether **21**, by analogy to the known stereochemical preference for Grignard addition to ketones in one stage from the less hindered side; see the discussion by H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).

[28] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

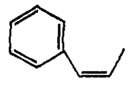
[29] The slow reaction observed during the attempted photosensitization of **8** with acetophenone may be due to chemical sensitization rather than any reaction by the triplet excited state of **8**. For a general discussion of the phenomenon of chemical sensitization, see P. S. Engel and B. M. Monroe, *Advan. Photochem.*, **8**, 245 (1971).

Discussion

The occurrence of skeletal rearrangements, the incorporation of deuterium from methanol-*O-d*, and the Markovnikov direction of addition in the photochemistry of the norbornenes **8** and **17** in methanol all imply that the initial step following photoexcitation is protonation of the olefin. An alternative four-center addition process is conceivable, but the formation of the rearranged products **20** and **22** indicates that at least some of the products are not formed *via* such a process, and it seems likely that each of the photoproducts is formed *via* reaction of a free carbocation intermediate as illustrated, for example, in Schemes II and IV.

The subsequent formation of ethers **11a**, **21**, and **22** through nucleophilic trapping by solvent of the appropriate carbocation intermediates has ample precedent in ground-state chemistry, and is paralleled in the photoprotonation of cyclohexenes, -heptenes, and -octenes.[2,3] The selective formation of ether **11a** to the exclusion of isomers **12a** and **13a** is the expected result of kinetic control in the trapping process.[20b] The formation of the reduction products **9**, **10**, **18**, and **19** apparently involves hydride abstraction from methanol by the carbocation intermediate. Although such a process has less precedent in ground-state chemistry, it regularly accompanies the photoprotonation of olefins.[2c,30,31]

The sensitization and fluorescence quenching data imply that the excited species of **8** and **17** undergoing protonation is a singlet. Two important questions remaining are why this excited state undergoes protonation and, secondly, why the triplet excited state generated through photosensitization is chemically inactive in methanol solution. These questions are perhaps best approached through a consideration of the photochemical properties of other styryl systems. Subsequent to the completion of this work, it has recently been reported that several acyclic styrene derivatives of types **25** and **26** also undergo photoprotonation on irradiation in methanol; again the photoreaction appears to occur *via* a singlet rather than triplet excited state.[33] This behavior parallels that reported here for the norbornenes **8** and **17**, but contrasts with that observed for 1-phenylcyclohexene and -heptene (**1a** and **b**, R = C_6H_5). We are thus faced with the seeming paradox that it is the latter olefins, which are *intermediate* in conformational flexibility between the rigid norbornenes **8** and **17** on one hand and the unconstrained acyclic analogs **25** and **26** on the other hand, that display divergent behavior.



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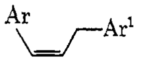

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The tendency of an excited singlet state of the norbornenes **8** and **17** and the acyclic analogs **25** and **26** to undergo photoprotonation suggests that the reactive state in these cases has charge-transfer character of type **27**, in which there is an increase of electron density at the β-carbon atom relative to the ground state. The failure of the triplet species of olefins **8**, **17**, **25**, and **26** generated by sensitized irradiation to undergo protonation suggests that the lowest lying triplet excited state of these olefins does not possess charge-transfer character and is perhaps even of a different electronic configuration than the reactive singlet excited state.

It remains then only to account for the divergent behavior displayed by 1-phenylcyclohexene and -heptene (**1a** and **1b**, R = C_6H_5). As proposed earlier,[2b] the photoprotonation observed on sensitized irradiation is probably the result of an initial photosensitized cis → trans isomerization of the olefin followed by ground-state protonation of the resulting highly strained *trans*-cycloalkene intermediate, in complete analogy with the photochemical behavior of other cyclohexene and -heptene analogs such as **1** (R = CH_3 or H), and hence does not involve charge-transfer behavior.

On direct irradiation, the cycloalkenes **1a** and **b** (R = C_6H_5) should likewise be able to undergo cis → trans isomerization, and the resulting trans isomer could, once again, undergo proton abstraction in methanol. Alternatively, intersystem crossing to the triplet manifold followed by cis → trans isomerization and subsequent protonation might occur. Either process is consistent with our observation that the fluorescence of 1-phenylcycloheptene (**1a**, R = C_6H_5) is not quenched in methanolic solution, even on acidification. However, the recent report that 1,3-cyclohexadiene quenches the photoprotonation of 1-phenylcyclohexene (**1a**, R = C_6H_5)[5d] indicates that the cis → trans isomerization occurs *via* initial decay to the triplet manifold, provided that no singlet quenching has occurred.[34] The failure of the excited singlet state of **1a** and **1b** (R = C_6H_5) to undergo direct protonation implies either (a) that it has a charge-transfer character but also has a shorter lifetime than the corresponding state generated on irradiation of the olefins **8**, **17**, **25**, and **26**, such that it is not sufficiently long-lived for an intermolecular process such as protonation to occur, or (b) that it does not have charge-transfer character. The possibilities cannot be distinguished from the available data and are the subject of continued study.

In addition to providing insight into the electronic distribution in excited states of styrene derivatives, the observation that these compounds undergo reaction with alcohols *via* a process involving protonation of an excited singlet species (a) provides yet another example in the ever-growing list of photoprocesses which involve an ionic mechanism and (b) affords a new mech-

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(30) J. A. Marshall and A. R. Hochstetler, *Chem. Commun.*, 296 (1968).

(31) The lack of precedence in other ground-state processes perhaps arises because the carbocation intermediate generated by protonation of the trans olefin is initially formed with a different geometry and substantially greater energy than one formed in other ways, such as acid-induced protonation of the cis olefin. Another possible factor in the photoprotonation process is the concomitant generation of methoxide anion, which would be expected to transfer hydride more readily than neutral methanol. The predominant formation of the 2-endo isomer **9** of phenylnorbornane is the expected stereochemical result of hydride transfer to the cation **14** (ref 32).

(32) (a) K. Takeuchi and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 2693 (1968); (b) F. A. Carey and H. S. Tremper, *Tetrahedron Lett.*, 1645 (1969).

(33) (a) N. Miyamoto, M. Kawanisi, and H. Nozaki, *ibid.*, 2565 (1971); (b) S. S. Hixson, *ibid.*, 4211 (1971); *J. Amer. Chem. Soc.*, **94**, 2505 (1972); *Tetrahedron Lett.*, 277 (1973).

(34) 1,3-Cyclohexadiene is particularly effective in quenching the fluorescence of some aromatic hydrocarbons; see L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665 (1966).

anistic pathway by which photoprotonation processes can occur. It fully suggests that a number of additional systems known to possess excited states displaying charge-transfer character will undergo photoprotonation on irradiation in alcoholic solution. These are the objects of further investigation.

Experimental Section[35]

Irradiation of 2-Phenyl-2-norbornene (8). A. In Methanol. In a typical run, a 150-ml methanolic solution containing 3.0 g of freshly distilled olefin **8** and 600 mg of hexadecane was irradiated for 6 hr. The formation of some polymeric material was suggested by the appearance of a faint opalescence in some cases. Gas chromatographic analysis revealed the continued presence of a small amount of starting olefin **8** (4%) and the formation of new peaks corresponding to a mixture of the norbornanes **9** and **10** (18%), the ether **11a** (47%), and an unidentified minor product (~2%). A control run revealed that no detectable reaction occurred in the absence of irradiation. Likewise, allowing the reaction mixture to stand in the dark after a 6-hr irradiation period resulted in no further change. No peak corresponding in retention time to ethylene glycol was observed.

Isolation of the first major component by preparative gas chromatography afforded a colorless liquid which displayed a gas chromatographic retention time and infrared and nmr spectra identical with those obtained from a 2.6:1 mixture of 2-*endo*- (**9**) and 2-*exo*-phenylnorbornane (**10**), prepared as described below. Similar isolation of the second product component afforded methyl 2-*exo*-phenylnorbornyl ether (**11a**) as a colorless liquid: bp 94–95° (0.4 mm); λ_{max} 212 and 216 nm (ϵ 4400) and 259 (460); nmr spectrum τ 2.75 (m, 5, C_6H_5), 7.37 (s, 3, CH_3O), 7.67 and 7.77 (2 br m, 2, CH-1 and -4), 8.07 (2 m, 1, J = 9.1, CH-7), and 8.29 (s, 2, CH_2-3);[36] *m/e* principal bands at 202, 170, 142 (base), 141, 121, 115, 104, 77, and 67. The relative intensities of mass spectral peaks varied greatly with experimental conditions.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.7; H, 9.0.

This material was identical in all respects with a specimen prepared independently by treatment of alcohol **13b**[11] with concentrated hydrochloric acid followed by a methanolic solution of potassium carbonate, using the general procedure previously reported for the preparation of the alcohol **11b**;[12] *m/e* 202.1347 (calcd for $C_{14}H_{18}O$, 202.1358).

B. In Aqueous Methanol. A 150-ml methanolic solution containing 2.5 g of olefin **8** and 22 ml of water was irradiated as described above for 6 hr. The oily residue obtained on removal of the methanol and water was chromatographed on Activity II alumina. Exhaustive elution with hexane afforded 1.94 g of a colorless liquid which showed no hydroxyl absorption in the infrared. Exhaustive elution with ether afforded 0.3 g of a colorless oil which exhibited strong hydroxyl absorption. Further purification by preparative gas chromatography followed by recrystallization from hexane afforded 2-*endo*-phenyl-2-norbornanol (**11b**) as colorless rods, mp 63.5–64°, unchanged on admixture with an authentic specimen;[12] lit.[12] mp 61–62°. Gas chromatographic analysis of the hexane aliquots revealed the presence of ether **11a**, a mixture of the 2-phenylnorbornanes **9** and **10**, and recovered olefin **8** in yields of 51, 12, and 5%, respectively.

C. In Methanol-*O-d*. A solution containing 1.00 g of olefin **8** in 25 g of methanol-*O-d* was irradiated for 8 hr in a quartz flask suspended approximately 3 in. from a Hanovia 450-W medium-pressure lamp. Gas chromatographic analysis revealed the presence of peaks corresponding to ether **11a**, a mixture of the 2-phenylnorbornanes **9** and **10**, and recovered olefin **8** in yields of 58, 8, and 19%, respectively. Each of these components was isolated by preparative gas chromatography and found by mass spectral analysis to have the deuterium composition outlined in Table I.

Isolation of the first product component afforded a mixture of the 2-phenylnorbornanes **9** and **10** as a colorless liquid. The nmr spectrum was similar to that of material obtained as described in part A except for a sharpening of the benzylic proton band of **9** at τ 6.82 (broad singlet with width at half height of 12 Hz) and an almost complete loss of the H_{3x} band at τ 8.04;[15] *m/e* 173 (23), 106 (38), 105 (100), 104 (24), 92 (65), 91 (36), 82 (34), and 67 (34).

Isolation of the second product component afforded ether **11a** as a colorless liquid which exhibited an nmr spectrum similar to that of material obtained as described in part A except for an attenuation of the band at τ 8.29 to an integration corresponding to 1.0 ± 0.1 proton; *m/e* 203 (51), 171 (33), 143 (72), 142 (100), 141 (32), 134 (29), 121 (48), 105 (47), and 67 (27).

Finally, isolation of the recovered olefin **8** afforded a colorless liquid which exhibited an nmr spectrum similar to that of an authentic specimen except for an attenuation of the H_3 doublet at τ 3.90.

D. With Sensitizer. Irradiation of a 75-ml methanolic solution containing 1.5 g of olefin **8** and 1.5 g of acetophenone through a Pyrex filter sleeve for 4 hr resulted in an 86% recovery of acetophenone, a 47% recovery of olefin **8**, and a 2% yield of a mixture of the 2-phenylnorbornanes, as determined by gas chromatographic analysis. There was no detectable formation of ether **11a**. Irradiation of olefin **8** under identical conditions in the absence of acetophenone afforded a 43% recovery of olefin **8**, a 4% yield of ether **11a**, and a 2% yield of 2-phenylnorbornane. Irradiation of acetophenone under identical conditions in the absence of olefin **8** for only 1.5 hr resulted in only a 39% recovery. Similar irradiation of 1.5 g each of olefin **8** and acetophenone in 75 ml of methanol-*O-d* afforded 2-phenylnorbornane as a colorless liquid which was shown by mass spectroscopic analysis to have the following composition: 82% d_0 and 18% d_1.

Finally, irradiation of 2.0 g of olefin **8** and 1.0 g of fluorene in 100 ml of methanol for 8 hr through a Pyrex filter resulted in a 71% recovery of olefin **8**. There was no detectable formation of any photoproducts.

2-Phenyl-2-norbornene-*3-d* (8-*3-d*). A. Preparation. Treatment of 2-norbornanone (**16**) with trifluoroacetic acid-*d* as described previously[19] afforded **16**-*3-d*$_2$ as colorless crystals having the following deuterium composition: 6% d_0, 24% d_1, and 70% d_2. Treatment of this material with phenylmagnesium bromide in the usual fashion afforded alcohol **13**-*3-d*$_2$ as colorless prisms, mp 44–44.5°. A deuterium analysis was not determined for this material since a molecular ion could not be obtained in the mass spectrum. Treatment of this material with thionyl chloride–pyridine for 10 min at −10° afforded a colorless liquid which was shown by gas chromatographic analysis to consist of a 1:6.8 mixture of 1-phenylnortricyclene-*3-d*$_2$ and 2-phenyl-2-norbornene-*3-d* (**8**-*3-d*). Isolation of the minor component by preparative gas chromatography afforded a colorless liquid which exhibited infrared and nmr spectra similar to those of an authentic specimen of 1-phenylnortricyclene.[11] Isolation of the major component afforded a colorless liquid which exhibited an infrared spectrum similar to that of an authentic specimen of 2-phenylnorbornene (**8**). The nmr spectrum was similar except for a marked attenuation of the doublet at τ 3.85. Mass spectral analysis revealed the following composition: 17% d_0 and 83% d_1.

B. Irradiation. A solution containing 0.5 g of purified olefin **8**-*3-d* in 75 ml of methanol was irradiated for 0.5 hr. Gas chromatographic analysis revealed the continued presence of olefin (13%) and two photoproducts obtained in yields of 17 and 36%. Isolation of each of these components by preparative gas chromatography followed by mass spectrometric analysis yielded the deuterium composition outlined in Table II. Isolation of the minor product afforded a colorless oil which exhibited an nmr spectrum similar to that of the mixture of the 2-phenylnorbornanes **9** and **10** obtained as described in part A except for the bands at τ 6.82 (d, J = 10.5) and 8.04 (br s). The presence of the 2-exo isomer

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[35] Infrared spectra were obtained on neat samples with a Perkin-Elmer 257 or Infracord spectrophotometer, and ultraviolet spectra in ethanol solution with a Cary 14 spectrophotometer. Fluorescence spectra were obtained on nondegassed solutions using a Perkin-Elmer MPF-2A spectrophotometer. Gas chromatographic analyses were performed on an Aerograph Model 90-P instrument using 10 ft × 0.25 in. columns packed with 20% Carbowax 20M on 60–80 mesh Chromosorb W or 10% XE-60 silicone on 60–80 mesh acid-washed DMCS-treated Chromosorb W. Melting points were obtained on a micro hot stage and are calibrated and corrected. Nuclear magnetic resonance spectra were determined in chloroform-d_3 solution with a Varian HA-100 spectrometer, using tetramethylsilane as an internal standard. Mass spectra were obtained using an Atlas CH-4 or SM-1 spectrometer. For deuterium analyses the P − 1 and P − 2 peaks were minimized by lowering the electron energy (10–12 eV). Unless otherwise indicated, all irradiations were conducted with 150 ml of solution using a Hanovia 450-W medium-pressure mercury arc and a water-cooled Vycor immersion well. Vigorous stirring of the reaction mixture was effected by the introduction of a stream of nitrogen through a jet opening in the bottom of the outer jacket. Yields were determined by gas-chromatographic analysis relative to hexadecane, which was employed as an internal standard.

[36] Indicates multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet, and br = broadened), integration, coupling constant (Hz), and assignment.

10 as 18% of the mixture was revealed by the characteristic broadened triplet at τ 7.32.

Isolation of the major component afforded a colorless liquid which exhibited an nmr spectrum similar to that of ether **11a** except for an attenuation in the integral of the H_3 band at τ 8.29 (1.2 ± 0.1 protons). Finally, isolation of the recovered starting material afforded a colorless liquid which exhibited an nmr spectrum similar to that of olefin **8** except for an attenuation in the integral of the doublet at τ 3.80 (0.5 ± 0.1 proton).

Independent Preparation of Methyl 2-*exo*-2-Phenylnorbornyl-*3*-d_2 Ether (11a-*3*-d_2). Treatment of a similar specimen of alcohol **11b**-*3*-d_2 with hydrochloric acid followed by methanolic potassium carbonate as described above and subsequent purification by preparative gas chromatography afforded colorless needles, mp 95.5–97° (sublimation), which exhibited an infrared spectrum similar to that for ether **11a**. The nmr spectrum was also similar except for an attenuation of the integration of the H_3 band at τ 8.29 (0.7 ± 0.1 proton). Mass spectral analysis revealed the following composition: 3% d_0, 65% d_1, and 32% d_2.

2-*endo*-Phenylnorbornane (9). A solution containing 0.5 g of olefin **8** and 8 ml of ethanol was stirred with 10 mg of 10% palladium on charcoal in an atmosphere of hydrogen. Absorption ceased after 0.95 equiv. Removal of the catalyst by filtration and of the solvent by evaporation afforded a colorless liquid which was further purified by short-path distillation at 102° (3 mm) to afford a colorless liquid which exhibited a single peak on gas chromatographic analysis: λ_{max} 6.24 and 13.08 μ and 211 nm (ϵ 6700), 216 (6300), and 261 (230); nmr spectrum τ 6.82 (m, 1, CH-2x), 7.64 (m, 2, CH-1 and -4), and 8.04 (triplet of quartets, 1, J = 12.5 and 2.2 Hz, CH-3x); m/e 172 and 104 (base peak).[7]

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.3; H, 9.5.

2-*exo*-Phenylnorbornane (10). Aluminum chloride catalyzed treatment of 2-norbornene with benzene as described previously[8] afforded a colorless liquid: λ_{max} 6.24 μ; nmr spectrum τ 2.92 (s, 5, C_6H_5), 7.32 (t, 1, J = 7.0 Hz, CH-2), and 7.66 (s, 2, CH-1 and -4); m/e 172 (37), 104 (100), 92 (50), 91 (28), 81 (37), and 67 (24).

Methyl 2-*endo*-2-Phenylnorbornyl Ether (13a). Treatment of alcohol **13b**[11] with sodium hydride followed by methyl iodide according to the procedure of Dauben, *et al.*,[37] followed by purification by preparative gas chromatography, afforded ether **13a** as a colorless liquid: λ_{max} 6.24 and 9.28 μ; nmr spectrum τ 2.7 (m, 5, C_6H_5) and 7.21 (s, 3, CH_3O); m/e 202.1340 (calcd for $C_{14}H_{18}O$, 202.1358), 133, 121, 104, 91, 77, and 67.

Methyl 2-*exo*-1-Phenylnorbornyl Ether (12a). A sample of 1-phenyl-2-*exo*-norbornanol (**12b**),[11] colorless prisms, mp 70–71° (sweat), was obtained by treatment of a commercial specimen of the corresponding acetate with lithium aluminum hydride, lit.[11] mp 69.5–70°. Treatment of this material with sodium hydride followed by methyl iodide as described above afforded ether **12a** as a colorless liquid: λ_{max} 6.24 and 9.18 μ; nmr spectrum τ 2.88 (s, 5, C_6H_5), 6.83 (br s, 1, CH-2n), 7.24 (s, 3, CH_3O), 7.74 (br s, 1, CH-4), and 7.99 (d, 1, J = 9 Hz, CH-7s); m/e 202.1337 (calcd for $C_{14}H_{18}O$, 202.1358), 170, 142, 128, and 91.

Acid-Catalyzed Addition of Methanol to 2-Phenyl-2-norbornene (8). To 10 ml of a methanolic solution containing 1.8×10^{-4} *M* sulfuric acid was added 0.24 g of olefin **8** at 25°. Monitoring of the solution by gas chromatographic analysis revealed the following degrees of conversion of **8**: 1 hr 65%; 2 hr 79%; and 3 hr 82%. There was not substantial change on further standing. Isolation of the major product by neutralization and concentration of the solution followed by preparative gas chromatography afforded a colorless liquid which was shown by analysis of its nmr spectrum to consist of a mixture of ethers **11a** and **12a**.[20] Three additional unidentified minor products were formed in yields of less than 1% each.

In a separate experiment, a solution containing 1.0 g of olefin **8** in 50 ml of methanol-*O-d* was allowed to stand in the dark under an atmosphere of nitrogen at 48° for 5 hr. Gas chromatographic analysis revealed the formation of no detectable products and mass spectrometric analysis of the recovered olefin revealed the presence of no detectable amount of deuterium.

2-Phenyl-2-bornene (17). A. Irradiation. In a typical experiment, a 75-ml methanolic solution containing 1.5 g of olefin **17**[22] was irradiated for 2.5 hr. Gas chromatographic analysis revealed a rapid disappearance of olefin **17** (4% recovery) and the appearance of six product peaks.[38] The products were isolated by preparative gas chromatography.

Isolation of the first component afforded 3,3-dimethyl-2-methylene-1-phenylnorbornane (1-phenylcamphene) (**20**) as colorless blades: mp 35–37°; λ_{max} 6.02, 6.22, and 11.22 μ; nmr spectrum τ 2.85 (s, 5, C_6H_5), 5.52 and 5.87 (2s, 2, CH_2), 7.80 (br d, 1, J = 5 Hz, CH-4), and 8.89 (s, 6, 2CH_3); lit.[25a,b] colorless oil; with similar nmr spectrum except that the methyl peaks are reported to appear as two separate singlets.[25c]

Isolation of the second component afforded a 5.8:1 mixture of 2-*endo*- (**18**) and 2-*exo*-phenylbornane (**19**) as a colorless liquid which exhibited an nmr spectrum similar to that of pure isomer **18** (obtained as described below) except for the presence of bands at τ 9.25, 9.18, and 7.15, which are assigned to the exo isomer **19**.

Isolation of the third component afforded methyl 2-*exo*-2-phenylbornyl ether (**21**) as a colorless liquid: λ_{max} 6.24, 9.28, 13.16, and 14.20 μ; nmr spectrum τ 2.75 (br m, 5, C_6H_5), 7.23 (s, 3, CH_3O), 7.76 (br d, 1, J = 7 Hz, CH-4), 8.87 (s, CH_3), and 9.13 (s, 6, 2CH_3); m/e 244.1823 (calcd for $C_{17}H_{24}O$, 244.1827), and principal peaks at 135, 134 (base), 133, 95, and 91. This material was identical with a specimen prepared independently by treatment of the corresponding alcohol[22] with sodium hydride followed by methyl iodide as described above.[27]

Finally, isolation of the last principal component afforded methyl 2-*exo*-(1-phenyl-2,3,3-trimethylnorbornyl) ether (**22**) as colorless prisms: mp 37.5–40°; nmr spectrum τ 2.87 (br s, 5, C_6H_5), 7.44 (s, 3, CH_3O), and 8.92, 8.96, and 9.05 (3 s, 3CH_3); m/e 244.1828 (calcd for $C_{17}H_{24}O$, 244.1827) and principal peaks at 169, 143 (base), 142, 101, 91, 43, and 41.

Through a combination of gas chromatographic and nmr analyses it was shown that photoproducts **18–22** were formed in yields of 11, 2, 20, 20, and 5%, respectively.[23]

B. Acid-Catalyzed Isomerization. A solution containing 276 mg of olefin **17** and 1.0 ml of concentrated sulfuric acid in 9.0 ml of methanol was stirred for 68 hr under an atmosphere of nitrogen at 25°. Gas chromatographic analysis of a neutralized specimen revealed the continued presence of olefin **17** and the formation of three principal products and three minor products. Isolation of the first principal component by gas chromatography afforded 2-phenyl-1,7,7-trimethyltricyclo[2.2.1.0^{2,6}]heptane (2-phenyltricyclene) (**23**) as a colorless liquid: λ_{max} 6.21, 10.99, 13.09, and 14.29 μ; nmr spectrum τ 2.91 (m, 5, C_6H_5), 7.92 (two triplets, 1, $J \sim$ 10.0 and 1.5 Hz, CH-4), 8.18 (pair of multiplets, 1, $J \sim$ 10 Hz), 8.41 (m, 1), and 9.05, 9.10 and 9.16 (3 s, 3CH_3); m/e 212.1558 (calcd for $C_{16}H_{20}$, 212.1565), 169, 155, 142, 141, 115, 91, and 77.

Isolation of the second principal component followed by sublimation at 130° (760 mm) afforded 1-phenylcamphene (**20**)[26] as long colorless blades with a phenolic odor: mp 35.5–36.5°; λ_{max} 253 and 258 nm (ϵ 440); m/e 212 (30), 169 (100), 154 (36), 91 (25), and 58 (50). The infrared and nmr spectra were identical with those described above.

Isolation of the final principal component afforded an unidentified methyl ether as a white amorphous solid: mp 31.5–32°; λ_{max} 6.22, 9.00, 13.14, and 14.27 μ; nmr spectrum τ 2.80 (br m, 5, C_6H_5), 6.78 (s, 3, CH_3O), and 9.05, 9.20, and 9.33 (3 s, 9, 3CH_3); m/e 244.1828 (calcd for $C_{17}H_{24}O$, 244.1827) and principal peaks at 212, 169, 160, 129, 91, 73, and 55.

Gas chromatographic analysis revealed the following composition: **23**, 18%; **17**, 9%; **20**, 46%; unidentified ether, 25%; and minor photoproducts, 2%. Repetition of the above reaction using 0.1 ml of sulfuric acid followed by gas chromatographic analysis of a neutralized aliquot revealed the presence of isomers **23**, **17**, and **20** in the ratio 1.0:4.2:20.5, respectively. This composition was unchanged in another aliquot withdrawn after 166 hr. The unidentified ether and several other minor products were present in yields of less than 1% each.

2-*endo*-Phenylbornane (18). In accordance with the procedure previously described,[24b] a solution containing 120 mg (0.568 mmol) of olefin **17** in 10 ml of ether was added to a solution containing 26 mg (1.14 g-atom) of sodium in 15 ml of liquid ammonia. The resulting mixture was stirred for 10 min, then 5 ml of absolute ethanol was added over a period of 10 min. Removal of the solvents by evaporation followed by dissolution of the resulting residue in ether, extraction with 5% hydrochloric acid followed by distilled water, drying over saturated sodium chloride solution followed by

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[37] W. G. Dauben, J. H. Smith, and J. Saltiel, *J. Org. Chem.*, **34**, 261 (1969).

[38] In addition, a peak corresponding in retention time to 2-phenyltricyclene appeared at intermediate reaction times (1% yield). This product disappeared as conversion of olefin **17** neared completion.

anhydrous sodium sulfate, and concentration by distillation afforded 160 mg of a pale yellow liquid. Final purification by preparative gas chromatography afforded 2-*endo*-phenylbornane (**18**) as a colorless liquid: λ_{max} 6.22, 12.92, 13.68, and 14.28 μ; nmr spectrum τ 2.88 (br s, 5, C_6H_5), 7.01 (quartet of doublets, 1, J = 11.2, 5.5, and 2.1 Hz, CH-2), 7.87 (triplet of triplets, 1, J = 12.2 and 3.5 Hz, CH-3), and 8.98, 9.07, and 9.28 (3 s, 9, $3CH_3$); *m/e* 214.1724 (calcd for $C_{16}H_{22}$, 214.1721).

1-Phenyl-2-*endo*-3,3-trimethylnorbornane (24). A solution containing 227 mg (1.07 mmol) of 1-phenylcamphene (**20**) in 10 ml of ethanol was stirred over 10 mg of 10% palladium on charcoal in an atmosphere of hydrogen. Absorption ceased after 1.1 equiv. Removal of the catalyst by filtration and of the solvent by distillation afforded a colorless liquid which was further purified by short-path distillation at 91–92° (0.55 mm) to afford a colorless liquid which exhibited a single peak on gas chromatographic analysis: λ_{max} 6.22, 13.23, and 14.27 μ; nmr spectrum τ 2.91 (s, 5, C_6H_5), 7.83 (br d, 1, J = 9.5 Hz, CH-4), 8.98 and 9.17 (2 s, 6, $2CH_3$), and 9.36 (d, 3, J = 7.5 Hz, CH_3-2); *m/e* 214.1725 (calcd for $C_{16}H_{22}$, 214.1721).

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Photochemistry of Diazonium Salts. I. Synthesis of 4-Fluoroimidazoles, 4-Fluorohistamine, and 4-Fluorohistidine[1]

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Abstract: Imidazolediazonium ions, prepared by diazotization of aminoimidazoles in tetrafluoroboric acid solution and irradiated *in situ*, decompose with formation of fluoroimidazoles in 30–40% yield. This procedure has been applied to the synthesis of 2-fluoroimidazole, 4-fluoroimidazole, and ethyl 4-fluoroimidazole-5-carboxylate. The ester, in turn, has served as the starting point for various transformations, including the synthesis of 4-fluorohistamine and 4-fluorohistidine. The fluorinated amino acid parallels histidine as a substrate for several enzymes and, in the case of histidine–ammonia lyase, serves as a competitive inhibitor. To date, fluorinated imidazoles have been obtained only by the photochemical method.

A wide variety of fluorinated analogs of biologically significant compounds have been synthesized and studied as potential enzyme inhibitors and as therapeutic agents.[2] Of the possible replacements for hydrogen in carbon–hydrogen bonds, fluorine offers the unique advantage of effecting a marked change in electron density distribution and related properties, but with a minimal change in molecular size or shape.[3] This combination of properties is proposed to be the basis for the effectiveness of drugs such as fluorouracil and the fluorosteroids.[2] While numerous ring-fluorinated aromatic and heteroaromatic systems have been prepared and studied as biochemical analogs, ring-fluorinated imidazoles have not been accessible for this purpose.[4] Since the imidazole ring plays a key role in biological structure and function (histidine, histamine, purine precursors, etc.), we were prompted, some years ago, to initiate a study of synthetic approaches to fluoroimidazoles.

In our hands, the more obvious synthetic routes[5] to fluoroimidazoles afforded only negative results, *e.g.*, (1) reaction of 4-bromo-5-nitroimidazole or of 4-bromo-5-carbethoxyimidazole with potassium fluoride, cesium fluoride,[6] or silver fluoride[7] gave either no halogen exchange or tarry polymers (at elevated temperatures);[8] (2) formation of the imidazole ring by reaction of acyclic α-fluoro-α-bromo ketones with formamide[9] failed; (3) thermal decomposition of imidazolediazonium fluoroborates,[10] such as **2**, with or without solvent and with or without metal catalysis, resulted either in no reaction or in intractable tars.

The diazonium fluoroborate **2** shows exceptional stability; in fact, treatment of the compound with mild base provides a colorless, neutral, *sublimable* material, which may be formulated as **3a** or, preferably, as **3b** (Scheme I).[11] Since diazo compounds are known to undergo facile photoextrusion of nitrogen,[12] we were

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[1] (a) This work was presented in part at a Symposium on Fluorine in Medicinal Chemistry, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971. (b) For a preliminary communication, see K. L. Kirk and L. A. Cohen, *J. Amer. Chem. Soc.*, **93**, 3060 (1971).

[2] (a) P. Goldman, *Science*, **164**, 1123 (1969); (b) F. Weygand and W. Oettmeier, *Usp. Khim.*, **39**, 622 (1970); *Russ. Chem. Rev.*, 290 (1970); (c) D. F. Loncrini and R. Filler, *Advan. Fluorine Chem.*, **6**, 43 (1970).

[3] Generally accepted van der Waals radii are 1.20 Å for hydrogen and 1.35 Å for fluorine. A fluorine atom attached to an sp^2 carbon is probably somewhat smaller.

[4] Fluorobenzimidazoles, in which the fluorine is attached to the benzene ring, have been reported: (a) K. L. Kirk and L. A. Cohen, *J. Org. Chem.*, **34**, 384 (1969); (b) E. C. Fisher and M. M. Joullié, *ibid.*, **23**, 1944 (1958).

[5] (a) M. Hudlicky, "Organic Fluorine Chemistry," Plenum Press, New York, N. Y., 1970; (b) A. E. Pavlath and A. J. Leffler, "Aromatic Fluorine Compounds," Reinhold, New York, N. Y., 1962.

[6] N. N. Vorozhtsov, Jr., and G. G. Yakobson, *Zh. Obshch. Khim.*, 31, 3705 (1961).

[7] A. G. Beaman and R. K. Robins, *J. Org. Chem.*, **28**, 2310 (1963).

[8] Studies were also conducted with various imidazoles in which one ring-nitrogen atom carried a reversible protecting group; however, no blocking group was found capable of surviving the conditions needed for halogen exchange.

[9] H. Brederick and G. Theilig, *Chem. Ber.*, **86**, 88 (1953).

[10] A. Roe, *Org. React.*, **5**, 193 (1949).

[11] *Cf.* 5-diazoimidazole-4-carboxamide: Y. F. Shealy, R. F. Struck, L. B. Holum, and J. A. Montgomery, *J. Org. Chem.*, **26**, 2396 (1961).

[12] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., p 471.