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THE PHOTOCHEMISTRY OF BENZOTRICYCLO[3.1.0.0^{2,6}]HEX-3-ENE [1]

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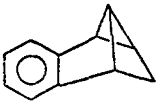
Abstract: Irradiation of 1 in methanol with λ 254 nm yields 3 and 4 as the main primary products which result from the excited singlet state by initial cyclopropane bond homolysis, but no primary photosolvolysis products.

It was recently reported that benzotricyclo[3.1.0.0^{2,6}]hex-3-ene (1) in methanol does not solvolyze to the ether 2 under ground or electronically excited-state conditions.[2] This information prompts us to communicate our results on the photochemistry of 1. The substrate was prepared by the photo-di-π-methane rearrangement of benzonorbornadiene (3) (obtained from o-bromofluorobenzene and cyclopentadiene [3]) in dry acetone as triplet photosensitizing solvent, [4] in a yield >98%.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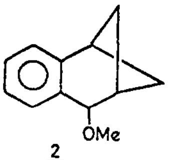
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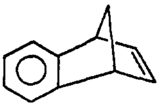
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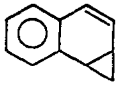
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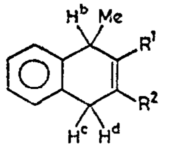
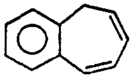

8 a R^1=OMe; R^2=H^a
b R^1=H^a; R^2=OMe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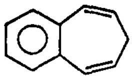
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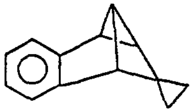
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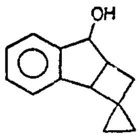
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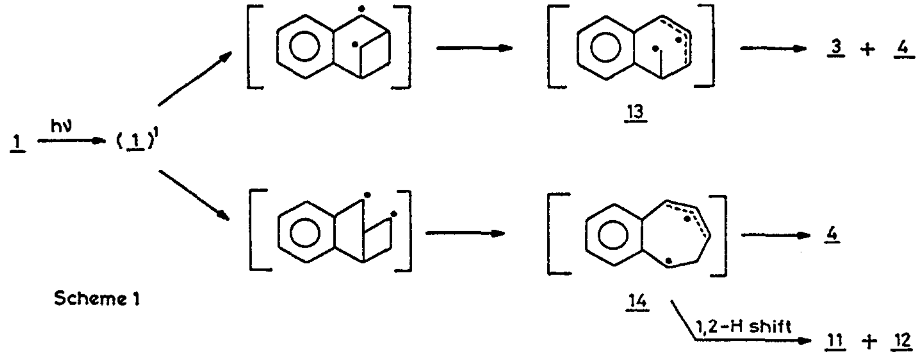
Irradiation of 1 in methanol with λ 254 nm[5] resulted in the formation of benzonorbornadiene (3), benzonorcaradiene (4), naphthalene (5), 1- and 2-methylnaphthalene (6 and 7), 1-methyl-2-methoxy-1,4-dihydronaphthalene (8a), two compounds 9 and 10 of non-identified structure, [6] and some minor unidentified products. [7] With the exception of 8a, the same products, but in a different ratio, were obtained using hexane, acetone-water (9:1 v/v) or acetic acid as solvent, e.g. the relative yield of 3 in hexane is higher, but in acetone-water lower than in methanol. Triplet photosensitization of 1 using acetone-water (9:1 v/v) as solvent with λ 300 nm for 140 h did not lead to any detectable conversion, indicating that the photo-isomerization of 1 probably proceeds from the excited singlet state.[8] The close to 100% yield in which 1 is obtained from 3 by acetone triplet photosensitization is in line with this conclusion.

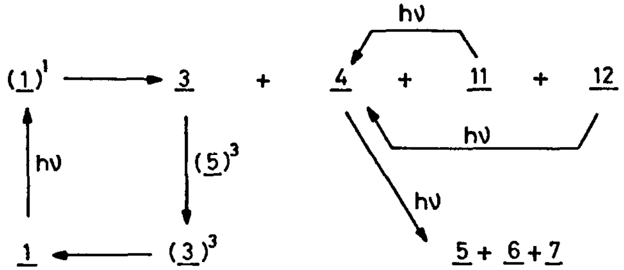
The product mixture was analyzed by GLC.[11] The products 4, 5, and 8 were isolated by preparative GLC;[12] 4 was obtained admixed with 6 and some 7, especially at high conversion, e.g. for 31 h of irradiation the 4:6:7 ratio is 4:1: $\leqslant$0.2. The products were identified by comparison of their GLC retention times (as with 3-7), ^{1}H NMR data (as with 5-7), and mass spectral fragmentation pattern (as with 3 and 5-7) with those of authentic samples. The ^{1}H NMR spectral data of 4 were identical with the reported ones.[13] The structure of 8a was assigned on the basis of the following ^{1}H NMR data (CD_2Cl_2) δ : 7.4-7.0 (m, 4H, H_{arom}), 6.71 (s, 1H, H^a), 4.25 (q, J=6.4 Hz, 1H, H^b), 3.35 (br.s, 2H, H^c+H^d), 3.23 (s, 3H, OCH_3 , and 1.36 (d, J=6.4 Hz, 3H, $CHC\underline{H}_3$), and mass spectral data (70 eV) m/z : 174 ($M^{+\bullet}$, 30%), 159 (70%), 144 (15%), 143 (30%), 142 (25%), 141 (30%), 128 (30%), 116 (15%), 115 (35%), 59 (100%).[14]

The dependence of the relative amounts of products on the irradiation time[7] showed that 3, 4, 9, and 10 are primary products, that 5-8 are secondary ones, and that 3, 4, 9, and 10 upon prolonged irradiation are in part photoconverted again. The formation of 3 and 4 from 1 may be explained as shown in Scheme 1. The singlet excited state of 1 will undergo bond scission so as to form the conjugated bicyclic benzo-allylic biradicals 13 and 14 which by intramolecular cyclization yield 3 and 4. A 1,2-H shift of 14 would lead to 1,2- and 3,4-benzotropilidene (11 and 12).[6] The subsequent



Scheme 1

photoconversion of 4 will yield mainly naphthalene, and further 1- and 2-methylnaphthalene, and 1,2- and 3,4-benzotropilidene.[15] In fact, the yield of naphthalene increases rapidly with increasing irradiation time.[7] The conversion of 3 is remarkable, as 3 is photostable upon direct irradiation.[4,16] The conversion may proceed, however, as result of triplet photosensitization by the naphthalene products 5-7 with reformation of 1.[4,17] The photoconversion of the benzotropilidenes 11 and 12 was reported;[13,18] they both yield benzonorcaradiene 4. This then leads to the following reaction scheme (Scheme 2).



Scheme 2

The minor product 8a is a secondary one, probably formed by photomethanolysis of 3 or 4, since irradiation of 1-methylnaphthalene in methanol with λ 254 nm does not yield any 8a.

Finally, we want to stress that no primary photosolvolysis products were obtained from 1 neither at λ 254 nm using methanol, acetic acid or acetone-water (9:1 v/v) nor at λ 300 nm using acetone-water as solvent. This is remarkable since the formation of this type of products could be expected by analogy with the reported photosolvolysis (λ 254 nm) of the related 15 in acetone-water yielding 16.[19,20]

References and Notes:

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3. G. Wittig and E. Knauss, Chem.Ber. 1958, 91, 895.
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5. The irradiations were performed in quartz vessels using a Rayonet RPR 208 photochemical reactor equipped with eight RUL 2537 Å lamps under the exclusion of dissolved oxygen.
6. 9 and 10 are likely to be 1,2- and 3,4-benzotropilidene (11 and 12).
7. Typically, the respective reaction mixtures obtained after irradiation of 1 (2g) in methanol (150 ml) with λ 254 nm for 1.0, 4.0, 8.5, and 11.5 h contained 87, 65, 47, and 44% unconverted 1, 0.6, 1.4, 1.8 and 2.1% 3, 3.0, 7.0, 7.7, and 8.1% 4, 0.2, 1.2, 3.2, and 4.8% 5, <0.2, 0.4, 1,9,

and 2.7% 6, 0.0, 0.1, 0.3, and 0.6% 8a, 1.7, 2.4, 2.8, and 2.7% 9, and 1.7, 2.3, 2.1, and 2.0% 10.

8. The energy transfer from triplet excited acetone (E_T = 79-82 kcal/mol[9]) to 1 will be of moderate efficiency, since the E_T of 1 will be ca. 81 kcal/mol, i.e. the value for phenylcyclopropane.[10] In fact, acetone triplet photosensitized isomerizations of simple phenylcyclopropanes were observed.[11]
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11. S.S. Hixson and J. Borovsky, J.Am.Chem.Soc. 1976, 98, 2840.
12. For the quantitative GLC analysis a 2m x 1/8 in. stainless steel column, packed with 10% SE 30 on Chromosorb WAW-DMCS 80-100 mesh was employed which was temperature programmed from 50-150°C with a rate of 5°/min using He as carrier gas at a flow rate of 20 ml/min. For the preparative GLC separation a 5 m x 1/4 in. copper column with 15% SE 30 on Chromosorb WAW, operated at 180°C using a He flow rate of 75 ml/min, was used.
13. M. Pomerantz and G.W. Gruber, J.Am.Chem.Soc. 1967, 89, 6798.
14. The ^{1}H NMR data and mass spectral data do not exclude the compound to be the 3-methoxy isomer 8b.
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16. L.A. Paquette, D.M. Cottrell, and R.A. Snow, J.Am.Chem.Soc. 1977, 99, 3723.
17. Irradiation (λ 254 nm) of 3 (0.1 ml) with added naphthalene (0.1 g) in methanol (9 ml) did lead to the formation of 1 in a yield of 35% at most, as 1 is photoconverted again to 3 and 4.
18. M. Pomerantz and G.W. Gruber, J.Am.Chem.Soc. 1967, 89, 6799.
19. J. Ipaktschi, Tetrahedron Letters, 1970, 3183.
20. In our hands 15 failed to photohydrolyse to 16.

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