Photochemistry of 2-Methylene-1,2,3,4-tetrahydro-1,4-methanonaphthalene in Protic Media. A Novel Photoinduced Anti-Markovnikov Addition to the Double Bond[1]

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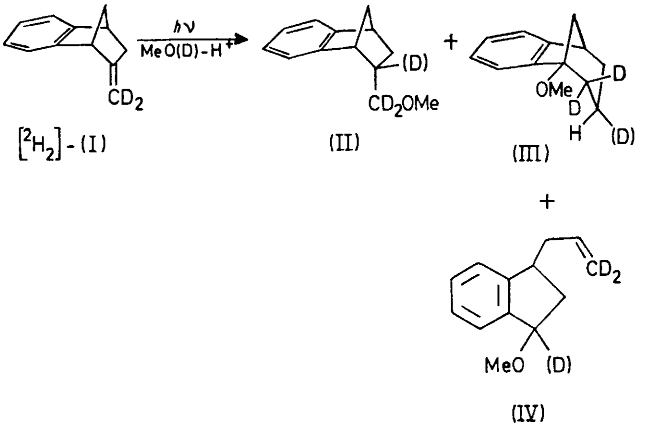
Summary Irradiation of 2-methylene-1,2,3,4-tetrahydro-1,4-methanonaphthalene (I) in acidic methanol leads to three products (II), (III), and (IV); the formation of (II) represents a novel anti-Markovnikov addition of methanol across the methylene double bond.

Previously[2] we reported on the photorearrangement of the title compound (I) upon irradiation at 254 nm in hydrocarbon media. We now report that irradiation in acidic methanol† leads to three new products, the major component of which (II) results from anti-Markovnikov addition across the double bond. The products, all confirmed by independent synthesis, are shown in Scheme 1; the deuterio derivatives are those formed from [$^2H_2$]-(I) with MeOH, and from (I) with MeOD [deuterium from MeOD shown as (D)]. (Assignment of the position of the deuterium atoms follows in a straightforward manner from analysis of the n.m.r. spectra).

Quantum efficiencies, Φ, for the formation of (II), (III), and (IV) are: $2{\cdot}66 \times 10^{-2}$; $1{\cdot}21 \times 10^{-2}$; and $5{\cdot}70 \times 10^{-3}$, respectively. The excited states responsible for these products have been determined by xenon perturbation.[3] Compounds (III) and (IV) are (identically) enhanced by xenon (as are the products formed in hydrocarbon media[3]);



Scheme 1

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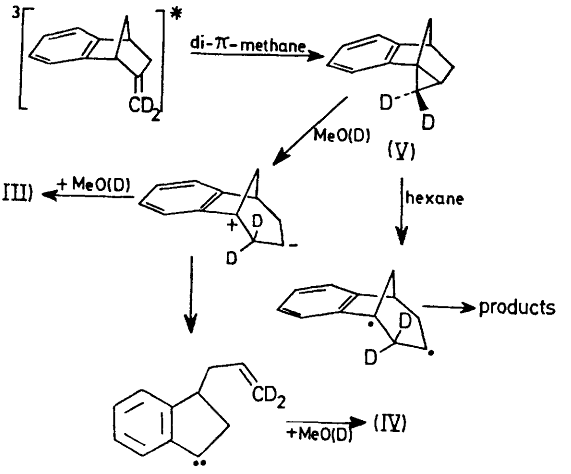
† Typically $1{\cdot}3 \times 10^{-2}$ M-(I) and 5×10^{-4} N-HCl. The same products are formed in basic methanol but at considerably lower (30—300 fold) rates. Irradiation in non-acidified methanol gives erratic results because of the ready photochemical formation of varying amounts of acid (P. J. Kropp, E. J. Reardon, Jr., Z. L. F. Gaibel, K. F. Williard, and J. H. Hattaway, Jr., *J. Amer. Chem. Soc.*, 1973, **95**, 7058, footnote 11. Also, P. Yates, *Pure Appl. Chem.*, 1968, **16**, 93). The products formed in hexane are absent in acidic methanol, but do appear in neutral or basic methanol and in acetic acid–dioxan. These products have been found to be unstable to acid in the dark. The expected Markovnikov product, *endo*-2-methyl-*exo*-2-methoxy-1,2,3,4-tetrahydro-1,4-methanonaphthalene, is slowly (over several weeks) formed in the dark.

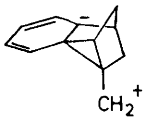
these are primarily (though not necessarily completely[3]) triplet derived. However, (II) is quenched by xenon, indicating that this product arises from an excited singlet state.

The formation of (III) and (IV) may be rationalized by invoking the previously proposed[2] di-π-methane intermediate (V); heterolysis of the highly strained cyclopropyl linkage in the polar, protic media, replaces the homolysis which occurs in hexane[2] (Scheme 2).

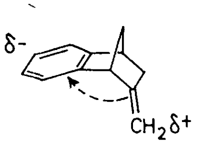


SCHEME 2

However, the anti-Markovnikov addition of methanol to the excited singlet state of (I) represents a totally new reaction pathway which requires a novel polarization of the double bond.[4] There are several, not necessarily mutually exclusive, ways of rationalizing such polarization. For example, a true σ bond may be formed, in a di-π-methane fashion, to give (VI); it has been suggested[5] that the singlet-derived di-π-methane intermediate should have zwitterionic character, and (II) may represent the trapping of such a zwitterion. Alternatively, the vinyl–phenyl interaction may be more diffuse (VII) perhaps approaching that of a singlet exciplex;‡ in such cases, charge transfer from olefin to the phenyl group is known to occur.[6] [We have earlier noted[2] the 67% reduction of the fluorescence and singlet lifetime of (I) (measured in hexane) relative to a saturated analogue].



(VI)



(VII)

Anti-Markovnikov photoaddition to (I) has been observed with other nucleophiles. Irradiation of (I) in a 5% solution of LiCl in 70% dioxan–water leads to *endo*-2-chloromethyl-1,2,3,4-tetrahydro-1,4-methanonaphthalene and irradiation in 5% acetic acid–dioxan solution gives the acetoxy derivative in 65% isolated yield.

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‡ 6-Phenylhex-2-ene, a molecule which rapidly forms an intramolecular singlet exciplex (W. Ferree, Jr., J. B. Grutzner and H. Morrison, *J. Amer. Chem. Soc.*, 1971, **93**, 5502), does not add methanol under these reaction conditions.

[1] For previous paper in the series, 'Organic Photochemistry,' see H. Morrison, D. Clark, J. Otten, M. Pallmer, and C. S. Yeh, *Mol. Photochem.*, in the press.

[2] F. Scully, J. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, 1973, **95**, 5100.

[3] H. Morrison, T. Nylund and F. Palensky, *J.C.S. Chem. Comm.*, 1976, 4.

[4] Other examples of 'anti-Markovnikov' excited state addition are (a) S. S. Hixson, *Tetrahedron Letters*, 1971, 4211; (b) K. Fujita, K. Matsui, and T. Shono, *J. Amer. Chem. Soc.*, 1975, **97**, 6256; (c) Y. Shigemitsu and D. R. Arnold, *J.C.S. Chem. Comm.*, 1975, 407.

[5] H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *J. Amer. Chem. Soc.*, 1974, **96**, 1459. H. E. Zimmerman, R. J. Boettcher, N. E. Buehler, and G. E. Keck, *ibid.*, 1975, **97**, 5635; L. Salem, *Israel J. Chem.*, 1975, **14**, 89.

[6] F. D. Lewis and C. E. Hoyle, *J. Amer. Chem. Soc.*, 1975, **97**, 5950 and references therein. For possible related examples, see ref. 4(c) and J. J. McCullough and W. S. Wu, *J.C.S. Chem. Comm.*, 1972, 1136.