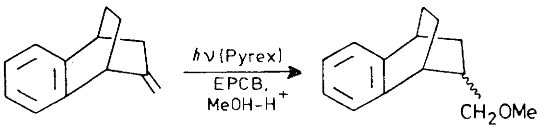
Photosensitized Anti-Markovnikov Addition of Methanol to Homoconjugated Aryl-olefins[1]

By David D. Neidigk and Harry Morrison*
(*Department of Chemistry, Purdue University, W. Lafayette, Indiana* 47907)

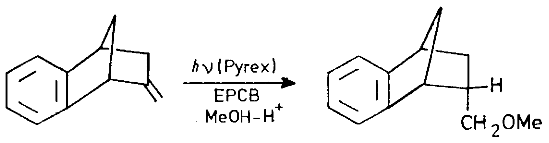
Summary Photolysis of ethyl *p*-cyanobenzoate in the presence of 2-methylene-1,2,3,4-tetrahydro-1,4-ethanonaphthalene (I) or 2-methylene-1,2,3,4-tetrahydro-1,4-methanonaphthalene (II) leads to anti-Markovnikov addition of solvent (methanol) across the double bond.

Although there have been several recent reports[2] of photosensitized anti-Markovnikov additions to double bonds, to date these reactions have only been successfully initiated when the olefin is conjugated to an aromatic ring. We now report that photolysis of a methanolic solution of (I), ethyl *p*-cyanobenzoate (EPCB), and a trace of sulphuric acid, using Pyrex filtered light so as to excite selectively the ester, leads to the reaction shown in equation (1). Likewise, the [2.2.1] analogue (II) also adds methanol when sensitized by EPCB [equation (2)]; the reaction is 25% less efficient than with (I) and gives only the *endo* ether. A mechanism analogous to that proposed by Arnold[2] is presumed to be operative, *i.e.* electron transfer from (II) to EPCB*, attack by methanol on the resultant radical-cation (IV) to give (V), and back transfer of an electron from EPCB$^-$ to (V) to give an anion which is then protonated to form the product.



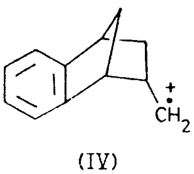
(1)

(I)

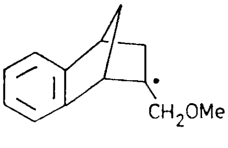


(2)

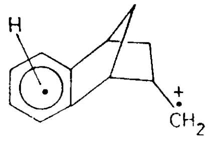
(II) (III)



(IV)



(V)



(VI)

There are two interesting features of this reaction. (1) The reaction does not work for 2-methylenebicyclo-[2.2.1]heptane, *i.e.* the presence of an aromatic ring is critical; this may be due to a homoconjugative stabilization of the radical-cation (IV). Alternatively, since the photoelectron spectroscopy derived ionization potentials for (II) are 8·40 (benzene), 8·90 (benzene), and 9·23 (olefin) eV,[3] the initial electron transfer from (II) to EPCB* could be from the benzene ring. (2) We recently reported[4] that (II) can be made to undergo anti-Markovnikov addition using direct excitation (*i.e.*, no sensitizer is necessary). By contrast we now find that the [2.2.2] analogue (I) does not show such addition in the absence of sensitizer. Clearly, although direct excitation and EPCB sensitization of (II) both yield (III), the similarity of the two reactions is more apparent than real. We have suggested[5] that in the direct photolysis, there is an acid-assisted, charge-transfer interaction between the chromophores, which eventually leads to (VI). Our observations with (I) confirm that the role of the aromatic ring in facilitating formation of (IV) is distinct from its ability to promote formation of (VI). The latter process is much more sensitive to stereoelectronic factors (the [2.2.2] system has a *ca.* 5° increase in the angle formed by intersection of the p-orbitals on C–2 and C–6). The structural differences between (I) and (II) do not affect **2**,6-bonding, since (I) and (II) are equally efficient in their 'di-π-methane' chemistry.[2,6]

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[1] Abstracted from the M.S. thesis of D.D.N., Purdue University, 1978. For previous paper in the series 'Organic Photochemistry,' see J. G. Otten, C. S. Yeh, S. Byrn, and H. Morrison, *J. Amer. Chem. Soc.*, 1977, **99**, 6353.

[2] A. J. Maroulis, Y. Shigemitsu, and D. R. Arnold, *J. Amer. Chem. Soc.*, 1978, **100**, 535 and references therein.

[3] F. Palensky, Ph.D. thesis, Purdue University, 1977.

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[5] T. Nylund, Ph.D. thesis, Purdue University, 1978.

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