Photolysis of 3-Ferrocenyl-1-(4′-methoxyphenyl)prop-1-ene in Methanol

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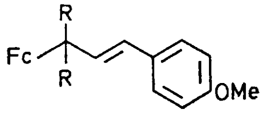
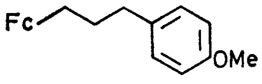
Summary Photolysis of 3-ferrocenyl-1-(4′-methoxyphenyl)prop-1-ene in methanol gives two ethers (**3a**) and (**4a**) the former by a 1,3-hydride transfer mechanism; both ethers undergo secondary photolysis to 1-ferrocenyl-3-(4′-methoxyphenyl)propane.

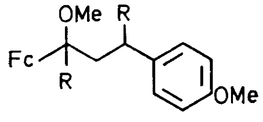
PREVIOUSLY we reported that photochemical addition of alcohols, in the absence of acid, to simple ferrocenylolefins produced ethers which independently photolysed to alkanes.[1] It was obvious from these results that the ferrocenyl group was capable of stabilising radicals on C-1 of a carbon chain.[2] Therefore in the absence of examples of the interaction of ferrocene with radicals (or cations) on C-3 of such a chain an examination of the photochemistry of 3-ferrocenyl-1-(4′-methoxyphenyl)prop-1-ene (**1a**) in methanol was undertaken.



(1) a, R = H
b, R = D



(2)



(3) a, R = H
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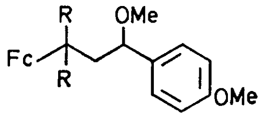
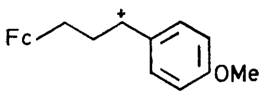
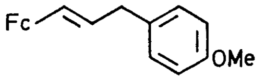


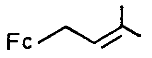
(4) a, R = H
b, R = D



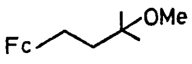
(5)



(6)



(7)



(8)

Fc = ferrocenyl

Photolysis† of this alkene (**1a**) gave, in addition to recovered starting material (43%), three products (**2**) (1%), (**3**) (13%), and (**4**) (38%).‡ The alkane (**2**) is most probably formed by secondary photolysis of both ethers [(**3a**) and (**4a**)] in accord with the results obtained from our earlier study,[1] and this was readily verified by independent photolysis of the two ethers.

The formation of ether (**4a**) is readily explained in terms of photochemically induced ionic addition of methanol in a manner similar to that reported for other olefins.[3] The specificity of addition affording ion (**5**) is controlled by the electron-donating properties of the methoxyphenyl group. The other ether (**3a**) could arise by a similar ionic addition to the isomeric olefin (**6**), however, no evidence for this isomerisation was found following n.m.r. analysis of recovered starting material.

Amongst the alternative routes§ to ether (**3a**) a 1,3-hydride migration in ion (**5**) was considered and tested utilising olefin (**1b**). This photolysis gave an alkane fraction (2·5%) and two ethers identified by n.m.r. and mass spectral analysis as (**3b**) (6%) and (**4b**) (24%).¶ Thus, although the number of well documented 1,3-hydride migrations is small,[4] the results obtained in this study seem to confirm such a mechanism.

Recently, attention has been paid to the photo-reactions of diarylpropenes in alcoholic, acid-free, conditions,[5] and it has been demonstrated that 1-(4′-methoxyphenyl)-3-phenylprop-1-ene adds alcohol in a like manner to our results with alkene (**1**). Hixson[5] suggests that the addition is influenced by intramolecular interaction of the two chromophores. It would be attractive to have definite evidence for similar interaction in alkene (**1**) but little information can be gleaned from the u.v. spectrum. There is, however, some chemical evidence for an interaction in 1-ferrocenyl-3-methylbut-2-ene (**7**) since photolysis† brings about addition to afford 1-ferrocenyl-3-methoxy-3-methylbutane (**8**) (21%).

The award of a maintenance grant by the SRC to C. Baker is acknowledged.

(*Received, 27th September* 1972; *Com.* 1655.)

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† Photolyses were carried out in methanol solution (200—300 ml., *ca.* 0·015M) in an immersion apparatus using a quartz well and a 450 watt medium pressure Hg arc lamp. Solutions were degassed for 1 h before irradiation by a purge of purified nitrogen.

‡ The identification of the two ethers was resolved by independent synthesis of (**3a**).

§ Another route to both ethers (**3a**) and (**4a**) is by prior isomerisation of the alkene (**1a**) to a cyclopropane. No evidence was found for this and in addition 1-ferrocenyl-1-methyl-2,2-diphenylcyclopropane was stable to the conditions of photolysis.

¶ Satisfactory elemental or mass spectral analyses were obtained for all new compounds reported.

[1] C. Baker and W. M. Horspool, *Chem. Comm.*, 1971, 615.

[2] The stabilisation by ferrocene of cations on C-1 is well known. See M. Cais, *Organometallic Chem. Rev.*, 1966, **1**, 435.

[3] J. A. Marshall, *Accounts Chem. Res.*, 1969, **2**, 33.

[4] A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *J. Amer. Chem. Soc.*, 1960, **82**, 6366.

[5] S. S. Hixson, *J. Amer. Chem. Soc.*, 1972, **94**, 2505, 2507.