Photolysis of Ferrocenyl-olefins and -ethers

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Summary The photolysis of ferrocenylethylene and 2-ferrocenylpropene in ethanol to afford photolabile ferrocenylethers is described.

INTEREST has been shown recently in the photolysis of ferrocene derivatives.[1-5] These reports have dealt with both preparative matter and aspects of ferrocene photolysis concerning the influence of the iron atom on intersystem crossing.[5] The population of ferrocenylolefin triplet states was of considerable interest to us in the light of the reports of radical abstraction reactions occurring during photolysis of 1,1-diphenylethylene.[6]

We report here the results obtained from the photolysis† of ferrocenylolefins (**1a**) and (**1b**) and ferrocenylethers (**2**) in alcoholic solution. The results are summarised in the Table and the Scheme. The photolysis of the olefins [(i) and (ii) in Table] produced ethers (**2**) and alcohols (**3**) which could be formed from the cation (**6i**). Such a cation could arise by protonation of the olefinic excited state following photon absorption, in a similar manner to that reported for other systems.[7] The radical products (**4**) and (**5**) could not be accommodated by such a scheme and, in the absence of ferricinium ion formation which would have been the result of promotion of an electron from iron to the cationic site to

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† Photolyses were carried out under nitrogen in an immersion apparatus with quartz filter and a 450 W medium-pressure mercury arc lamp.

form ferrocenyl radicals, an alternative route was sought

Photolysis of the ethers (**2**) in alcohols demonstrated that radical products arose from this source but the yield was no better than that from olefin, and, moreover, the rate of disappearance of the ether was very slow Subsequently it was found by the photolysis of ether (**2b**) in methanol (vii) that in addition to the product formed by radical reaction there was a much more efficient ether exchange reaction which resulted in the formation of ether (**2c**) ‡

TABLE

Product (%) from the photolysis of ferrocenyl-olefins and -ethers in alcohols

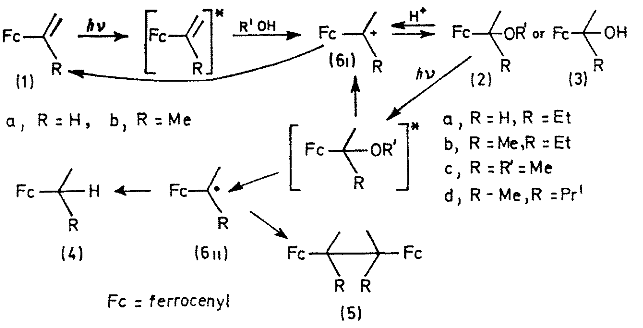
	Olefin or ether	t/h	Solvent	Products (%)[a]				
				(**1**)	(**2**)	(**3**)	(**4**)	(**5**)
(i)	(**1a**)	69	EtOH	a(14)[b]	a(58)	a(9)[d]	a(4)	a(4)[c]
(ii)	(**1b**)	36	EtOH	b(13)[b]	b(65)	b(2)	b(4)	b(4)
(iii)	(**2b**)	36	EtOH	b(16)	b(40)[b]	b(27)	b(7)	b(4)
(iv)	(**2b**)	36	EtOH–H_2O	b(4)	b(41)	b(48)	b(<1)	b(<1)
(v)	(**2c**)	36	MeOH	b(10)	c(37)[b]	b(10)	b(9)	b(7)
(vi)	(**2d**)	48	Pr^{i}OH	b(30)	d(33)[b]	b(24)	b(6)	
(vii)	(**2b**)	14	MeOH	b(10)	c(53)	b(17)	b(5)	

[a] Products are always accompanied by a certain amount of decomposed materials All new compounds gave satisfactory analytical and spectral data

[b] Recovered starting material

[c] An oily product assigned this structure (**5a**) has been reported recently by Sonada *et al*[8] Their assignment based on n m r evidence [τ, 5 68 (2H, m), 5 93 and 6 01 (18H, s), and 8 56 and 8 62 (6H, both d)] is incorrect and the compound is bis(1-ferrocenylethyl)ether The crystalline compound isolated by us shows the following signals at τ 6 01, 6 05(s), 6 26 (18H, m), 7 5 (2H, m), and 8 88 and 8 99 (6H, both d) which are consistent with the proposed structure

[d] The formation of the alcohols does take place in the presence of water (iv) However the amount formed in dry solvent is small and decomposition on the column during separation brings about formation of the alcohol at the expense of the ether [A N Nesmeyanov and I I Kritskaya, *Izvest Akad Nauk, S S S R , Ser Khim* 1964, 2160, (*Chem Abs* , 1964, **58**, 7971e)]



Therefore the reaction scheme proposed above is one in which the ether excited state affords both the cation (**6i**) (which gives olefin or alcohol or undergoes ether exchange) and the radical (**6ii**)

Aromatic ethers such as anisole[9] or phenyl benzyl ether undergo photochemical reaction of the Fries type[10] but such reactions appear to be restricted to phenyl ethers, methyl benzyl ether undergoes neither a photo-Fries reaction nor an ether exchange reaction on photolysis in ethanol

The foregoing results point to an involvement of the iron atom The exact nature of the effect in the partitioning of the excited state into carbonium ion and radical derived products is still being studied

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‡ The exact route by which the ether exchange process occurs is still in doubt Although thermal control experiments did not react, it is possible that photolysis of alcohol solutions might produce a trace of acid sufficient to catalyse the exchange

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