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PHOTOLYSIS OF FERROCENYL ETHERS

OPTIMUM CONDITIONS FOR THE FREE RADICAL REACTION

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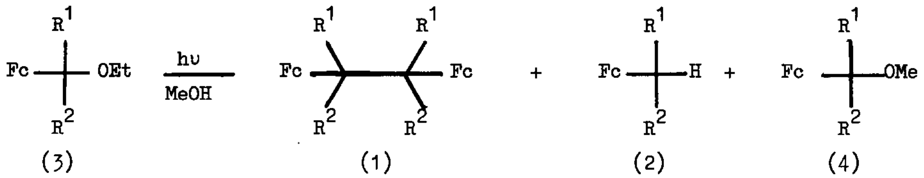
Recently we reported results dealing with the photochemical addition of alcohols to simple ferrocenyl olefins producing ethers as the primary photo-products.[1] These ethers were also photolabile and gave rise to products of reduction and dimerisation upon further irradiation. The reduction and dimeric products could best be accounted for by free radical paths which, under the reaction conditions chosen, were of quite minor importance (ca. 5%). The major reaction was an ether exchange reaction probably involving a cationic intermediate and gave rise, for example, to the formation of 2-ferrocenyl-2-methoxypropane from 2-ferrocenyl-2-ethoxypropane when methanol was used as the solvent. Dark thermal control reactions in methanol established that all the products were produced photochemically. However there was always the possibility, as shown by others[2,3] that acidic material was being produced during the photochemical experiments. The acid catalysis of at least part of the exchange reaction was subsequently demonstrated using methanol solutions of formic acid (4×10^{-3}M) whereby 2-ethoxy-2-ferrocenyl propane was converted quantitatively into 2-ferrocenyl-2-methoxypropane.

Optimum conditions for the photochemical formation of products (1 and 2) of the radical reaction were eventually found to require vanadous sulphate purified nitrogen[4] and sodium carbonate, as the acid scavenger, added to the methanolic solutions of the ethers (3) undergoing photolysis.[5] Utilisation of these reaction conditions raised the total yield of products (1 and 2) to 40%.

These reaction conditions were employed in a study of the influence of substituents on the formation of products (1 and 2) (Table 1). The results follow the expected



Scheme 1

Table 1 Influence of Substituents on the formation of products (1) and (2) from (3).

			Products (%)		
Ether (3)		(% recovered)	(1)	(2)	(4)
(a)	$R^1=R^2=H$	(61)	1.6	14	12
(b)	$R^1=H$, $R^2=Me$	(35)	2.0	15	24
(c)	$R^1=R^2=Me$	(0)	10.2	35	39
(d)	$R^1=Ph$, $R^2=H$	(0)	6.2	29	42
(e)	$R^1=Ph$, $R^2=Me$	(5)	-	34	41
(f)	$R^1=R^2=Ph$	(0)	-	70	12

pattern whereby the yield of products (1 and 2) (Scheme 1) increases as the ability of the substituent to stabilise the radical increases. Inevitably there is a decrease in the amount of radical dimerisation as the bulk of the substituent increases.

Even under the conditions where products derived from radicals are at a maximum, the ether exchange reaction still takes place, demonstrating the reaction to be a photochemical solvolysis.

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5. Irradiations using solid Na_2CO_3 (1.2 g.) as proton scavenger were carried out in an immersion apparatus using methanol solutions (200 ml., ca. 1.5×10^{-2}M), a quartz well, and a 450 watt medium pressure Hg arc. The carbonate was kept in suspension throughout the photolysis by magnetic stirring and agitation by N_2.