Irradiation of Diazofluorene in Alcohols: Unusual Behaviour of Fluorenyl Ethers

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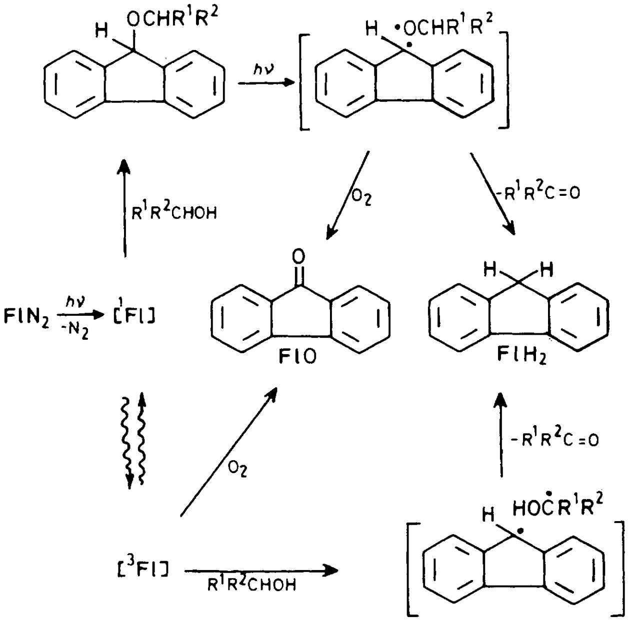
Fluorenyl ethers formed in the reaction of singlet fluorenylidene with alcohols undergo photocleavage to give fluorene and fluorenone, which formally arise from triplet fluorenylidene.

It is generally accepted[1,2] that singlet carbenes insert into the O–H bond of alcohols rather than the C–H bonds to give ethers while triplet carbenes abstract hydrogen from the C–H bonds of alcohols to give radical pairs which in turn undergo dimerization or abstraction of a second hydrogen atom. Consequently, the ratios of products arising from O–H insertion *vs.* hydrogen-abstraction in the reactions of carbenes with alcohols have been used[1–3] to estimate the steady-state concentration of singlet and triplet carbenes. During our studies[3] on the reaction of carbenes with alcohols, however, we found that the fluorenyl ethers (FlHOR) formed in the photolysis of diazofluorene ($\mathrm{FlN_2}$) in alcohols (ROH) were very photolabile, affording fluorene ($\mathrm{FlH_2}$) and fluorenone (FlO), both of which formally arise from triplet fluorenylidene (^{3}Fl).

Irradiation of an alcoholic solution of diazofluorene (20 M) in a Pyrex tube with a 300 W high-pressure Hg lamp at 10 °C until all the diazofluorene had been consumed (*ca.* 20 min) gave FlHOR, $\mathrm{FlH_2}$, and FlO. The product distributions apparently reflect the hydrogen-atom donor ability of the solvent alcohol employed (Table 1). Thus, the ratio of $\mathrm{FlH_2}$ to FlHOR significantly increased on going from MeOH to $\mathrm{Pr^iOH}$. This is consistent with the idea[1–3] that MeOH reacts mainly with the singlet fluorenylidene to give FlHOMe while hydrogen abstraction by the triplet from the α-C–H bond of the alcohol leading to $\mathrm{FlH_2}$ becomes significant in $\mathrm{Pr^iOH}$. However, the product distributions varied significantly with irradiation time (Table 1), and control experiments showed that the ether FlHORwas photolabile under the irradiation conditions to give $\mathrm{FlH_2}$ and FlO. Thus, when FlHOR, prepared by refluxing fluoren-9-yl bromide in the alcohol ROH, was irradiated in benzene through a Pyrex filter, $\mathrm{FlH_2}$ and FlO were formed in a ratio depending on the alkyl group R; $\mathrm{FlHOPr^i}$ decomposed rapidly upon irradiation to give mainly $\mathrm{FlH_2}$ while the decomposition of $\mathrm{FlHOBu^t}$ was much slower and resulted in almost exclusive formation of FlO (Table 2). These results imply that FlHOR either underwent disproportionation to give $\mathrm{FlH_2}$ and the aldehyde (or ketone) or was oxidized to FlO upon irradiation. This assumption is supported by the finding that irradiation of $\mathrm{FlDOCD_3}$ in benzene or MeOH resulted in the exclusive formation of $\mathrm{FlD_2}$ and that photolysis of $\mathrm{FlHOCH_2Ph}$ gave roughly equal amounts of $\mathrm{FlH_2}$ and PhCHO. The radical pairs formed by cleavage of the C–O bond of FlHOR will disproportionate within the solvent cage if the alkoxy radical has an α-hydrogen atom, or will diffuse apart if the alkoxy radical has no α-hydrogen atom, FlH· being trapped by oxygen to give FlO (Scheme 1).

These results are unusual since most other ethers resulting from the reaction of typical arylcarbenes, *e.g.*, $\mathrm{Ph_2C}$:, PhCH:, and $\mathrm{Ph\ddot{C}CO_2Me}$, with alcohols were stable even under irradiation in a quartz tube. The reason for this difference between FlHOR and other ethers is as yet unknown.

These results may be related to the anomalous behaviour



Scheme 1. Fl = fluoren-9-ylidene

Table 1. Photolysis of 9-diazofluorene ($\mathrm{FlN_2}$) in alcohols.

		Relative yield (%)[a]		
ROH	Time/min	FlHOR	$\mathrm{FlH_2}$	FlO
MeOH	20	86.2	8.2	5.6
	40	61.7 (97.3)	28.7 (1.7)	9.6 (<1)
EtOH	20	68.0	22.5	9.4
	40	57.9 (93.8)	31.2 (5.2)	10.9 (<1)
$\mathrm{Pr^iOH}$	20	50.2	30.4	19.4
	40	41.3 (78.6)	37.2 (17.9)	21.5 (3.5)
$\mathrm{Bu^tOH}$	20	92.8	<1	6.2
	40	86.9 (94.5)	<1 (<1)	12.1 (4.5)
$\mathrm{PhCH_2OH}$[b]	20	5.5	69.1	25.4

[a] Total product yields are 70—85%. Other minor products detected were bifluorenyl and the azine FlN=NFl. Yields in parentheses are for irradiation with a Corning CS-052 filter, cut-off at 350 nm. [b] PhCHO was formed.

Table 2. Photolysis of fluorenyl ethers in benzene.

		Relative yield (%)[a]		
R in FlHOR	Time/min	FlHOR	$\mathrm{FlH_2}$	FlO
Me	20	42.3	50.4	7.3
	40	28.5	62.3	9.2
$\mathrm{CD_3}$[b]	40	38.0	50.4[c]	11.6
Et	20	34.0	55.3	10.7
	40	15.5	72.4	12.1
$\mathrm{Pr^i}$	20	1.5	70.9	27.6
$\mathrm{Bu^t}$	20	51.1	<1	47.9
	40	22.2	1.1	76.7

[a] Total product yields are 80—85%. Another minor product detected was bifluorenyl. [b] $\mathrm{FlDOCD_3}$. [c] $\mathrm{FlD_2}$. Neither FlHD nor $\mathrm{FlH_2}$ was detected within the limits of n.m.r. detection.

of fluorenylidene recently reported:[4] it has been suggested[4b] that singlet fluorenylidene generated in cyclohexane abstracts hydrogen to give FlH•; also, addition of alcohols[4d] causes the rates of decay of ^{3}Fl and of growth of FlH• to increase concomitantly.

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