Reinvestigation of the Decafluorobenzophenone–Isopropyl Alcohol Actinometer

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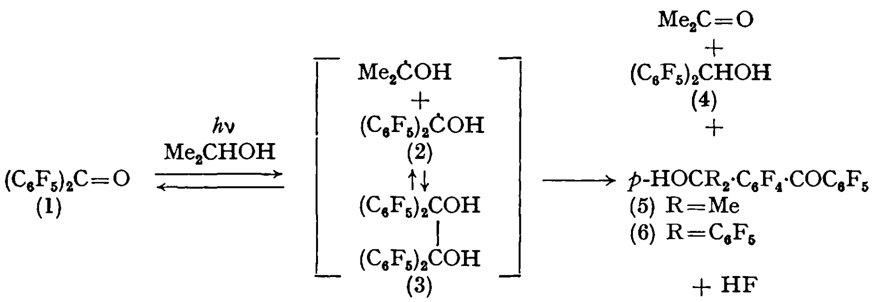
Summary The recommended actinometer decafluorobenzophenone in isopropyl alcohol is shown to be unsuitable.

PRODUCT analysis by chromatography with benzene on silica gel after the photolysis of decafluorobenzophenone (**1**) in degassed and non-degassed isopropyl alcohol solutions revealed that the compounds (**5**), m.p. 91—92°, and (**6**), m.p. 121—122°, were formed in addition to the previously reported[1] product (**4**), with an approximate ratio of 4 : 1 : 2 for (**4**) : (**5**) : (**6**). The structures of (**5**) and (**6**) were assigned on the basis of u.v., i.r., ^{1}H- and ^{19}F-n.m.r. (including double-resonance experiments), and mass spectral data.



$$(C_6F_5)_2C{=}O\ (1)\ \overset{h\nu}{\underset{}{\overset{Me_2CHOH}{\rightleftarrows}}} \left[\begin{array}{c} Me_2\dot{C}OH \\ + \\ (C_6F_5)_2\dot{C}OH \\ (2) \\ \uparrow\downarrow \\ (C_6F_5)_2COH \\ | \\ (C_6F_5)_2COH \\ (3) \end{array}\right] \longrightarrow \begin{array}{c} Me_2C{=}O \\ + \\ (C_6F_5)_2CHOH \\ (4) \\ + \\ p\text{-}HOCR_2\cdot C_6F_4\cdot COC_6F_5 \\ (5)\ R{=}Me \\ (6)\ R{=}C_6F_5 \\ +\ HF \end{array}$$

SCHEME

A red colour developed during irradiation which disappeared on shaking or flushing the solution with air and reappeared on standing. This observation correlates with the presence of the ketyl radical intermediate (**2**)[2], known to recombine in perfluoromethylcyclohexane[3] to the pinacol (**3**) which in alcoholic solvents forms the thermally stable compounds (**1**) and (**4**) [and presumably also (**5**) and (**6**) in the photomixture] (Scheme).

Our u.v. control spectra of the photoreaction were compatible with the formation of a multi-product mixture and, in particular, they did not confirm the occurrence of an isosbestic point at 326 nm which has been reported[1] and mistakenly ascribed to a virtually exclusive transformation of (**1**) into decafluorobenzhydrol (**4**).

In addition, the following facts show that—contrary to a further claim in the literature[1]—the photochemical quantum yield for the disappearance of (**1**) in isopropyl alcohol varies with the reaction conditions. The generally lower quantum yields in non-degassed solutions (Φ^{366} 0·22, Φ^{313} 0·34, Φ^{295} 0·39†) suggest that reaction of molecular oxygen with (**2**) provides for an additional path to (**1**), possibly *via* a hydroperoxide derivative. The dependence on excitation wavelength is explicable in terms of the formation of products which absorb in the same u.v. region as the starting material.

Our results are complementary to the previous reports[1–3] on the photolysis of decafluorobenzophenone, and in particular they invalidate recommendation[1] of the decafluorobenzophenone–isopropyl alcohol system as a suitable photochemical actinometer.

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† *Cf.* Φ 0·60[1] in degassed solution. All our quantum yields were determined with an electronically integrating actinometer (ref. 4) and v.p.c. analysis on 5% SE-30 on Chromosorb G-AW-DMCS.

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