A New Actinometer: Decafluorobenzophenone–Isopropyl Alcohol

By NICOLAE FILIPESCU, JACK P. PINION, and FREDRICK L. MINN*
(*Department of Chemistry, The George Washington University, Washington, D.C.* 20006)

Summary The clean photoreduction in propan-2-ol of decafluorobenzophenone to decafluorobenzhydrol and the ease of g.l.c. determination of the extent of conversion suggest this system as a new actinometer.

WE suggest the use of decafluorobenzophenone photoreduction in isopropyl alcohol as a convenient actinometer at wavelengths between 290 and 370 nm, a near-u.v. region widely used in organic photochemistry. Unlike benzophenone, $(C_6F_5)_2CO$ is reduced to decafluorobenzhydrol, which is perfectly stable under g.l.c. conditions and has a retention time substantially longer than that of the parent ketone. This allows easy separation and accurate analysis of their mixture on practically any common g.l.c. column.

Decafluorobenzophenone (Aldrich), purified by sublimation, was irradiated in Spectrograde isopropyl alcohol (Fisher) at wavelengths longer than 290 nm. This region was used because the photoproduct $(C_6F_5)_2CHOH$ absorbs below 285 nm (see Figure) and undergoes further photochemical reaction. The only isolated product was decafluorobenzhydrol, identified by elemental analysis, mass and n.m.r. spectra, and comparison of its i.r. spectrum with that of a chemically prepared sample. The quantum yield of the $(C_6F_5)_2CO \rightarrow (C_6F_5)_2CHOH$ photoreaction was determined in an optical-train arrangement against the ferrioxalate actinometer.[1] Samples (10^{-2} M) in 1 cm quartz cuvettes were irradiated with light from a 120 w high-pressure Hg arc passing through a Bausch and Lomb high-intensity monochromator while a stream of nitrogen was bubbled through the solutions both for stirring and for partial degassing.† Within the recommended wavelength range the transformation seems uncomplicated by side reactions and is of constant quantum yield $\Phi = 0{\cdot}60 \pm 0{\cdot}01$. Changes in the u.v. absorption spectrum of dilute degassed $(C_6F_5)_2CO$ solutions in propan-2-ol on successive irradiations show two isosbestic points at 228 and 326 nm and a smooth transformation from $(C_6F_5)_2CO$ to $(C_6F_5)_2CHOH$ with virtually no build-up of transitory intermediates. This contrasts with benzophenone, for which the initial hydrogen abstraction by the lowest n,π^* triplet is followed by almost exclusive coupling of the $(C_6H_5)_2\dot{C}OH$ and $(CH_3)_2\dot{C}OH$ radicals in the solvent cage.[2] The insignificance of the analogous coupling reaction for $(C_6F_5)_2CO$ is probably caused by a shifting of the odd-electron density from the *para*- (or *ortho*-)carbon atoms in $(C_6H_5)_2\dot{C}OH$ to the fluorine substituent in $(C_6F_5)_2\dot{C}OH$, as shown, for example, in valence bond structure (**1**). Furthermore, electrostatic repulsion between the *ortho*-fluorines on the two benzene rings and between them and the hydroxylic oxygen may prevent somewhat the planarity required in the quinoid system of the enol intermediate. The limited solubility of decafluorobenzophenone in isopropyl alcohol may preclude preparation of optically thick actinometer solutions, especially at longer wavelengths; this limitation may be alleviated by examination of other solvent systems.‡ Nevertheless, convenience and accuracy make this an attractive actinometer.

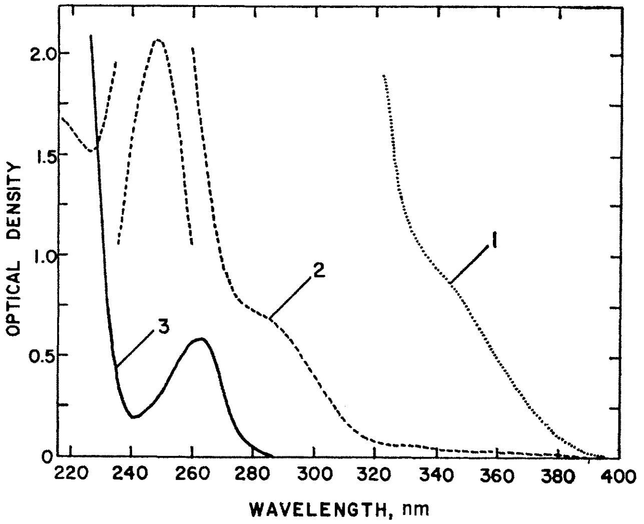
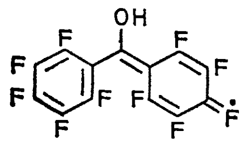


FIGURE. *U.v. absorption spectra of decafluorobenzophenone* (1) $5{\cdot}5 \times 10^{-3}$M, (2) $2{\cdot}2 \times 10^{-4}$M, *and decafluorobenzhydrol* (3) $2{\cdot}2 \times 10^{-4}$M *in isopropyl alcohol.*



(1)

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† No substantial differences were found between the behaviour of degassed and non-degassed samples.

‡ Although $(C_6F_5)_2CO$ is much more soluble in $(CF_3)_2CHOH$ (Pierce), photoreduction in this system was more complicated, formation of several photoproducts being indicated by g.l.c.

[1] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, *A*, **235**, 518.

[2] J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Amer. Chem. Soc.*, 1959, **81**, 1068; N. Filipescu and F. L. Minn, *ibid.*, 1968, **90**, 1544 and references therein.