

Photohydroxyalkylation of Hexafluorobenzene. Evidence for Substitution and Addition Mechanism

Marko Zupan\*, Boris Šket and Barbara Pahor

Department of Chemistry and "Jožef Stefan" Institute,  
University of Ljubljana, Ljubljana, Yugoslavia

(Received in UK 30 September 1977; accepted for publication 27 October 1977)

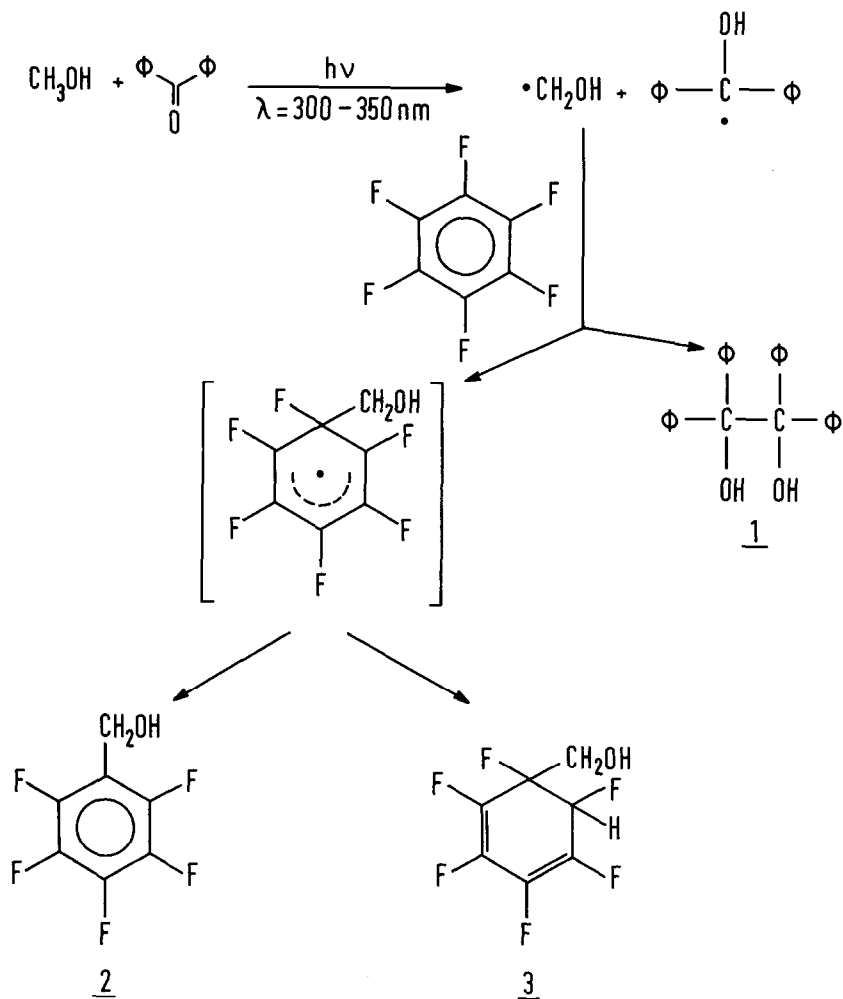
The light-induced substitution reactions of arylfluorides have been recently reviewed<sup>1</sup>. Bryce-Smith and coworkers<sup>2</sup> have recently observed cine-substitution by nucleophilic substitution of fluorobenzene and difluorobenzenes with primary and secondary amines, and found evidence for the addition-elimination mechanism. Irradiation of solutions of hexafluorobenzene in cyclohexane and cyclooctane gives hydrogen fluoride and a complex mixture containing cyclohexylpentafluorobenzene and other radical coupling products<sup>3</sup>.

We now report that a 24-hour irradiation of a solution of hexafluorobenzene in methanol in the presence of benzophenone with  $\lambda = 300 - 350$  nm at  $T = 25^\circ\text{C}$ , leads to the formation of three products. A white crystalline product, precipitating when the solution was evaporated in vacuo to a third, was filtered off and easily recognized as 1,1,2,2-tetraphenyl-1,2-dihydroxyethane (**1**). The filtrate was evaporated in vacuo and the crude reaction mixture was analyzed by  $^{19}\text{F}$  nmr spectroscopy and separated by preparative tlc. The main product formed (**2**, 48 %, liquid product), shows in its  $^{19}\text{F}$  nmr three signals:  $\delta F = -150.0$  ppm (2F, dd),  $-159.75$  ppm (1F, t),  $-168.0$  ppm (2F, td) with the coupling constants 24 Hz and 9 Hz, and in its  $^1\text{H}$  spectrum a singlet signal at  $\delta = 4.76$  ppm for two protons and a broad singlet for one proton at  $\delta = 3.61$  ppm. The mass spectrum of product **2** shows the following fragments:  $m/e$ : 198 ( $M^+$ , 100 %, calcd. for  $\text{C}_7\text{F}_5\text{H}_3\text{O}$   $m/e$  198.0104, found  $m/e$  198.0104), 181 (65), 179 (19), 177 (57), 150 (36), 117 (24), 99 (22). From the spectroscopic data we have established that hydroxymethylpentafluorobenzene was formed. A minor product formed (**3**, 20 %, oily product) shows in its  $^{19}\text{F}$  nmr spectrum four multiplets, corresponding to six fluorine atoms:  $\delta F = -139.5$  ppm (2F, dm,  $J = 27$  Hz),  $-154.9$  ppm (2F, dm,  $J = 27$  Hz),  $-167.25$  ppm (1F, td,  $^3J_{\text{FH}} = 24$  Hz,  $^3J_{\text{FF}} = 24$  Hz),  $-169.9$  ppm (1F, dd,  $^2J_{\text{FH}} = 50$  Hz,  $^3J_{\text{FF}} = 24$  Hz), with a very similar mass spectrum to that of compound **2**. Product **3** was converted by heating into product **2**. On the basis of the spectroscopic data and chemical transformation, we established the structure of product **3** as 1-hydroxymethyl-1,2,3,4,5,6-hexafluorocyclohexadiene-3,5. Separation of the crude reaction mixture of products **2** and **3** by preparative glc gave only product **2**.

Reduction of the irradiation time from 24 hours to 6 hours or prolongation to 60 hours affected only the overall yield of the products, but not the ratio of the substitution and addition products ( $2/3 = 2/1$ , determined by  $^{19}\text{F}$  nmr), thus reducing the possibility of the formation of substitution product (**2**) by photoelimination of **3**, as was suggested by the photonucleophilic substitution reactions of fluorobenzene and difluorobenzenes<sup>2</sup>. On the basis of the above mentioned observations, the mechanism presented in the Scheme is suggested: in the presence of benzophenone a hydroxymethyl radical is formed, which then reacts with hexafluorobenzene, forming radical species, transforming by two different pathways to **2** and **3**.

Being interested in the effect of the structure of the alcohol on the photoreaction, we studied also the reactions with ethanol, isopropanol, cyclohexanol and t-butanol. All reactions, except of that with t-butanol, after separation by glc, resulted in hydroxymethyl derivatives, i.e. 1-hydroxy-1(pentafluorophenyl)ethane (28 %, liquid product), 2-hydroxy-2(pentafluorophenyl)propane (28 % of liquid product), 1-hydroxy-1(pentafluorophenyl)cyclohexane (30 % of liquid product). The effect of the structure of the alcohols on the reaction pathways, and of sensitizers and temperature on the above mentioned photoreactions, is in progress.

## SCHEME



## References:

1. J.Cornelisse and E.Havinga, *Chem. Rev.*, **75** (1975), 353.
2. D.Bryce-Smith, A.Gilbert, and S.Krestonosich, *J.C.S., Chem.Comm.*, **1976**, 405.
3. D.Bryce-Smith, B.E.Connett, A.Golbert, and E.Kendrick, *Chem. and Ind.*, 855 (1966).