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Irradiation of 1-hydroxyalkane solutions of pentafluoropyridine in the presence of benzophenone resulted in regiospecific substitution at position 4, thus forming 2,3,5,6-tetrafluoro-4-(1-hydroxyalkyl)pyridine.

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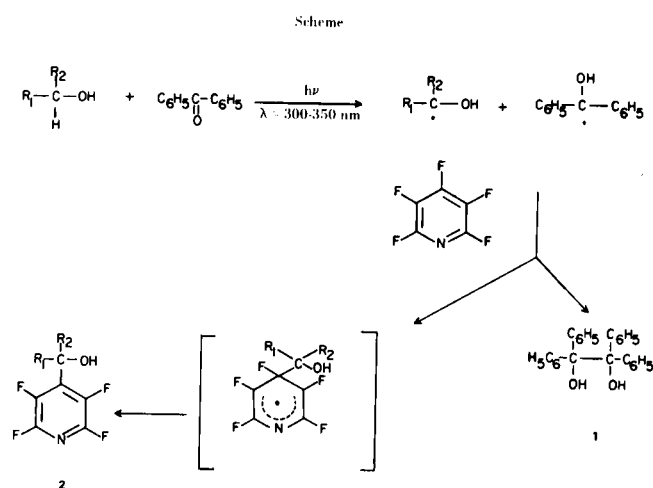
Sir:

Bryce-Smith and coworkers (1) have recently found that 2-fluoropyridine readily reacted with diethylamine and *t*-butylamine, thus forming *N*-substitution products exclusively and no evidence for ring-substitution, which was observed by reactions with difluorobenzenes (2), was found. On the other hand, 2-fluoropyridine gave with triethylamine (1) a 2:1 mixture of 2-diethylaminopyridine and *N,N*-diethyl-1-(2-pyridyl)ethylamine.

We now report that a 24 hour irradiation of a methanol solution of pentafluoropyridine in the presence of benzophenone at $\lambda = 300\text{--}350\text{ nm}$ and $T = 25^\circ$ leads to the formation of two products, the first a white crystalline product, precipitating when the solution was evaporated *in vacuo* to a third, which 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}F nmr spectroscopy, purified by preparative glc and 47% of a liquid product was isolated. Product 2 shows in the ^{19}F nmr two multiplets at $\delta\text{ F} = -93.75\text{ ppm}$ (2F, AA'XX' type of spectrum), -151.5 ppm (2F, AA'XX' type of spectrum) and in its ^1H nmr spectrum a singlet signal at $\delta = 4.7\text{ ppm}$ (2H) and a broad singlet at 3 ppm (1H). The mass spectrum of product 2 shows the following fragments: m/e 181 (M^+ , 100%, Calcd. for $\text{C}_6\text{H}_3\text{NOF}_4$ m/e 181.0151, Found m/e 181.0147), 180 (33), 164 (37), 160 (58), 151 (28), 143 (52), 142 (47), 121 (37), 100 (28), 86 (20), 84 (23), 82 (38), 75 (22), 69 (28). From the spectroscopic data and comparison of nmr data with other 2,3,5,6-tetrafluoro-4-substituted pyridines (3), we established that 4-hydroxymethyltetrafluoropyridine was formed.

Being interested in the effect of the structure of the alcohol on the photoreaction, we found that reaction with ethanol and 1-propanol resulted in the formation of 2,3,5,6-tetrafluoro-4(1-hydroxyalkyl)pyridine in high yield, while reaction with 2-propanol and cyclohexanol resulted in 4-substituted products in very low yield, under the conditions mentioned above, while the reaction with *t*-butyl alcohol failed. In the presence of higher amounts

of benzophenone and a longer irradiation time (50 hours), the reaction did not proceed to disubstituted products. On the basis of the above mentioned observations, the mechanism presented in the Scheme is suggested: in the presence of benzophenone, the hydroxyalkyl radical is



formed, which then reacts with pentafluoropyridine, forming radical species, transforming in the next step to 4-substituted products. Under the conditions mentioned above we were unable to detect the photoaddition products. However, studies of the effect of the structure of the alcohols on the reaction pathways, and of sensitizers and temperature on the above mentioned photoreactions are in progress.

REFERENCES AND NOTES

- (1) D. Bryce-Smith, A. Gilbert, and S. Krestonosich, *Tetrahedron Letters*, 385 (1977).
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- (3) J. Lee and K. G. Orrell, *J. Chem. Soc.*, 582 (1965).