

GENERATION OF CARBENIUM IONS BY PHASE TRANSFER CATALYSIS.
A CONVENIENT PREPARATION OF BENZYLIC FLUORIDES.

Donald Bethell, Kenneth McDonald and K. Sundarraja Rao

Robert Robinson Laboratories, The University, P.O.Box 147,
Liverpool L69 3BX.

(Received in UK 22 February 1977; accepted for publication 14 March 1977)

Phase transfer catalysis has achieved spectacular preparative success.¹ In all cases, quaternary ammonium or phosphonium salts have been used to transport an anion from an aqueous solution in which its sodium or potassium salt is soluble into an organic solvent in which it is not. The chemical reaction is then usually thought to take place in the organic phase, the transferred anion acting typically as a nucleophile or as a base. Reactive carbon intermediates generated by this means have been either carbanions or carbenes produced from them. We now report the generation of carbenium ions using a typical phase transfer catalyst, tetrabutylammonium perchlorate, in water/methylene chloride by the reaction of hydrogen difluoride ion with aryldiazoalkanes. The product mixture contains the corresponding benzylic fluoride as a major and easily separable component, and the procedure can in some cases provide a convenient alternative to the existing methods of preparation of such fluorides.²

We illustrate the procedure with the preparation of diphenylmethyl fluoride, a compound whose preparation surprisingly has not previously been described.

To an aqueous solution of potassium hydrogen difluoride (6g. in 100 ml.) was added tetrabutylammonium perchlorate (0.5g) and a solution of diazodiphenylmethane (5g.) in methylene chloride (100 ml.). The reaction mixture was stirred magnetically in the dark at room temperature until all the diazoalkane had reacted (48 hr.). Evaporation of the organic layer yielded an orange oil from which diphenylmethyl fluoride (2.5g) was distilled (b.p. 80-83°/0.15 mm). Analysis: found C 83.8, H 5.95; $C_{13}H_{11}F$ requires C 84.1, H 5.93%. NMR spectrum in $CDCl_3$: 1H , δ 7.30 (s, 10H), 6.43 (d, 1H, $^2J_{HF}$ 48 Hz); ^{19}F , 37.2 ppm downfield from $PhCH_2F$ (d, $^2J_{HF}$ 48 Hz). Analytical gas chromatography gave the following composition: Ph_2CHF , 50%. Ph_2CHOH 10%, PH_2CO , 4%. $Ph_2C:CPh_2$, 1%, residue [the composition of which appeared from mass spectrometric examination to be $(Ph_2C)_n$ with n at least 5] 35%. The method has been successfully applied to the preparation of 2- and 4-bromodiphenylmethyl fluorides.

For comparison, decomposition of diazodiphenylmethane at the same concentration in water-saturated methylene chloride containing toluene-*p*-sulphonic acid (0.012M) gave Ph₂CHOH (23%), Ph₂C:O (10%), Ph₂C:CPh₂ (24%), and residue (43%).³ The product proportions are closely similar to those of the non-fluorinated products from the KHF₂ phase transfer reaction, if the yields of the olefin and residue are combined. The inference is that the products arise in both reactions by partitioning of the diphenylmethylation between the available nucleophiles in the organic phase.

Treatment of diazophenylmethane with KHF₂ as described above but at 0°C resulted in a very rapid reaction. Work up as before gave benzyl fluoride (14%; b.p. 42°/12 mm) together with benzyl alcohol, benzaldehyde, benzalazine and stilbene. By contrast, 9-diazofluorene at room temperature showed no detectable decomposition after fourteen days.

References.

1. E.V. Dehmow, Angew. Chem. Int.Ed., 1974, 13, 170; J. Dockx, Synthesis, 1973, 443.
2. C.M. Sharts and W.A. Sheppard. Org. Reactions, 1974, 21, 125; C.L. Liotta and H.P. Harris, J. Amer. Chem. Soc., 1974, 96, 2250 and references therein.
3. cf. D. Bethell and J.D. Callister, J. Chem. Soc. 1963, 3808 who found only Ph₂CHOH and Ph₂C=CPh₂ using aqueous acetonitrile as solvent.