Reaction of Perfluoroalkyl Carbanions with Benzenediazonium Chloride

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Summary In the presence of caesium or potassium fluorides, perfluoro-olefins react with dry benzenediazonium chloride in dimethylformamide giving benzeneazoperfluoroalkanes.

REACTIONS of perfluoroalkyl carbanions, generated by reversible nucleophilic addition of a fluoride ion to fluoro-olefins, are an effective method for the introduction of perfluoroalkyl groups into organic compounds.[1] We have found that perfluoroalkyl carbanions react smoothly with dry benzenediazonium chloride in dimethylformamide, giving benzeneazoperfluoroalkanes (41—53%) [equation (1)].

$$R_f^- + N \equiv \overset{+}{N}\text{–Ph} \rightarrow R_f\text{–N=N–Ph} \qquad (1)$$

(**1**) $R_f = (CF_3)_3C$, (**2**) $R_f = (CF_3)_2CF$,

(**3**) $R_f = \overline{CF_2 \cdot CF_2 \cdot CF_2 \cdot CF}$

Dry benzenediazonium chloride[2] was added slowly to a slurry of caesium or potassium fluoride in a solution of the fluoro-olefin in DMF, the reaction being noticeably exothermic, especially with perfluoroisobutene. Benzeneazoperfluoroalkanes are yellow liquids [(**1**) b.p. 52 °C, 8 mmHg; (**2**) b.p. 46 °C, 8 mmHg; and (**3**) b.p. 46 °C, 4·5 mmHg] which are stable at room temperature, although some decomposition of (**3**) occurs after storage for a long time.

Satisfactory analytical data for all these compounds were obtained. Their i.r. spectra include the following absorption bands: 1460(m), 1480(w), 1520(s, br), and 1600(w) [for (**3**) 1590]; in the mass spectra an intensive peak $m/e = 105$ (PhN_2), as well as weak molecular ions peaks are observed. The ^{19}F n.m.r. spectra (from external CF_3CO_2H) have signals at −11 p.p.m.(s) for (**1**), 0 p.p.m(d), +89 p.p.m. (heptet) for (**2**) [J (CF_3–F) 4·8 Hz], and five signals for the perfluorocyclobutyl group in (**3**). ^1H n.m.r. spectra show signals for the phenyl nucleus in the δ 6·20—7·62 p.p.m. region (Me_4Si).

The reaction is a method for the synthesis of benzeneazoperfluoroalkanes; compounds of the type CF_3–N=N–Ar were previously obtained by condensation of trifluoronitrosomethane with aromatic amines.[3]

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