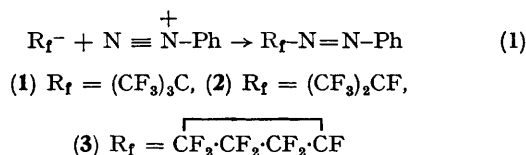


## Reaction of Perfluoroalkyl Carbanions with Benzenediazonium Chloride

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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.<sup>1</sup> We have found that perfluoroalkyl carbanions react smoothly with dry benzenediazonium chloride in dimethylformamide, giving benzeneazoperfluoroalkanes (41–53%) [equation (1)].



Dry benzenediazonium chloride<sup>2</sup> 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  $m/e = 105$  ( $\text{PhN}_2$ ), as well as weak molecular ions peaks are observed. The <sup>19</sup>F n.m.r. spectra (from external  $\text{CF}_3\text{CO}_2\text{H}$ ) have signals at –11 p.p.m.(s) for (1), 0 p.p.m.(d), +89 p.p.m. (heptet) for (2) [ $J$  ( $\text{CF}_3$ –F) 4.8 Hz], and five signals for the perfluorocyclobutyl group in (3). <sup>1</sup>H n.m.r. spectra show signals for the phenyl nucleus in the  $\delta$  6.20–7.62 p.p.m. region ( $\text{Me}_4\text{Si}$ ).

The reaction is a method for the synthesis of benzeneazoperfluoroalkanes; compounds of the type  $\text{CF}_3\text{--N=N--Ar}$  were previously obtained by condensation of trifluoronitrosomethane with aromatic amines.<sup>3</sup>

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<sup>3</sup> S. P. Makarov, A. Ya. Yakubovich, V. A. Ginsburg, A. S. Filatov, M. A. Englin, N. F. Privezentseva, and T. Ya. Nikiforova, *Doklady Akad. Nauk S.S.S.R.*, 1961, **141**, 357.