A New Aromatic Rearrangement

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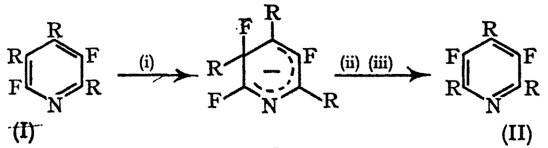
WE have described[1,2] reactions in which carbanions, generated by reactions of fluoride ion with fluoro-olefins, reacted with polyfluoro-aromatic compounds in a process which is a nucleophilic analogue of Friedel–Crafts reactions. As an extension to this analogy we now describe the migration of polyfluoroalkyl groups within an aromatic system, initiated by fluoride ion. This is analogous to the acid-induced rearrangements of alkylbenzenes.

The reaction of perfluoropyridine with perfluoropropene, initiated by potassium fluoride, has been found to give a mixture of isomeric tri-substituted compounds and we

$$C_3F_6 + C_5F_5N \xrightarrow[\text{Autoclave } 130^\circ]{\text{KF–Sulpholan}} C_5F_4N(C_3F_7) + C_5F_3N(C_3F_7)_2 + C_5F_2N(C_3F_7)_3 + \text{olefin dimers and trimers}$$

we have recently found that the yield of tri-substituted compounds is increased (to 40%) by injecting the olefin into the autoclave at the reaction temperature. A detailed analysis of the n.m.r. spectra of these isomers[3] has now established their structures to be (I) and (II). Haszeldine[4] has also claimed that these isomeric products are formed with a preponderance of (I) and attributed this to steric effects favouring this isomer. However, we have established that, under the conditions of the polyfluoroalkylation reaction, isomer (I) can be rearranged to (II) by potassium fluoride. Clearly then, isomers (I) and (II) are the products of kinetic and thermodynamic control, respectively. Also, isomer (I) may be obtained in large excess under conditions of a short reaction time. That isomer (II) is, indeed, the more thermodynamically stable is quite consistent with the unusually large steric requirements of the perfluoroisopropyl group, indicated by variable temperature n.m.r. studies.[5]



(I) (II)

R=CF(CF$_3$)$_2$

(i) KF–sulpholan, 130°; (ii) CF(CF$_3$)$_2$-migration; (iii) $-F^-$.

Some cross-over products were observed in the rearrangement of (I) to (II) in the presence of an excess of perfluoroquinoline, which is known to be easily polyfluoroalkylated,[6] and indicates an intermolecular process.

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[5] R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, L. H. Sutcliffe, and G. J. T. Tiddy, *Chem. Comm.*, in the press.
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