A New Intramolecular Nucleophilic Arylation: Synthesis of Octafluoro-9-fluorenone

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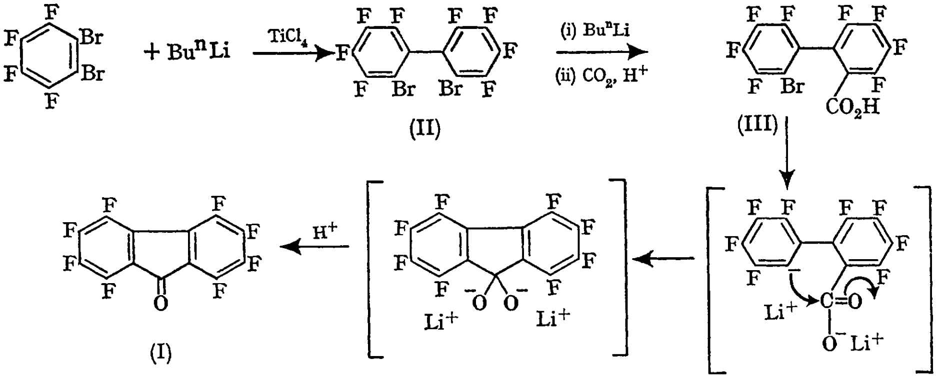
IN a recent Communication,[1] we discussed the dramatic enhancement of equilibrium acidities of hydrocarbons by polyfluoroaryl substitution. Since polycyclic aromatic hydrocarbons are generally more acidic than similar open-chain hydrocarbons (*e.g.* fluorene, pK_a 22·83 *cf.* diphenylmethane, pK_a 33·1),[2] owing to more favourable resonance stabilization of the resulting anion, it was of interest to examine the perfluorophenyl analogues of fluorene and 9-substituted fluorenes. The acidities of the latter compounds would be expected to be unusually high for hydrocarbons.

To gain entry into the fluorinated fluorene series, we prepared octafluoro-9-fluorenone (I), a key compound for subsequent preparative steps by a novel cyclization reaction. The reaction of lithium salts of aliphatic carboxylic acids with organolithium reagents affords a convenient method for the preparation of ketones.[3] It has also been shown that perfluoroalkyl carboxylic acids react with Grignard reagents[4] and phenyl-lithium[5] to provide perfluoroalkyl ketones, generally in good yields. The rate of reaction is enhanced in the latter cases by the electron-attracting perfluoroalkyl group which increases the electrophilic character of the carbonyl carbon atom and renders it more susceptible to attack by the nucleophilic organometallic reagent. However, completely fluorinated ketones have not been prepared by this route.

We have taken advantage of this method to prepare compound (I):



2,2′-dibromo-octafluorobiphenyl (II) was prepared from 1,2-dibromotetrafluorobenzene.[6] Reaction of (II) with an equimolar concentration of n-butyllithium in ether at −78° gave the bromocarboxylic acid (III), m.p. 158—160° (sealed capillary), in 66% yield (*M*, calc., 421; found, 415), after carbonation. This is a very sensitive reaction, since dilithiation occurs readily.[7] The acid (III) was treated with two equivalents of n-butyl-lithium at $-78°$ and the mixture acidified to give (I), yellow crystals, m.p. 247—248° (sealed capillary, sublimes readily).

Compound (I) was readily converted into its 2,4-dinitrophenylhydrazone, m.p. 239—240° (decomp.), in contrast to the behaviour of the more sterically hindered decafluorobenzophenone, which fails to form this derivative. The infrared spectrum of (I) in $CHCl_3$ revealed carbonyl absorption at 1737 s and 1721 w $cm.^{-1}$ and the visible-ultraviolet spectrum exhibited λ_{max} (dioxan) 375, 330, 316, 302, 297sh, and 290sh $m\mu$, very similar to that of 9-fluorenone.

The formation of this cyclic aromatic ketone represents, to our knowledge, the first report of an *intramolecular* nucleophilic arylation reaction involving attack on a carboxylate salt. Moreover, compound (I) appears to be the first example of a perfluorinated ketone prepared by this method.

Under similar conditions, 2′-bromobiphenyl-2-carboxylic acid, the hydrogen analogue of (III), failed to yield 9-fluorenone. We suggest that the reaction was successful with (III) because the substituted tetrafluorophenyl group enhances the electrophilicity of the carbonyl carbon atom, thus encouraging facile nucleophilic attack by the favourably disposed incipient carbanionoid species.

The ready availability of (I) now makes possible the preparation of a new class of compounds which contains the perfluorinated fluorene moiety.

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