Carbanionic Character of Decafluorobenzhydryl Bromide. Behaviour Towards Nucleophiles

By ROBERT FILLER* and FRANK P. AVONDA

(Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616)

Summary Decafluorobenzhydryl bromide (**1**) reacts with nucleophiles to give 1,1,2,2-tetrakis(pentafluorophenyl)-ethane (**2**) as the predominant product; there is no evidence of products derived from initial nucleophilic displacement on the carbon of (**1**).

WE report that decafluorobenzhydryl bromide (**1**) reacts with nucleophiles such as cyanide ion and triphenylphosphine to give 1,1,2,2-tetrakis(pentafluorophenyl)ethane (**2**)† as the predominant product. This result may be compared with the behaviour of the non-fluorinated analogue, benzhydryl bromide (**3**), which reacts with these nucleophiles by S_N2 displacement at carbon. These observations are summarized in equations (1) and (2).

$$\underset{(\mathbf{3})}{Ph_2CHBr} + Y^- \longrightarrow Ph_2CHY + Br^- \qquad (1)$$

$$\underset{(\mathbf{1})}{(C_6F_5)_2CHBr} + Y^- \longrightarrow \underset{(\mathbf{2})}{[(C_6F_5)_2CH]_2} + YBr \qquad (2)$$

$$Y = CN^-, Ph_3P:$$

We believe that reaction (2) arises by positive halogen transfer resulting from nucleophilic attack on halogen (S_NX reaction[1]) as, *e.g.*, in the case of CF_3I,[2] to give the stabilized carbanion (**4**),[3] which then attacks unchanged bromine at carbon to form the bimolecular product (**2**) [equation (3)].

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† We have consistently obtained samples of (**2**) with m.p. 249—250°, 30° higher than that recorded in ref. 4.

$$Y^- + \mathbf{(1)} \longrightarrow YBr + \underset{\mathbf{(4)}}{(C_6F_5)_2\bar{C}H} \xrightarrow{(1)} \mathbf{(2)} \qquad (3)$$

The isolation of CNBr in good yield on reaction of **(1)** with cyanide ion provides support for this interpretation. We found no evidence of products derived from initial nucleophilic displacement on carbon, *viz.*, $(C_6F_5)_2CHY$. A small amount of $(C_6F_5)_2CH_2$, formed by protonation of the carbanion, is often encountered.

A further indication of the unusual stability of **(4)** is observed when **(1)** reacts with n-butyl-lithium at −70° and the mixture is carbonated. Compound **(2)** was isolated with no evidence of a carboxylic acid. In contrast **(3)** forms a less stable carbanion, which is converted on carbonation into diphenylacetic acid.

From similar studies by Vorozhtsov and his co-workers[4] on $(C_6F_5)_2CHCl$, it is clear that a broad spectrum of reagents with widely different nucleophilicities react with $(C_6F_5)_2$-$CHX(X = Cl, Br)$ to give the anomalous product **(2)**, rather than the variety of products obtained from $(C_6H_5)_2$-CHX and the appropriate nucleophile.

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