

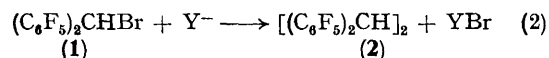
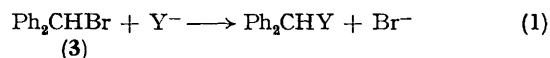
Carbanionic Character of Decafluorobenzhydryl Bromide. Behaviour Towards Nucleophiles

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

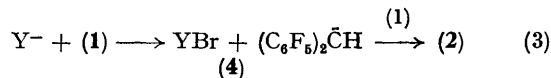
We report that decafluorobenzhydryl bromide (1) reacts with nucleophiles such as cyanide ion and triphenylphosphine to give 1,1,2-tetrakis(pentafluorophenyl)ethane (2)† as the predominant product. This result may be compared with the behaviour of the non-fluorinated analogue, benzhydryl bromide (3),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



Y = CN^- , Ph_3P :

We believe that reaction (2) arises by positive halogen transfer resulting from nucleophilic attack on halogen (S_NX reaction¹) 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)].

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



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-workers⁴ on $(C_6F_5)_2CHCl$, it is clear that a broad spectrum of reagents with widely different nucleophilicities react with $(C_6F_5)_2CHX$ ($X = Cl, Br$) to give the anomalous product (2), rather than the variety of products obtained from $(C_6H_5)_2CHX$ and the appropriate nucleophile.

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² J. Banus, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1951, 60.

³ R. Filler and C. S. Wang, *Chem. Comm.*, 1968, 287.

⁴ N. N. Vorozhtsov, jun., V. A. Barkhash, and S. A. Anichkina, *Doklady Nauk SSSR*, 1966, **166**, 598.