Tetrahedron Letters No.29, pp. 2481-2482, 1969. Pergamon Press. Printed in Great Britain.

An Unusual Benzyne Reaction[1]

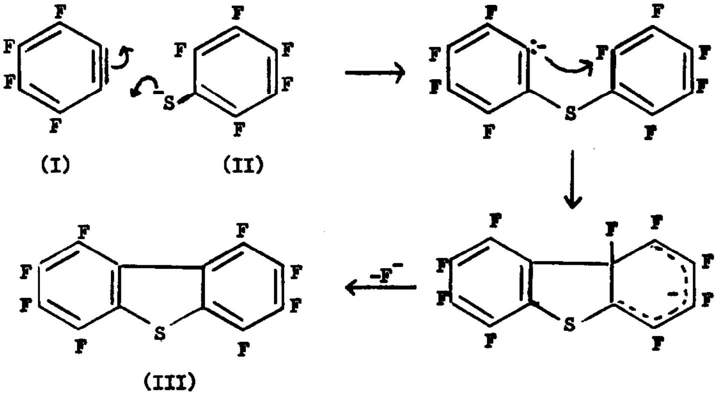
R.D. Chambers and D.J. Spring

University Science Laboratories, South Road, Durham.

(Received in UK 29 April 1969; accepted for publication 23 May 1969)

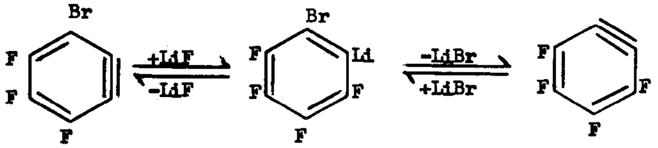
We report here a process involving nucleophilic addition to tetrafluorobenzyne with concomitant nucleophilic aromatic cyclisation of the resulting anion.

In previous work we have studied some of the chemistry of perfluoro-dibenzothiophen[2] and the derived -dibenzofuran.[3] The dibenzothiophen (III) was synthesised[2] by an Ullmann coupling of bis(2-bromotetrafluorophenyl)sulphide, itself not readily available.[4] We now find that (III) can be prepared in ~70% yields in a one-step process by the reaction of tetrafluorobenzyne (I) (generated by thermal decomposition of pentafluorophenyl-lithium) and pentafluorothiophenolate anion (II). The procedure involved the addition of two equivalents of butyl-lithium, dropwise, to an equimolar mixture of bromopentafluorobenzene and pentafluorothiophenol in 5:1 ether:hexane, maintained at 0°C. The reaction mixture was then allowed to stir overnight before work-up, giving (III).



The mechanism for this reaction appears to involve nucleophilic attack of (II) on (I) with subsequent cyclisation by an internal nucleophilic aromatic substitution. Nucleophilic addition to other benzynes is very well documented,[5] but the product isolated usually arises from a step equivalent to only the first part of the process outlined above. However, the outstanding characteristic of polyfluoroaromatic compounds is their susceptibility to nucleophilic attack and sulphur as a substituent activates this process,[6] which probably accounts for a related cyclisation reaction between (II) and diethyl acetylene dicarboxylate, to yield the benzo[b]thiophen system.[7]

Since (II) appears to be a very efficient trapping agent for (I), we have also applied this process to trapping the decomposition products of 2-bromotetrafluorophenyl-lithium. The major product was (III) (~40% of the total products), the other products arising from reaction with (IV). This contrasts with the results of other workers using furan[8] and polyfluoroaryl-lithiums[9] as trapping agents, but otherwise under similar conditions, when the products almost entirely arose from reaction with (IV). This was attributed[8] to LiF being insoluble in the solvent used and to LiBr being soluble, thus effectively making elimination of LiBr reversible and LiF irreversible. Our results indicate that (II)



(IV) (I)

traps the benzyne before this equilibrium is properly established since LiBr elimination would be expected to be more facile than that of LiF.

1. Part XI of the series 'Polyfluoroaryl Organometallic Compounds'. Part X, R.D. Chambers and D.J. Spring, Tetrahedron, 25, 565 (1969).

2. R.D. Chambers, J.A. Cunningham and D.J. Spring, Tetrahedron, 24, 3997 (1968).

3. R.D. Chambers, J.A. Cunningham and D.J. Spring, J. Chem. Soc. (C), 1550 (1968).

4. R.D. Chambers, J.A. Cunningham and D.A. Pyke, Tetrahedron, 24, 2783 (1968).

5. 'Dehydrobenzene and Cycloalkynes' by R.W. Hoffmann, Academic Press, 1967, p.99 ff.

6. R.D. Chambers and D.J. Spring, unpublished results.

7. G.M. Brooke and Md. A. Quasem, J. Chem. Soc. (C), 865 (1967).

8. E.J. Soloski and C. Tamborski, J. Organometal. Chem., 10, 385 (1967).

9. S.C. Cohen, D.E. Fenton, A.G. Massey and D. Shaw, J. Organometal. Chem., 8, 1 (1967).