Diels–Alder Reactions of Tetrafluorobenzyne with Aromatic and Heteroaromatic Compounds

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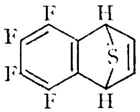
WE have already reported the Diels–Alder reaction of tetrafluorobenzyne with furan;[1] this Communication records similar reactions of thiophen, 1-methylpyrrole, and durene.

Thiophen reacts readily at 25° with an ethereal solution of pentafluorophenyl-lithium,[1] to give a clear solution. At this temperature decomposition of pentafluorophenyl-lithium to tetrafluorobenzyne occurs rapidly.[2] Separation of the products by preparative gas chromatography at 180° gave only 1,2,3,4-tetrafluoronaphthalene (40% yield).[1] Separation by alumina chromatography, however, gave 1,2,3,4-tetrafluoronaphthalene (35%), pentafluorothiophenol (*ca.* 1%), and an unidentified compound containing fluorine and sulphur (*ca.* 5%). The latter has a proton n.m.r. consistent with structure (I) and decomposes when warmed to 1,2,3,4-tetrafluoronaphthalene and sulphur,[3] but is so unstable even at room temperature that further characterisation has been impossible. This process provides the best route to 1,2,3,4-tetrafluoronaphthalene and its derivatives,[4] and we believe it to be the first recorded example of the participation of thiophen in a Diels–Alder reaction. The powerful dienophilic character of tetrafluorobenzyne is clearly shown since under the same conditions benzyne, from *o*-fluorophenyl-lithium, yields only 2-fluorobiphenyl and triphenylene.[3]

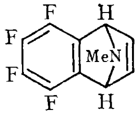
There have been reports of reactions of benzyne with 1-substituted pyrroles[5] to give mainly naphthylamine and carbazole derivatives but no 1,4-dihydronaphthalen-1,4-imines have been isolated. The reactions of tetrafluorobenzyne with 1-methylpyrrole were thus of interest.

A crystalline stable solid (m.p. 75—76°; 52% yield) was obtained, which was soluble in acid and could be reprecipitated on basification. Elemental analysis was satisfactory for the imino-compound. Its ^{19}F n.m.r. spectrum showed two groups of peaks at 150 and 161·4 p.p.m., relative to CCl_3F, attributable to four aromatic fluorine atoms. The proton n.m.r. spectrum showed three peaks at 2·1, 4·8, and 6·8 p.p.m. (relative to external tetramethysilane) in the ratio of 3 : 2 : 2 (the adduct of furan and tetrafluorobenzyne[1] showed two peaks at 4·7 p.p.m. and 6·6 p.p.m. corresponding to bridgehead and vinylic protons), these peaks may be assigned therefore to the *N*-methyl, the bridgehead, and the vinylic protons, respectively. The u.v. spectrum was in accord with the bridgehead structure; therefore we suggest that the product is the bridged imine (II). A report has just appeared of a stable bridged imino-compound isolated from the reaction of benzyne and 1-benzyltetramethylpyrrole.[6]

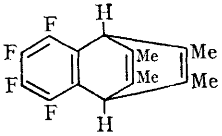
Durene has also been treated with tetrafluorobenzyne, giving a crystalline solid (m.p. 150—151°; 41% yield), easily separated from excess of durene by sublimation. The ^{19}F n.m.r. spectrum showed peaks at 137 p.p.m. attributable to four fluorine atoms, the proton n.m.r. spectrum showed two peaks at 1·8 and 4·4 p.p.m. (relative to external tetramethylsilane) in the integral ratio of 6 : 1. These peaks are attributable to methyl and bridgehead protons, respectively. Elemental analysis and molecular-weight measurements (Rast) agree with structure (III).



(I)



(II)



(III)

Similar experiments have been completed giving the expected adducts from benzene, hexafluorobenzene, toluene, the isomeric xylenes, and pyridine as substrates.

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[1] P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1962, 3227.

[2] D. D. Callander, P. L. Coe, and J. C. Tatlow, *Tetrahedron*, in the press.

[3] P. L. Coe and A. J. Uff, unpublished results.

[4] P. L. Coe, G. M. Pearl, and J. C. Tatlow, unpublished results.

[5] G. Wittig and W. Behnisch, *Chem. Ber.*, 1958, **91**, 2358; G. Wittig and B. Reichel, *Chem. Ber.*, 1963, **96**, 2851; E. Wolthuis, D. Vander Jagt, S. Mels, and A. de Boer, *J. Org. Chem.*, 1965, **30**, 190.

[6] E. Wolthuis and A. de Boer, *J. Org. Chem.*, 1965, **30**, 3225.