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ARYNE CHEMISTRY Part XV[1]

THE CLEAVAGE OF ETHERS AND THIOETHERS BY ARYNES

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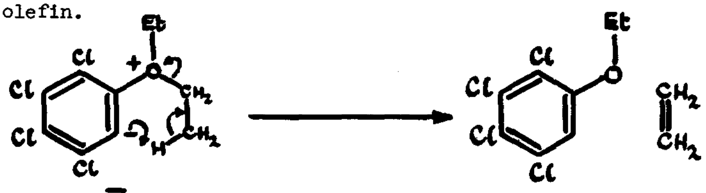
The cleavage of thioethers by benzyne has been reported previously.[2] Ethers have been much used as solvents in reactions involving arynes yet no products resulting from the cleavage of these compounds have been reported. The tetrahalogenobenzynes are even more electrophilic than benzyne,[3] and it might be anticipated that the weakly nucleophilic ethers would be cleaved.

Diethylether reacts with tetrachlorobenzyne, generated from tetrachloroanthranilic acid, to yield 2,3,4,5-tetrachlorophenetole in 63% yield. When the reaction mixture was quenched with deuterium oxide no incorporation of deuterium was detected in the product. A plausible mechanism involves abstraction of a proton β- to oxygen, by the initially formed betaine (I) followed by elimination of an olefin.



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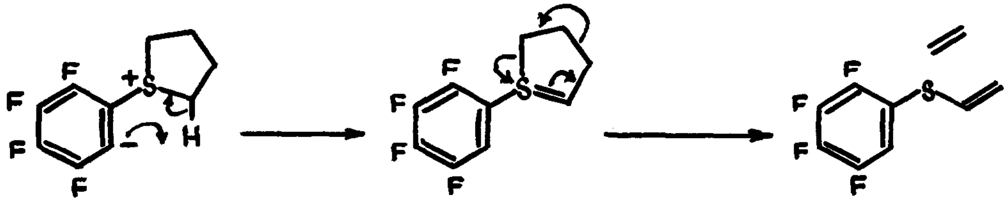
Similarly, n-butyl methyl ether, t-butyl methyl ether, and cyclohexyl methyl ether yield 2,3,4,5-tetrachloroanisole. Cyclohexene was isolated in the case of the reaction with cyclohexyl methyl ether, and was identified by comparison with a standard sample by gas chromatography.

The abstraction of an α-proton to form an ylid is well known with thioethers. Thus tetrafluorobenzyne reacts with tetrahydrothiophen to yield 2,3,4,5-tetrafluorophenyl vinyl sulphide. This reaction is analogous to the reported decomposition of a tetrahydrosulphonium salt in basic media,[4] which has recently been rationalised by Baldwin.[5]



The driving force for the abstraction of a proton α- to a positively charged sulphur would be the formation of the ylid. The absence of suitable d-orbitals on oxygen would presumably preclude a similar reaction involving tetrahydrofuran. Scale molecular models indicate that the abstraction of a proton β- to oxygen, in a betaine derived from an aryne and tetrahydrofuran, would be difficult. It was not surprising therefore that little cleavage of tetrahydrofuran by tetrachlorobenzyne occurred. The major product from this reaction was found to be 2,3,4,5-tetrachlorophenyl-3'methyl-butyl ether, formed by the addition of 3-methylbutan-1-ol- to tetrachlorobenzyne. 3-Methylbutyl nitrite was used as the source of nitrosating agent in the aprotic diazotisation. A small amount of an unknown compound was detected by gas chromatography. Reduction of the crude reaction mixture by hydrogen in the presence of palladium on carbon gave a product which was shown to contain 2,3,4,5-tetrachlorophenyl-n-butyl ether by comparison with a standard sample, on columns with widely differing polarities.

Our further studies are concentrated in delineating the cleavage reactions, in particular using those ethers which have no β-hydrogens, and those thioethers having no α-hydrogens.

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