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ARYNE CHEMISTRY. PART XXV.[1]

SOME REACTIONS OF TETRAFLUOROBENZYNE WITH METHOXYBENZENES AND THE PHOTOLYSIS AND THERMOLYSIS OF SOME OF THE PRODUCTS

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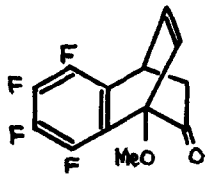
Recent interest in reactions of tetrahalogenobenzynes, in particular with 2,3-dimethoxynaphthalene,[2] prompts us to report some of our results in this area. Reactions of arynes involving, (2+2+2)π cycloadditions,[3] and (2+2)π cycloadditions,[4] have also been much studied recently.

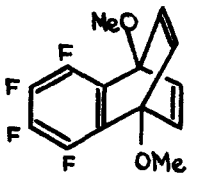
We,[5] and others[6,3b] have shown that tetrafluorobenzyne reacts with toluene to give a mixture of 1,4-cycloadducts in which the non-bridgehead adduct predominates (ratio 4:1). With p-xylene only the non-bridgehead adduct was detected. On the other hand, reactions of tetrahalogenobenzynes with anisole,[5,3b,7] resulted in the formation of adducts in which the bridgehead adduct predominated (ratio 4:1 with tetrafluorobenzyne). It was of interest therefore to study reactions of tetrafluorobenzyne with other alkoxybenzenes, and we now report reactions with the three isomeric dimethoxybenzenes and 1,3,5-trimethoxybenzene.

o-Dimethoxybenzene was found to give one major product (1) in 44% yield and m-dimethoxybenzene gave only one product (2) in 62% yield. p-Dimethoxybenzene gave three products, one of which was the adduct (3), isolated in 18% yield, having two bridgehead substituents, and the second product, isolated in 31% yield, was the diketone (4) derived by hydrolysis of the di-enol ether (5). In certain of our experiments we have isolated enol ethers but these compounds are hydrolysed extremely rapidly, as indicated by infra-red and ^{1}H n.m.r. spectroscopy.

The structures of the compounds (1)——(4) were established largely by analysis, and infra-red and ^{1}H n.m.r. spectroscopy (Table). Mass spectrometry showed that the major cleavage of the molecular ions of the adducts (1) and (2) occurs by the loss of ketene. We therefore studied the photolysis and thermolysis of (1) and (2) which gave the naphthalene (6) in almost quantitative yield in each of the four reactions. Similar pyrolytic and photolytic reactions have been reported recently.



(1)



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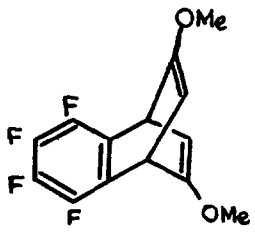

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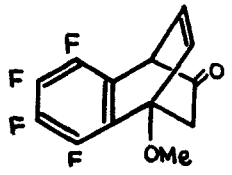
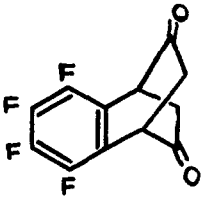
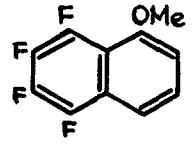


(2)

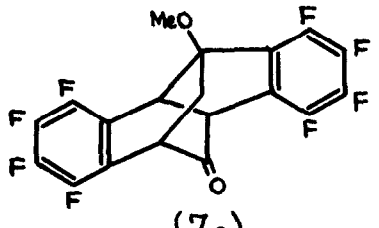


(4)

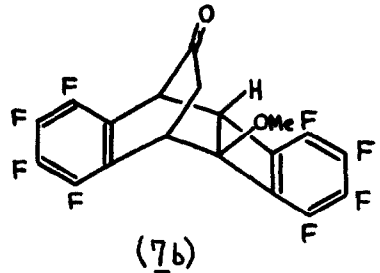


(6)

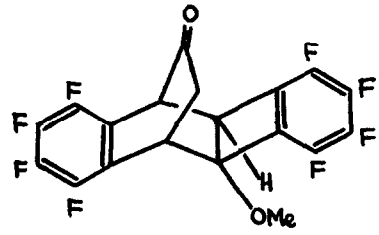
The third product in the reaction of tetrafluorobenzyne with p-dimethoxybenzene (isolated in 8% yield) was shown, by analysis and mass spectrometry, to have the molecular formula $C_{19}H_8F_8O_2$ and therefore was derived originally from p-dimethoxybenzene and two molecules of tetrafluorobenzyne. The infra-red spectrum showed the presence of a carbonyl group (ν_{max} 1745 cm^{-1}) and we therefore considered structures (7a, b, and c).



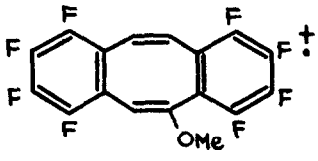
(7a)



(7b)



(7c)



(8)

The addition of tetrafluorobenzyne to the bis-enol ether (5) could occur by an orbital symmetry controlled (2+2+2)π cycloaddition[9] to yield after hydrolysis (7a). The compounds (7b and c) could arise by (2+2)π cycloaddition of tetrafluorobenzyne to one enol-ether residue in (5). Hydrolysis of the initial product would again give a ketone. Comparison of the i.r. and ^{1}H n.m.r. data for the compound (7) with the data for a number of other compounds at hand suggests the exclusion of the structure (7a). Similarly the loss of ketene from the molecular ion of (7) would require the rearrangement of (7a) [M^+. -42=50% of M^+.] and suggests that the initial cleavage occurs to form the ion (8). The spectral data presently available suggests that the structure (7c) is more likely for this chiral molecule.

TABLE

^{1}H n.m.r. spectra, chemical shift data (τ)

Compound			-OMe	$-CH_2-CO-$	other
1	5.4	3.26	6.3	7.9	
2	5.36	3.04-3.52	6.38	7.7	
3		3.0	6.24		
4	5.7			7.34	
7	5.59 and 6.31		6.6	8.0	5.61

Although the diketone isomeric with the compound (4) was not detected in the reaction of *m*-dimethoxybenzene with tetrafluorobenzyne such a product would be predicted to undergo interesting reactions. We therefore carried out a reaction of tetrafluorobenzyne with 1,3,5-trimethoxybenzene. The di-enol ether (9) was not isolated, and after the removal of unreacted 1,3,5-trimethoxybenzene we isolated the phenolic acid (10) in 40% yield (ν_{max} 3500-2500, and 1700 cm^{-1}). The reaction of (10) with diazomethane gave (11) which was more easily characterised: ν_{max} 2860 and 1750 cm^{-1}; λ_{max}^{MeOH} 266 ($\log_{10}\epsilon$ 3.69), 275 (3.79), 286 (3.72), 318 (3.19), and 331 (3.27) n.m.; τ 2.8 (1H), 2.96 (1H), 5.94 (2H, d., $|J|_{H-F}$= 5.9 Hz.), 6.1 (3H), and 6.28 (3H).

The phenolic acid (10) is undoubtedly formed from the di-enol ether (9) by hydrolysis followed by a retro-Claisen condensation followed by aromatisation as shown in the scheme.

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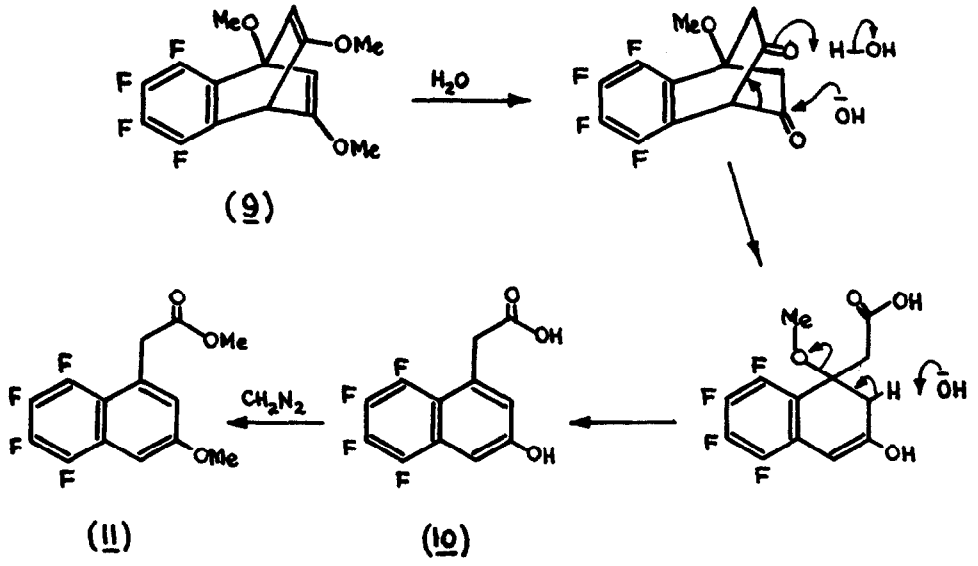

(9) (10) (11)

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