Reactions of Arynes with Carbonyl Compounds

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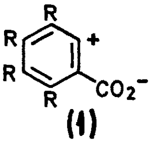
Summary Arynes, generated by a number of methods, react with cinnamaldehyde to form flavenes; with benzaldehyde and p-methoxybenzaldehyde, 2,4-diaryl-1,3-benzodioxan derivatives are obtained, while, using p-nitrobenzaldehyde in the presence of acetone, a 2,2-dimethyl-4-p-nitrophenyl-1,3-benzodioxan derivative has been isolated.

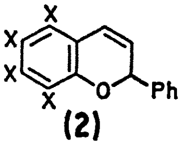
1,3-BENZODIOXAN-4-ONES have been isolated when o-carboxybenzenediazonium salts were decomposed in the presence of aqueous solutions of carbonyl compounds.[1] Similarly the formation of 2,2-diphenyl-3,1-benzo-oxathian-4-one from thiobenzophenone and benzenediazonium-2-carboxylate,[2] and other reactions,[3] imply the intermediacy of (1; R = H). We have previously reported the reactions of tetrachlorobenzyne, generated from tetrachloroanthranilic acid, with $\alpha\beta$-unsaturated aldehydes.[4] It was possible that these reactions were *arynoid*,[5] also involving the intermediacy of (1; R = Cl), since benzenediazonium-2-carboxylate is known to decompose to benzyne in a stepwise manner.[6]

We now report that benzyne, generated from benzothiadiazole 1,1-dioxide,[7] diphenyliodonium-2-carboxylate,[8] or from anthranilic acid,[9] reacted with cinnamaldehyde to form flavene[10] (2; X = H) in *ca.* 15% yield. Similarly (2; X = Cl)† was formed in 32% yield. Thus these reactions do involve arynes.[11]

We have also obtained 1,3-benzodioxan derivatives by the aprotic diazotisation of tetrachloroanthranilic acid[12] in the presence of other simpler carbonyl compounds. The absence of products analogous to those reported,[1,2] also implies that tetrachlorobenzyne is involved in these reactions. We obtained (3; R = Ph), and (3; R = p-C_6H_4·OMe) each in *ca.* 20% yield in reactions using benzaldehyde or p-methoxybenzaldehyde.



(1)



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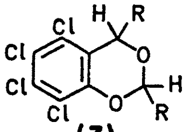

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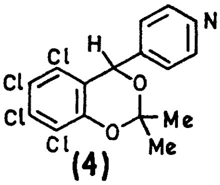

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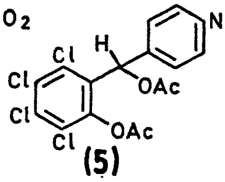
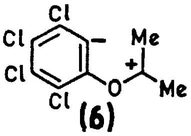


(5)



(6)

An indication of the mechanism of the reactions of tetrachlorobenzyne with aromatic aldehydes is given by the fact that no analogous adduct has been isolated at present using p-nitrobenzaldehyde. However, in the presence of acetone (4) was obtained in 5% yield. The structure of (4) is evident from the cleavage with sulphuric acid in acetic anhydride which yielded (5), and this suggests that the 1,4-dipolar intermediate (6) is involved in this reaction, and that similar intermediates may be involved in our other reactions.

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† Satisfactory analytical and spectroscopic data were obtained for all the new compounds reported.

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