The Rearrangement of Benzo-1,3-dioxan Derivatives to Benzofurans

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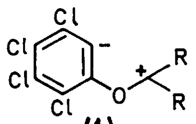
Summary The cleavage of 4-acetyl-2,2,4-trialkylbenzo-1,3-dioxans and derivatives yield benzofurans; the proof of structures and certain mechanistic features are discussed.

WE have shown that tetrachlorobenzyne reacts with simple carbonyl compounds to form benzo-1,3-dioxan derivatives which are probably formed *via* a dipolar intermediate of the type (**1**).[1] We now report that tetrachlorobenzyne reacts with acetone in the presence of butan-2,3-dione to yield (**2**;R^1 = R^2 = Me)† in 25% yield. Similar adducts were obtained (**2**; R^1 = R^2 = Et and R^1 = Me, R^2 = Et) when the acetone was replaced by diethylketone or ethyl methylketone. Each of these adducts gave the same product (**3**; R = OAc) on cleavage with sulphuric acid in acetic anhydride, and an alternative product (**3**; R = Br) in high yield with hydrobromic acid in acetic acid. Acetone (or diethylketone or ethyl methylketone) was detected in the reaction mixtures and isolated as its 2,4-dinitrophenylhydrazone.

The adducts (**2**) were reduced by sodium borohydride to the carbinols (**4**) and these were cleaved to 4,5,6,7-tetrachloro-2,3-dimethylbenzofuran (**3**; R = Me) as were the corresponding acetates of (**4**).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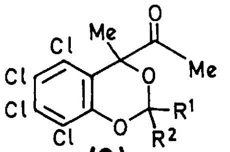
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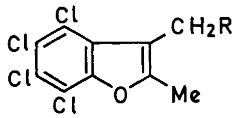
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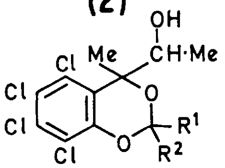
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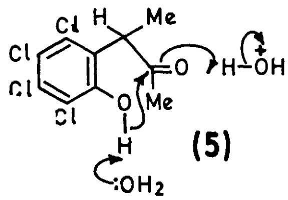
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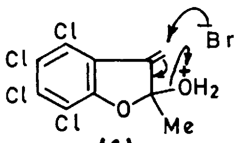
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The structures of the compounds (**3**; R = OAc, Br, and H) are evident from the following spectral data and chemical interconversions. Thus, compound (**3**; R = H) had a mass spectrum which showed the presence of four chlorine atoms (major molecular ion *m/e* 284). The u.v. spectrum showed the expected benzofuran chromophore λ_{max} (hexane) 272, 293, and 305 nm (ϵ 13,300, 3270, and 1530), and the ^1H n.m.r. spectrum showed the presence of two methyl resonances at τ 7·6 and 7·7. The compound (**3**; R = OAc) was converted into (**3**; R = Br) with hydrobromic acid, and (**3**; R = Br) was converted into (**3**; R = D) with lithium aluminium hydride. Reduction of (**3**; R = Br) with lithium aluminium deuteride gave (**3**; R = H) in which the singlet in the ^1H n.m.r. spectrum at τ 7·7 was replaced by the expected two proton triplet. The methyl resonance in 3-methylbenzofuran occurs at higher field than in the 2-isomer.[2]

The reaction of (**4**; $R^1 = R^2$ = Me) with deuteriosulphuric acid in acetic anhydride did not result in any deuterium incorporation into (**3**; R = H). We therefore suggest that the ring closure to form (**3**; R = H) involves the cyclisation (**5**) and that in the related cleavages which yield (**3**; R = OAc and Br) the formation of the benzofuran involves the expulsion of water in the final step as shown (**6**) for the formation of (**3**; R = Br).

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

[1] H. Heaney and C. T. McCarty, preceding Communication.

[2] Personal communication from Prof. J. A. Elvidge.