Reaction of 1,3-Dioxolans with Halogens: Formation of 1,3-Dioxolan-2-ylium Polyhalides

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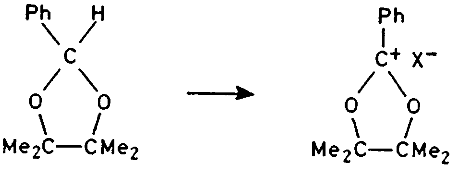
Summary Halogens and interhalogens oxidise 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolan (**1**) to the appropriate 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolan-2-ylium polyhalides (**2**)—(**6**).

SEVERAL reports of the conversion of 1,3-dioxolans into bromohydrin esters upon treatment with *N*-bromosuccinimide (NBS),[1—6] *NN*-dibromobenzenesulphonamide,[7] and even bromine[1] have appeared in recent years. While 1,3-dioxolan-2-yl radicals,[2] 1,3-dioxolan-2-ylium cations,[3,4] and 2-bromo-1,3-dioxolans[5] have been suggested as possible intermediates, available evidence[3,8] has indicated that carbocations rather than radicals are preferred as intermediates in the ring-opening step of NBS reactions. A recent report[8] that the appropriate 1,3-dioxolan-2-ylium tribromide could be isolated from the reaction of the *p*-nitrobenzylidene acetal of norbornane-2-*exo*-3-*exo*-diol with bromine has prompted us to report some preliminary results of the reactions of 1,3-dioxolans with halogens and interhalogens. The results are outlined in the Scheme and in the Table.



(1)

(2) X = Br_3
(3) X = I_3
(4) X = ICl_2
(5) X = IBr_2
(6) X = ICl_4

SCHEME

TABLE. Reaction of 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolan (**1**) with some halogens and interhalogens.[a]

Reagent	Reaction time/h	Product	Isolated yield/%	Colour	M.p./°C (uncorrected)
Cl_2	1	—	0	—	—
Br_2	1	(**2**)	95	Orange	83—84
I_2	6	(**3**)	58	Brown	138·5
ICl	1	(**4**)	90	Yellow	118—120
IBr	1	(**5**)	65	Orange	114—115
ICN	2	—	0	—	—
ICl_3	1	(**6**)	77	Yellow	135—138

[a] The dioxolan (**1**) (8 mmol) and the reagent (40 mmol) were stirred together in chloroform (20 ml) with initial cooling of the solution and then at room temperature for 1—6 h before diethyl ether (80 ml) was added. The resulting precipitate was filtered off and washed thoroughly with ether.

The dioxolan (**1**) reacted vigorously with bromine, evolving HBr. Addition of ether precipitated an orange crystalline material which upon mild acid or base hydrolysis gave pure pinacol monobenzoate. The n.m.r. and i.r. spectra and elemental analysis of the precipitated material were indicative of 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolan-2-ylium tribromide (**2**). This result confirms the finding of Plénat and his coworkers[8] that 1,3-dioxolan-2-ylium cations are intermediate in the reaction of 1,3-dioxolans with bromine. When 2-phenyl-1,3-dioxolan was treated similarly with bromine, the intermediate 2-phenyl-1,3-dioxolan-2-ylium tribromide could not be isolated and the product was 2-bromoethyl benzoate (96%). The stability of the 1,3-dioxolan-2-ylium cation (**2**) may be attributed to steric hindrance by the methyl groups towards bromide attack at the C(4) or C(5) positions which occurs readily in the corresponding 4,5-unsubstituted intermediate.

Iodine reacted more slowly with the dioxolan (**1**) to give a brown precipitate of the 1,3-dioxolan-2-ylium tri-iodide (**3**). Iodine monochloride and iodine monobromide both reacted vigorously affording HCl and the yellow dichloroiodate(I) (**4**), and HBr and the orange dibromoiodate(I) (**5**), respectively. Cyanogen iodide failed to react with the dioxolan (**1**) and after 2 h only the starting material was recovered. Iodine trichloride reacted smoothly liberating HCl and the yellow tetrachloroiodate(III) (**6**).

These novel reactions show that 1,3-dioxolans are generally reactive towards halogens and interhalogens and, at least in the case of 2-phenyl-4,4,5,5-tetramethyl-1,3-dioxolan (**1**), the intermediate 1,3-dioxolan-2-ylium cation may be isolated in association with the appropriate polyhalide anion.

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