Bromodeacylation accompanying Substitution in the Bromination of Aryl Acetates

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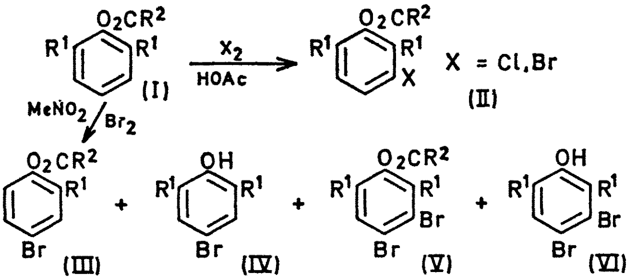
Summary Brominations of some 2,6-dialkylphenyl acetates in nitromethane give the 4-bromo-2,6-dialkylphenyl acetates together with the corresponding 4-bromo-2,6-dialkyl phenols, whereas 3-substitution predominates for the corresponding brominations and chlorinations in acetic acid.

REACTIONS, the overall course of which can be described as halogeno-deacylation with rearrangement, and classified by analogy as S_E2', are well known in naphthalene derivatives,[1,2] though their detailed courses have only been investigated in outline. Although there are hints in the literature[3] that such processes may be accessible also in the benzene series, no clear cases have been established up till now as far as we are aware.

The directing effects of ester groups, O·COR, have not been investigated very extensively, but the benzoyloxy-group (R = Ph) is activating for molecular chlorination, though considerably less so than alkyl groups.[4] In 2,6-dialkylphenyl esters (I) therefore, the normal position of substitution would probably be expected to be the 3-position (activated by two alkyl groups); we have established that the chlorination and bromination of some esters of this kind in acetic acid give mainly (though not exclusively) the expected derivatives (II; R^1 = Me, Pr^i; R^2 = 3,5-$(NO_2)_2 \cdot C_6H_3$, Me, Ph, *p*-Me·C_6H_4). Bromination of the benzoates in $MeNO_2$ was found to take the analogous course; but for the acetates (R^1 = Me, Pr^i; R^2 = Me), substitution occurred in the 4-position, to give the acetate (III), accompanied by the phenol (IV), and the di-substituted derivatives (V), (VI). Analysis by t.l.c. and g.l.c. showed, for example, that 2,6-di-isopropylphenyl acetate and bromine (each 0·1M) in $MeNO_2$ at 25° after *ca.* 30% reaction had given 4-bromo-2,6-di-isopropylphenyl acetate (66%), 4-bromo-2,6-di-isopropylphenol (27%), and 3,4-dibromo-2,6-di-isopropylphenol (6%); traces of 3-bromo-2,6-di-isopropylphenyl acetate, 3,4-dibromo-2,6-di-isopropylphenyl acetate, and of material of very high retention-time (probably formed by addition) were also detected.



The reactions were slow, and appeared to be heterolytic in character, as judged by the fact that the reactions were catalysed by added iodine or pyridine; the product ratio was very little changed by irradiation, or by the presence or absence of oxygen, nitrogen, or peroxides. Bromide ion, added either as hydrogen bromide or as tetraethylammonium bromide, markedly catalysed the reaction. The acetates (starting material and products) were not affected by the hydrogen bromide formed under the conditions of the reaction; but, in nitromethane saturated with hydrogen bromide or with water, a greater proportion of phenol was formed.

We presume that the phenols (IV) and (V) are formed by prototropic rearrangement of dienone intermediates, which themselves must be obtained by a reaction which formally is of the S_E2' type, but in which external bromide ion can act as a catalyst, presumably by assisting in the displacement of the acetyl group. As far as we are aware, this is the first clear example of bromination by this route in the benzene series, though Barton and his co-workers[5] have described fluoro-deacylations which may be related. In the present case, in which the electrophilic group enters *para-* to the acetate group, the cyclic transition state involving electrophilic attack synchronous with displacement of the acetyl group possible in some early examples[1,2] is unlikely to be involved.

We recognise, of course, that any such categorisation begs the question of whether there are further intermediates involved, and if so, what their nature is. The same is true of other categorisations (*e.g.* S_E2, S_N2', *etc.*). Addition–elimination sequences could contribute to the formation not only of the S_E2' but also to the S_E2 products described in the present work; we hope to clarify the nature of the reaction path further by search for these and for other possible intermediates, and by kinetic studies.

The present results suggest a re-interpretation (*cf.* ref. 6) of some unexpected orientational differences[7] between chlorination and bromination of biaryl esters.

Starting materials and products were characterised by standard methods; ^1H n.m.r. spectroscopy distinguished clearly between 3- and 4-substituted esters and phenols.

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