Intermediates in the Chlorination of Phenols and their Derivatives

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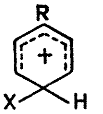
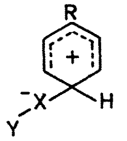
Summary Some unusual reaction paths taken, and intermediates involved, in the chlorination of 3,4-dimethylphenol and its methyl ether and acetate are described.

ELECTROPHILIC aromatic substitution is most commonly discussed in terms of proton loss from intermediates having much carbonium ionic character (*e.g.*, I, II). It is, however, becoming increasingly clear that even when such intermediates are implicated at an early stage in the reaction path, their subsequent reactions can be complex, and can result in the formation of unexpected products. Among these reactions are included rearrangements involving 1,2-shifts;[1] rearrangements with modification of the unsaturated system giving displacement from a distant point in the molecule and sometimes leading to side-chain substitution;[2] and co-ordination with a nucleophile to give products of addition.[3] Observation of the latter process is critically dependent on the possibility of identifying the product before it has been able to undergo other reactions; these may lead back to starting materials or onward to more stable products, which may include the normal products of substitution, products of further addition, and products of rearrangement.

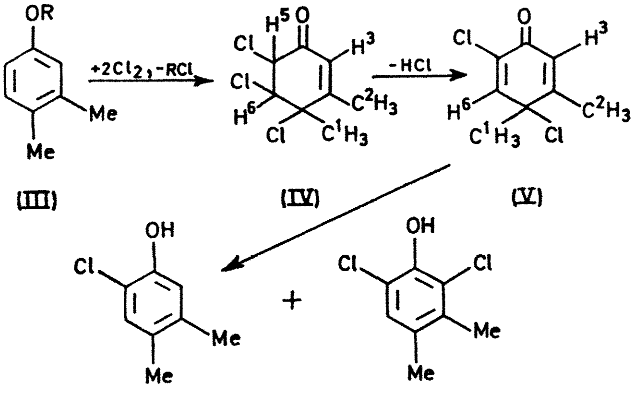


(I)

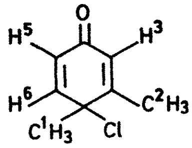


(II)

In an earlier communication[4] we described the bromination of 2,6-dialkylphenyl acetates, in which the orientation of substitution is abnormal in that 4-substituted derivatives rather than the expected 3-substituted analogues are formed. We have now extended these results by studying the chlorination of 3,4-dimethylphenol, of 3,4-dimethylphenyl acetate, and of 3,4-dimethylphenyl methyl ether (III; R = H, Ac, Me, respectively) in acetic acid. The ^{1}H n.m.r. spectrum of the crude product from each of these reactions showed the presence of an enone (IV) ^{1}H n.m.r. (60 MHz, C_6D_6) δ 1·37 (s, C^1H_3), 1·67 [d, $J(C^2H_3,H^3)$ 1·3 Hz, C^2H_3], 4·22 (AB quartet, H^5 and H^6, J_{AB} 11·6 Hz), 5·55 [q, $J(H^3, C^2H^3)$ 1·3 Hz, H^3]. This enone decomposed with loss of hydrogen chloride to form the dichlorodienone (V), which was isolated by chromatography on deactivated alumina, and was identified from its i.r. spectrum (CS_2): 1680 (C=O), 1615 (C=C), 660 cm^{-1} (C–Cl) and from its ^{1}H n.m.r. spectrum ($CDCl_3$), δ 1·82 (s, C^1H_3), 2·27 [d, $J(C^2H_3, H^3)$ 1·3 Hz, C^2H_3], 6·14 [q, J (H^3, C^2H_3) 1·3 Hz, H^3], 7·08 (s, H^6). It decomposes relatively slowly in acetic acid to give the phenols (VI) and (VII); on g.l.c. the course of decomposition is different and only phenol (VI) is formed.



Accompanying (IV) in the product of chlorination of (III; R = H) is a less stable dienone which was obtained only in admixture with more saturated adducts, and from its i.r. spectrum (CS_2) 1665 (C=O), 1630 cm^{-1} (C=C), and ^{1}H n.m.r. spectrum ($CDCl_3$) δ 1·77 (s, C^1H_3), 2·20 [d, $J(C^2H_3, H^3)$ 1·0 Hz, C^2H_3], 6·05 [m, $J(H^5, H^3)$ 2·0, $J(H^5, H^6)$ 10·0, $J(C^2H_3, H^3)$ 1·0 Hz, $\frac{1}{2}H^5 + H^3$], 6·21 [d, $J(H^5, H^3)$ 2·0 $J(H^5, H^6)$ 10·0 Hz, $\frac{1}{2}H^5$], 6·91 [d, $J(H^6, H^5)$ 10·0 Hz, H^6], has the structure (VIII). This adduct is decomposed in acetic acid to give a mixture of (VI) and (III; R = H).



(VIII)

Further components of the reaction mixture include other partly saturated (enone) adducts, apparently a complex mixture of polychlorides and acetoxy-polychlorides.

The formation of (VIII) from (III; R = H) exemplifies the availability of halogen substitution with rearrangement; the sequences giving (V) from (III; R = H, Ac, Me) must all include related steps. The formation of these and other more saturated products shows how ramified the reaction path can become, and indicates that sequences commencing with addition can make significant contributions to the reaction path. We report these results because of current interest in unusual paths for aromatic substitutions, of which a notable example is in the field of nitration in acetic anhydride[5] to give intermediates closely related in structure to those which we have now reported.

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