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COMPETITIVE MODES OF DECOMPOSITION OF 1-HALOGEN-1-ALKYL BENZENONIUM IONS (1a)

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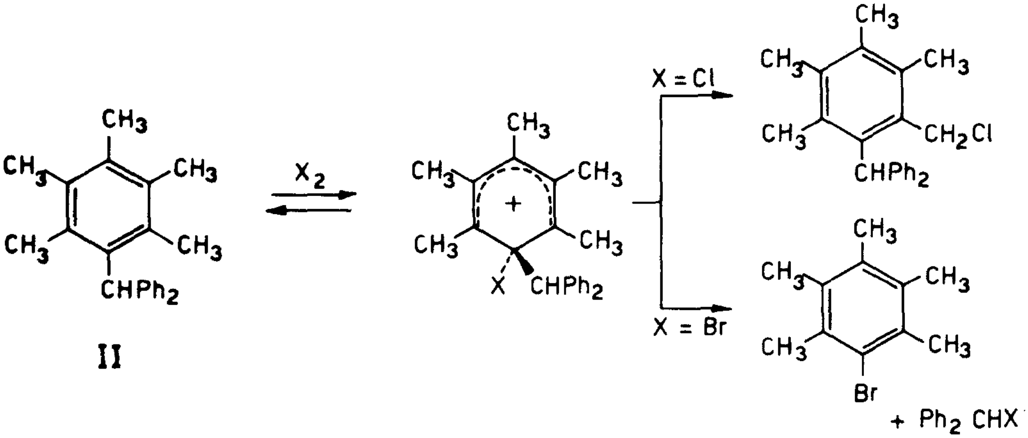
In the electrophilic halogenation of methylbenzenes side-chain substitution is known to compete with nuclear hydrogen replacement more effectively in chlorination than in bromination (2). This is now well understood in view of the discovery (1b) of a substantial shift, relative to chlorination, of the slow step of the electrophilic bromination of hexamethylbenzene toward a rate-limiting decompostion of the intermediate benzenonium ion into side-chain products. The question has been raised (3) whether with an appropriate structure of hexasubstituted benzenes dealkylation can compete with side-chain halogenation reaction. To this end we have examined the aralkyl pentamethylbenzenes, $C_6Me_5CH(OH)Ph$ (I) and $C_6Me_5CHPh_2$ (II). The hydroxybenzyl group is known to be a good leaving group in bromination (4). Thus, on attack of the pentamethylbenzene ring by the electrophile the expected nuclearly substituted product, C_6Me_5Br, is formed together with benzaldehyde. Because of its high carbocation stability, the benzhydryl group (structure II) was also expected to be involved in competitive reactions. Both compounds were chlorinated and brominated in acetic acid solution in the dark. The results we have obtained are wholly consistent with the mechanistic differences between chlorination and bromination referred to above.

When compounds I and II were chlorinated (0.03 M in both reactants) the halogen was found in the side-chain in high yields (93 and 97%, respectively). Thus, despite the presence of a good aralkyl leaving group, the rearrangement of chlorine from nucleus to side-chain, which occurs in a fast step in this reaction, is still predominant.

In contrast, when bromine (0.04 M) was used, a quantitative yield of bromopentamethylbenzene resulted in agreement with the fact that in this case the decomposition of the benzenonium ion into any side-chain products becomes a rate limiting, slow step and is, therefore, completely overshadowed by the faster dealkylation of either the PhCHOH or Ph_2CH group. The two decomposition paths are shown in equation (1), in the case of the benzhydryl derivative.



II

(1)

These competitive modes of decomposition can also be detected within bromination itself. As it was shown in the preceding communication, the rate law in bromination is affected by the mechanistic details, the reaction being second-order in halogen when $k_2[B] \gg k_{-1}K_2[Br_2][Br^-]$, which seems to be the usual case for many nuclear displacements, and first-order in halogen when $k_{-1}K_2[Br_2][Br^-] \gg k_2[B]$, which applies to the side-chain reaction (1c). As the bromine concentration is decreased, the rate of the second-order reaction is expected to decrease more markedly than that of the first-order reaction. Accordingly, a noticeable amount of side-chain product was found at a lower Br_2 concentration (0.01 M).

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