The Reactions of Cerium(iv) Ammonium Nitrate and Cobalt(iii) Acetate with 1,2-Diphenylethanes in Acetic Acid. Evidence against the Involvement of Radical Cations in the Side-chain Oxidation of Alkylbenzenes by Co(OAc)₃

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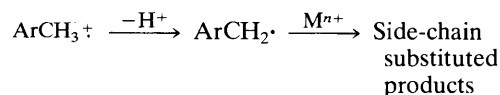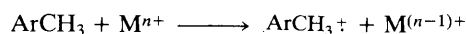
The oxidation of 1,2-diphenylethane and 2,3-dimethyl-2,3-diphenylbutane by cerium(iv) ammonium nitrate and Co(OAc)₃ in acetic acid show that a radical cation mechanism is plausible only in the reaction of the former oxidant.

One-electron oxidants can promote the side-chain oxidation of alkylaromatics by a mechanism involving a radical cation intermediate (Scheme 1). Unambiguous evidence for this mechanism has been found in the reactions of cerium(iv) ammonium nitrate (CAN),[1] silver(ii)[2] and, more recently, 12-tungstocobaltate(iii) ions.[3] The mechanism for the side-chain oxidations of toluene and other methylbenzenes promoted by Co(OAc)₃ is however, not yet defined: the earlier indications in favour of a radical cation mechanism[4] have been questioned by later results that suggest a hydrogen atom transfer process, leading directly to the benzylic free radical [equation (1)].[5]

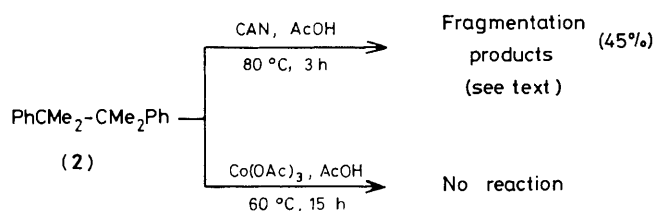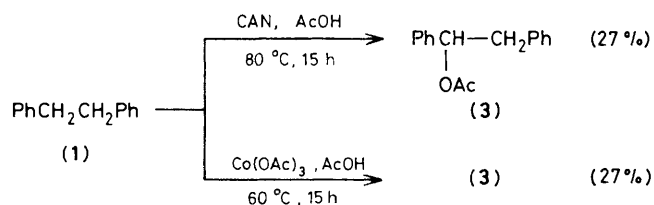$$ArCH_3 + Co^{III} \longrightarrow ArCH_2{\cdot} + H^+ + Co^{II} \quad (1)$$

In this note we report on results concerning the reactions of 1,2-diphenylethane (1) and 2,3-dimethyl-2,3-diphenylbutane (2) with CAN and Co(OAc)₃ in acetic acid that provide evidence against the involvement of radical cations in the reactions of the latter salt.

With (1) in AcOH, CAN and Co(OAc)₃ exhibit similar behaviour forming the side-chain substituted compound (3) as the main reaction product (Scheme 2).†

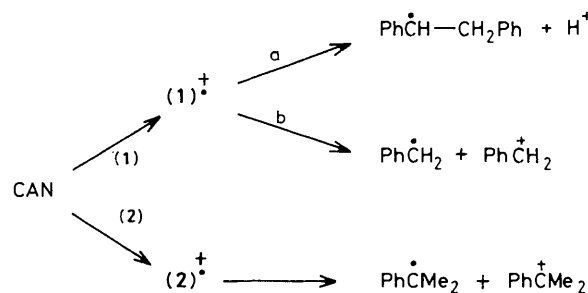$$ArCH_3 + M^{n+} \longrightarrow ArCH_3{\overset{+}{\cdot}} + M^{(n-1)+}$$

$$ArCH_3{\overset{+}{\cdot}} \xrightarrow{-H^+} ArCH_2{\cdot} \xrightarrow{M^{n+}} \text{Side-chain substituted products}$$

Scheme 1

Very small amounts (less than 2%) of benzyl acetate and benzaldehyde were also observed but they were probably derived from the subsequent reaction of (3). However, with (2) as the substrate the two oxidants behave in very different ways (Scheme 2). Whereas CAN reacts with (2) at a significantly faster rate than with (1), leading to fragmentation products (acetophenone, diacetate, and a mixed acetate-nitrate of 2-phenylpropane-1,2-diol†‡), the reverse situation is observed with Co(OAc)₃. More significantly (2) appears completely inert toward Co(OAc)₃ under the reaction conditions where substantial conversion of (1) takes place.

The results for the reaction of (1) and (2) with CAN can be easily explained on the basis of the radical cation mechanism. It is reasonable to assume that with the 1,2-diphenylethane radical cation, loss of the α-proton (Scheme 3, path a) is favoured over fragmentation (Scheme 3, path b).§ In (2) no α-hydrogen is present and hence the observed fragmentation is the only available pathway for the radical cation (Scheme 3).

In contrast, the radical cation mechanism does not fit with the results observed with Co(OAc)₃, being incompatible with the lack of reactivity of (2). These results are interpreted best by a mechanism, like that in equation (1), that involves a direct attack at the side-chain C–H bond.¶[9] Accordingly, side-chain acetoxylation takes place when α-hydrogen atoms are available [substrate (1)], but when these are replaced by methyl groups no reaction occurs.

Scheme 2

Scheme 3

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† Product analysis has been carried out by g.l.c. and n.m.r. comparison with authentic specimens. The concentration of the substrate was 0.021 M, that of the oxidant 0.042 M.

‡ Interestingly, the reaction products obtained with (2) are the same as those obtained in the reaction of either cumene or α-methylstyrene with CAN in acetic acid (unpublished observations from this laboratory). It is therefore likely that the tertiary carbocation from the fragmentation of (2), directly and after oxidation of the benzylic radical formed at the same time (Scheme 3), loses a proton to give α-methylstyrene that undergoes a CAN-induced addition reaction (ref. 6).

§ It is interesting to note that in aqueous acetonitrile, in the presence of 0.6 M HNO₃, 1,2-diphenylethane reacts with CAN to give fragmentation as the only observed reaction (ref. 7). Thus, it would seem that the nature of the solvent can significantly influence the decomposition mode of a radical cation.

¶ Another possibility is an electrophilic attack of cobalt(iii) salts at the C–H bond of the alkylaromatic compound (ref. 8).

It is interesting to note that a similar observation (lack of fragmentation products in the reaction with t-butyladamantane as compared to the extensive fragmentation found in the anodic oxidation of the same substrate) has been used to exclude a radical cation mechanism for the reactions of . cobalt(III) trifluoroacetate with alkanes.[9]

References

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