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THE $E_{RC}1$ REACTION: A RADICAL ANION — RADICAL CHAIN ELIMINATION PROCESS.[1]

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In a previous communication,[2] we reported that the reaction of *p*-nitrobenzylidene dichloride (I) with the 2-nitro-2-propanide ion (II) in dimethyl sulphoxide gives *inter alia*, the monosubstituted compound (III) *via* an $S_{RN}1$ process.[3] The steps involved are given in Scheme 1.

$$\underset{(I)}{ArCHCl_2} + \underset{(II)}{[CMe_2NO_2]^-} \longrightarrow [ArCHCl_2]^{\overline{\bullet}} + \overset{\bullet}{C}Me_2NO_2 \qquad (i)$$

$$[ArCHCl_2]^{\overline{\bullet}} \longrightarrow Ar\overset{\bullet}{C}HCl + Cl^- \qquad (ii)$$

$$Ar\overset{\bullet}{C}HCl + (II) \longrightarrow [ArCH(Cl)CMe_2NO_2]^{\overline{\bullet}} \qquad (iii)$$

$$[ArCH(Cl)CMe_2NO_2]^{\overline{\bullet}} + (I) \longrightarrow \underset{(III)}{ArCH(Cl)CMe_2NO_2} + (I)^{\overline{\bullet}} \qquad (iv)$$

Scheme 1 (Ar = p-$NO_2C_6H_4$)

This reaction was catalysed by light and inhibited by oxygen and *p*-dinitrobenzene as expected for the $S_{RN}1$ process. The radical anion of (I) has been proposed as an intermediate in the reaction of (I) with sodium hydroxide in methanol.[4] Two by-products were formed in the reaction of (I) with (II) and were identified as β,β-dimethyl-*p*-nitrostyrene (IV) and 2,3-dimethyl-2,3-dinitrobutane (V). Furthermore, attempts to improve the yield of (III) to greater than 40 - 50% by either increasing the ratio of (II):(I) or

$$\underset{(IV)}{p\text{-}NO_2C_6H_4CH{:}CMe_2} \qquad \underset{(V)}{Me_2C(NO_2)CMe_2NO_2}$$

by increasing the reaction time gave greater proportions of (IV) and (V). In fact the reaction of the dichloride (I) with three equivalents of the anion (II) gave an 85% yield of the styrene (IV) and an equivalent amount of (V) according to the overall equation

$$\text{(I)} + 3\text{(II)} \longrightarrow \text{(IV)} + \text{(V)} + \mathrm{NO_2^-} + 2\mathrm{Cl^-}$$

In order to elucidate the mechanism of formation of the styrene (IV) the reaction of the monochloro compound (III) with the anion (II) was studied under a variety of conditions. The reaction was found to be catalysed by light. In DMF at 5° the reaction gave (IV) in 96% yield when irradiated by a sunlamp whereas a control reaction "in dark" (reaction vessel wrapped in aluminium foil) had proceeded to only 8%. The reaction was also inhibited by *p*-dinitrobenzene. In DMSO at 20° "in dark", the reaction after 150 min gave the styrene (IV) in 90% and 18% yields respectively in the presence of 0 and 20 mol% of *p*-dinitrobenzene. In view of these and other similar catalytic and inhibition effects we propose the following mechanism (Scheme 2).

$$\mathrm{ArCH(Cl)CMe_2NO_2} + [\mathrm{CMe_2NO_2}]^- \longrightarrow [\mathrm{ArCH(Cl)CMe_2NO_2}]^{-\bullet} + \dot{\mathrm{C}}\mathrm{Me_2NO_2} \qquad \text{(i)}$$

$$[\mathrm{ArCH(Cl)CMe_2NO_2}]^{-\bullet} \xrightarrow{\text{slow}} \mathrm{Ar}\dot{\mathrm{C}}\mathrm{HCMe_2NO_2} + \mathrm{Cl^-} \qquad \text{(ii)}$$

$$\mathrm{Ar}\dot{\mathrm{C}}\mathrm{HCMe_2NO_2} + [\mathrm{CMe_2NO_2}]^- \longrightarrow \mathrm{ArCH{:}CMe_2}\ \text{(IV)} + \dot{\mathrm{C}}\mathrm{Me_2NO_2} + \mathrm{NO_2^-} \qquad \text{(iii)}$$

<u>or</u>

$$\mathrm{Ar}\dot{\mathrm{C}}\mathrm{HCMe_2NO_2} + \mathrm{A}^{-\bullet} \longrightarrow \mathrm{ArCH{:}CMe_2} + \mathrm{NO_2^-} + \mathrm{A} \qquad \text{(iv)}$$

$$\dot{\mathrm{C}}\mathrm{Me_2NO_2} + [\mathrm{CMe_2NO_2}]^- \longrightarrow [\mathrm{Me_2C(NO_2)CMe_2NO_2}]^{-\bullet}\ \ (\equiv \text{(V)}^{-\bullet}) \qquad \text{(v)}$$

$$\text{(V)}^{-\bullet} + \mathrm{ArCH(Cl)CMe_2NO_2} \longrightarrow \text{(V)} + [\mathrm{ArCH(Cl)CMe_2NO_2}]^{-\bullet} \qquad \text{(vi)}$$

Scheme 2 (Ar = *p*-$NO_2C_6H_4$)

The initiation step, (i), is the light catalysed step.[3] The loss of chloride ion from the radical anion in step (iii), normally the slow step in $S_{RN}1$ processes,[3,5] can here be demonstrated to be a relatively slow step. If it were a fast step then the electron transfer process in Scheme 1, step (iv) would not take place in the transformation of (I) to (III) with the result that the styrene (IV) would be the sole or at least major product in the conversion (I) → (III). The ratio of (III)/(IV) in reactions of the dichloride (I) with the salt (II) was *ca.* 8 : 1 in the early stages and steadily decreased as the reaction progressed indicating competition between step (iv), Scheme 1 and step (ii), Scheme 2. This result contrasts strikingly with the report by Bunnett[6] involving the $S_{RN}1$ reaction of dihalobenzenes in which the monosubstituted halobenzene radical anion intermediate preferentially loses a second halide ion before electron transfer takes place. Presumably the greater stability of the nitroaromatic radical anion allows sufficient time for successful competition between electron transfer and loss of chloride ion.

The benzylic radical formed in step (ii) (Scheme 2) accepts an electron from an electron donor which may be the 2-nitro-2-propanide ion (step (iii)) or one of the radical anions ($A^{\overline{\cdot}}$) present in the reaction mixture (step (iv)). This latter process is a chain terminating step and at low radical anion concentrations would be a minor pathway. (The benzyl anion, $Ar\bar{C}HCMe_2NO_2$, may be an intermediate in the loss of nitrite ion and concomitant styrene (IV) formation or the electron transfer and loss of nitrite may be synchronous processes). The step (v) is the well established radical-anion coupling process of aliphatic $S_{RN}1$ reactions[3] and the resultant radical anion, $(V)^{\overline{\cdot}}$, becomes the chain carrier for the chain propagating step (vi). The interruption of chain processes of this sort by *p*-dinitrobenzene and other inhibitors is well established.[3]

Further indirect evidence for the proposed mechanism is the failure of compounds of the type (I), where Ar = phenyl and substituted phenyl groups *without* nitro substituents, to give any trace of styrenes of the type (IV) under the same or more vigorous conditions.

We suggest the term "$E_{RC}1$", standing for *elimination, radical chain, unimolecular* for this process, which is unimolecular in the same sense as S_N1 and $S_{RN}1$.[5]

Other *p*-nitrobenzyl derivatives were found to undergo the $E_{RC}1$ reaction. In DMSO the methanesulphonate (VI; Ar = p-$NO_2C_6H_4$) at 20° in the dark, gave a 64% yield of the styrene (IV) and a 22% yield of the enol methanesulphonate (VII; Ar = p-$NO_2C_6H_4$) after 24 hours.

$ArCH(OSO_2Me)CMe_2NO_2$ (VI)

$ArC(OSO_2Me):CMe_2$ (VII)

At 20°, in the dark, in the presence of 20 mol% of *p*-dinitrobenzene the reaction was incomplete after 7 days and consisted of the starting material (VI), 18%, the styrene (IV), 29%, and the enol methanesulphonate (VII), 37%. The reaction conducted at 20° with sunlamp irradiation gave a 93% yield of the styrene (IV) in 1.5 hours. These results are readily explained by competing E2 and $E_{RC}1$ processes. The methanesulphonates (VI; Ar = Ph, or *p*-$MeO_2CC_6H_4$) under the same conditions gave no styrene products analogous to (IV).

Other nitrobenzylic derivatives, where the α and β substituents are Cl, Br, NO_2 and OSO_2Me are currently under further study.

FOOTNOTES AND REFERENCES

1) This investigation was supported by Grant No. C73/15098 from the Australian Research Grants Committee.

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