Reaction of 4-Nitrobenzyl and 4-Nitrophenyl(phenyl)methyl Halides with Potassium t-Butoxide

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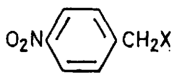
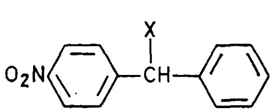
The reactions of 4-nitrobenzyl and 4 nitrophenyl(phenyl)methyl halides with t-butoxide in t-butyl alcohol solution give high yields of 4,4'-dinitrostilbene and 4,4'-dinitrotetraphenylethylene respectively. The initial reaction is the production of the carbanion which subsequently reacts in a first-order reaction. Evidence is presented which supports a radical anion chain mechanism for the reactions both in the presence and the absence of oxygen.

THE reaction of hydroxide ions with 4-nitrobenzyl chloride (Ia) does not give the expected substitution product, 4-nitrobenzyl alcohol. Instead, in the absence of air, high yields of 4,4'-dinitrostilbene are obtained. A number of kinetic studies have been carried out in order to elucidate the mechanism of this anomalous reaction and a wide range of mechanisms have been postulated. These include mechanisms involving carbenes,[1] a bimolecular displacement reaction in competition with a radical anion mechanism,[2] and those that exclude one [3] or all of these.[4]

The present investigation has examined the reactions of 4-nitrobenzyl (I) and 4-nitrophenyl(phenyl)methyl halides (II) with sodium and potassium t-butoxides in t-butyl alcohol. Previous investigations have used sodium hydroxide in dioxan–water mixtures in which the equilibrium concentration of carbanion produced by loss of a benzylic proton would be small compared with the concentration of the starting material. The use of t-butoxide as base ensures that most of the substrate will be present as the carbanion [5] and therefore enables the disappearance of this species to be measured spectrophotometrically at low concentrations. Since these concentrations are much lower than the concentration of dissolved air the effect of oxygen on the reactions can be readily observed. Also, since potassium t-butoxide is known [6] to be capable of donating an electron to nitroaromatic compounds, this study should be able to distinguish between the bimolecular displacement and radical anion mechanisms which a previous study [2] could not. The effect of the second phenyl group has been studied in view of the reports of the large steric and electronic influences of such substituents.[4,7]



(I)



(II)

a; X = Cl
b; X = Br

EXPERIMENTAL

Solvents.—t-Butyl alcohol and preparation of the t-butoxides were as previously described.[5]

t-Butyl [^{2}H]*alcohol*. t-Butyl borate, prepared by refluxing t-butyl alcohol with boric acid and benzene to remove water azeotropically,[8] was hydrolysed with excess of deuterium oxide. Distillation of the product gave an azeotrope which was initially dried with calcium hydride and finally distilled from potassium. The product, analysed by n.m.r., contained 97% t-butyl [^{2}H]alcohol.

Materials.—Commercial 4-nitrobenzyl chloride and bromide were recrystallised from ethanol, chloride m.p. 72—73 °C (lit.,[9] 72 °C), bromide 99—100 °C (lit.,[10] 99—100 °C).

4-*Nitrobenzyl fluoride*. Benzyl fluoride was reacted [11] with concentrated nitric acid in acetic anhydride for 2 h. Separation of the products on a silica gel column gave 4-nitrobenzyl fluoride, m.p. 38 °C (lit.,[11] 38.5 °C).

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[10] N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Amer. Chem. Soc.*, 1955, **77**, 6269.

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4-Nitrophenyl(phenyl)methyl chloride. This was prepared by the reaction of the alcohol with thionyl chloride in methylene chloride. Recrystallisation of the product from light petroleum (b.p. 40—60 °C) gave the crystalline product, m.p. 43 °C (lit.,[12] 43 °C).

4-Nitrophenyl(phenyl)methyl bromide. This was prepared by passing dry hydrogen bromide through a solution of the alcohol in dry benzene. Removal of the solvent and recrystallisation from light petroleum (b.p. 40—60 °C) gave the bromide, m.p. 74 °C (lit.,[12] 73—74 °C).

Effect of Bases.—Solutions of 4-nitrophenyl(phenyl)-methyl chloride and bromide in t-butyl alcohol were kept under nitrogen with potassium t-butoxide for 24 h at 55 °C. After this period the red colour initially produced had faded. The yellow-brown precipitate obtained on dilution with water was shown to be essentially one compound by t.l.c. After recrystallisation from benzene–light petroleum, the product had m.p. 199 °C, $\lambda_{max.}$ 360 and 265 nm and an n.m.r. spectrum consistent with 4,4′-dinitrotetraphenylethylene. The yields of crude material were >95% of the theoretical yield. In the presence of oxygen no ethylene was observed in the products which was mainly 4-nitrobenzophenone.

Under similar conditions 4-nitrobenzyl chloride and bromide gave yields of 4,4′-dinitrostilbene of >90% of the theoretical yield.

TABLE 1

Effect of base concentration on rate of disappearance of 4-nitrobenzyl chloride carbanion in the absence of oxygen at 29.9 °C

10^5[(Ia)]/M	10^2[KOBu^t]/M	10^2k/s^{-1}
1.18	0.88	2.72
1.18	1.32	2.88
26.4	1.65	2.92
2.94	2.19	2.85
10.6	3.3	2.87
26.4	12.5	2.75
		mean 2.84 × 10^{-2} s^{-1}

TABLE 2

Mean rate constants for the disappearance of 4-nitrobenzyl halide carbanions at 29.9 °C

Halide	Atmosphere	Solvent	No. of determinations	10^2k/s^{-1}
Chloride	Nitrogen	Bu^{t}OH	9	2.8 ± 0.08
Chloride	Air	Bu^{t}OH	6	0.56 ± 0.02
Chloride	Oxygen	Bu^{t}OH	6	1.41 ± 0.03
Bromide	Air	Bu^{t}OH	6	0.75 ± 0.05
Bromide	Nitrogen	Bu^{t}OH	7	9.0 ± 0.23
Bromide	Nitrogen	Bu^{t}OD	4	8.6 ± 0.18

TABLE 3

Mean rate constants for the disappearance of 4-nitrophenyl(phenyl)methyl halide carbanions at 56.5 °C

Halide	Base	Atmosphere	Solvent	No. of determinations	10^5k/s^{-1}
Chloride	KOBu^t	N_2	Bu^{t}OH	6	8.7 ± 0.33
Chloride	NaOBu^t	N_2	Bu^{t}OH	9	8.4 ± 0.13
Chloride	NaOBu^t	N_2	Bu^{t}OD	7	7.8 ± 0.30
Chloride	NaOBu^t	Air	Bu^{t}OH	7	7.8 ± 0.72
Bromide	NaOBu^t	N_2	Bu^{t}OH	7	9.5 ± 0.29

Kinetic Studies.—In all cases the rate of carbanion formation was faster than its rate of disappearance. The latter was determined using a Unicam SP 500 spectrophotometer at the wavelength of maximum absorption of the carbanion. Special cells [13] which enabled the reactants to be deoxygenated and thermostatted in the cell holder of the instrument before mixing were used. For the reactions with air and oxygen saturated solutions were obtained by bubbling the gas through the solutions for 30 min prior to mixing. All of the runs gave good linear first-order plots and the rate constants summarised in Tables 2 and 3 were calculated from these graphs.

RESULTS AND DISCUSSION

At high base concentrations all the compounds studied were virtually completely converted into the equilibrium concentration of their carbanions within 1 min of mixing. The rate of proton removal from (I) at low base concentrations (<10^{-2}M) was however slow enough to interfere slightly with the initial rate of disappearance of carbanion. Table 1 shows the values of the first-order rate constants obtained for the disappearance of the carbanion of (Ia) in the absence of oxygen. The zero-order dependence of the rate constant on base concentration is a characteristic of all the compounds (I) and (II) both in the presence and absence of oxygen. The production of stilbene is therefore first order in carbanion only.

$$\mathrm{ArCH_2X + Bu^tO^- \rightleftharpoons ArCHX^- + Bu^tOH}$$

The order of the reaction eliminates the possibility that the mechanism involves bimolecular displacement of the halide ion by the carbanion (Scheme 1) and also electron transfer from carbanion to unionised starting material (Scheme 2) if these reactions are rate determining as these would be second order in carbanion. It does not exclude the possibility that reprotonation of the carbanion is the rate-determining step in these reactions. The small solvent isotope effects observed (Tables 2 and 3) for both systems [1.08 for (Ia), 1.05 for (IIb)] do however eliminate this possibility as a substantial isotope effect would be expected for this reaction.

$$\mathrm{Bu^tOH + ArCHX^- \rightleftharpoons ArCH_2X + Bu^tO^-}$$
$$\mathrm{ArCHX^- + ArCH_2X \longrightarrow ArCHX\text{-}CH_2Ar + X^- + X^-}$$
$$\mathrm{ArCHX\text{-}CH_2Ar + Bu^tO^- \longrightarrow ArCH{=}CHAr + Bu^tOH + X^-}$$

SCHEME 1

$$\mathrm{Bu^tOH + ArCHX^- \rightleftharpoons ArCH_2X + Bu^tO^-}$$
$$\mathrm{ArCHX^- + ArCH_2X \longrightarrow ArCH_2X^{-\cdot} + ArCHX\cdot}$$
$$\mathrm{ArCH_2X^{-\cdot} \longrightarrow ArCH_2\cdot + X^-}$$
$$\mathrm{ArCH_2\cdot + ArCHX\cdot \longrightarrow ArCH_2\text{-}CHXAr}$$
$$\mathrm{ArCHX\text{-}CH_2Ar + Bu^tO^- \longrightarrow ArCH{=}CHAr + Bu^tOH + X^-}$$

SCHEME 2

The effect of changing the leaving group from chloride to bromide is much smaller than that expected from a mechanism in which the carbon–halogen bond is broken in the rate-determining step to give a carbene. The values observed for the bromide : chloride ratio [(I) = 3.1, (II) = 1.1] are far removed from the typical value

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[13] D. Bethell and R. J. E. Talbot, *J. Chem. Soc.* (*B*), 1968, 638.

of 50 given by Streitwieser.[14] A ratio of this order has been observed [15,16] in an intramolecular displacement reaction involving a carbanion although values much lower than this have been observed in similar reactions.[17] A carbene is an unlikely intermediate in this reaction as it would have to react with the carbanion to give the required product. Since the latter is present in low concentrations the most prominent reaction of an aromatic carbene would be to react with solvent or added alkene.[18] Previous attempts to trap the carbene with alkenes have also failed.

In view of the low dissociation constants of carbanion–alkali metal ion pairs [19] it is possible that dissociation of an ion pair could be the rate-determining step in the production of stilbene. This would account for the order of reaction, low bromide : chloride ratio, and solvent isotope effect. However Table 3 also shows that the rate is unaffected by the change from sodium to potassium t-butoxide and therefore a change in counter ion. This would not be expected if ion pair dissociation is important. Similarly the concentration of base has no effect on the rate of reaction of the carbanion both in the presence and absence of oxygen in contrast with previous observations.[19] Lastly such a mechanism could not account for the large decrease in the rate of disappearance of carbanion in the presence of air for (Ia) but a large increase in rate for (IIa).

One mechanism that can account for all of these observations is a chain reaction in which radical anions act as the chain carrier (Scheme 3). Radical anions are known to be produced by electron transfer from t-butoxide ions to 4-nitrotoluene. Also radical anions derived from (Ia and b) have been observed by polarography [20] and were shown to decompose rapidly to give the benzylic radical. Such radicals are stable enough not to react with solvent but they will react rapidly with carbanions [21] to produce radical anions. The chain is completed by electron transfer from this radical anion to another molecule of starting material. The slowest step in the propagation cycle is the loss of halide from radical anion and the rate for this step is $k[\mathrm{ArCH_2X^{-\cdot}}]$. The overall rate for this chain reaction will therefore depend on the radical anion concentration. If the initiation step is slow then it will control the radical anion concentration and hence the rate of disappearance of carbanion. This will lead to an overall first-order dependence on carbanion concentration. The rate will then be proportional to the concentration of unionised starting material which largely explains the slow reaction of (II) by comparison with (I) as a result of the low equilibrium concentration of (II). Since this equilibrium is rapidly established the lack of a solvent isotope effect is not surprising. The slowest reaction in the chain is probably loss of halide ion from the radical anion [rate constants (Ia) 10 $\mathrm{s^{-1}}$, (Ib) $>100\ \mathrm{s^{-1}}$] [14] which is at least 100 times faster than the observed rate thus reinforcing the proposal that initial radical anion formation is rate determining. The chain mechanism proposed in Scheme 3 is preferred to the alternative mechanism, proposed by Closs and Goh [2] in which two benzylic radicals combine. This is because the low concentration of radicals present in comparison with the concentration of carbanion favours reaction of radicals with the latter as the rate constants are similar. E.s.r. measurements on concentrated solutions of (I) and (II) in t-butyl alcohol and potassium t-butoxide in the absence of oxygen did not show the presence of any paramagnetic species. This could be due to the very low concentration of radicals present, a concentration of 10^{-9}M being sufficient to account for the observed rate of (II). The radicals previously observed [2] in this system are probably due to reactions involving oxygen. In order to determine whether radical anions could be produced and detected in this system 4-nitrobenzyl fluoride was subjected to the same conditions. It has already been shown [20] that the rate of loss of fluoride ion from the radical anion is 1 000 times slower than the loss of chloride. The increased stability of the radical anion should increase its concentration and allow it to be detected. It was observed that the initial yellow colour, due to the carbanion, rapidly changed to an intense purple. The e.s.r. spectrum of this solution consisted of an intense broad singlet. Immediate quenching of the purple solution with hydrochloric acid gave a quantitative yield of starting material. The purple colour faded very slowly in basic solution and some stilbene was found in the reaction mixture after two weeks at 30 °C.

Initiation

$$\mathrm{ArCH_2X + Bu^tO^-} \xrightarrow{\text{slow}} \mathrm{ArCH_2X^{-\cdot} + Bu^tO\cdot}$$

Propagation

$$\mathrm{ArCH_2X^{-\cdot}} \longrightarrow \mathrm{ArCH_2\cdot + X^-}$$

$$\mathrm{ArCH_2\cdot + ArCHX^-} \longrightarrow \mathrm{ArCH_2CHXAr^{-\cdot}}$$

$$\mathrm{ArCH_2CHXAr^{-\cdot} + ArCH_2X} \rightleftharpoons \mathrm{ArCH_2X^{-\cdot} + ArCH_2CHXAr}$$

$$\mathrm{ArCH_2CHXAr + Bu^tO^-} \longrightarrow \mathrm{ArCH{=}CHAr + Bu^tOH + X^-}$$

SCHEME 3

The dependence of the rates of disappearance of carbanion on oxygen concentration also support a radical anion chain mechanism. For the benzyl halides (I) the reaction is slower under air than under nitrogen while for the diphenyl halides (II) reaction under air is much faster than under nitrogen. In the latter case production of radical anion would be hindered by the low equilibrium concentration of (II) and the reaction of carbanion with

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[14] A. Streitwieser, *Chem. Rev.*, 1956, **56**, 571.

[15] A. C. Knipe and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1968, 67.

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[19] D. Bethell, R. J. E. Talbot, and R. G. Wilkinson, *Chem. Comm.*, 1968, 1528.

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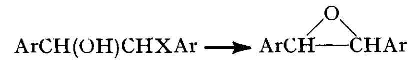
[21] R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Amer. Chem. Soc.*, 1965, **87**, 4520; G. A. Russell and W. C. Danen, *ibid.*, 1968, **90**, 347.

oxygen would predominate over radical anion formation. As a result of the faster rate of stilbene formation in (I) this rate is similar in magnitude to that of the reaction of the carbanion with oxygen. This is supported by the products of reaction in the presence of air, (II) gives no stilbene while (Ia) gives [22] 25%. Thus when oxygen is present there will be competition between oxygen and carbanion for the benzylic radical and if the oxygen concentration is high enough all of the radicals will be removed and the chain length will be reduced to unity (Scheme 4). The higher rate of reaction of (I) with air in comparison with (II) reflects the increased stability of the carbanion derived from (II).

$$\mathrm{ArCHX^- + O_2 \longrightarrow ArCHX\cdot + O_2\cdot}$$
$$\mathrm{ArCHX\cdot + ArCHX^- \longrightarrow ArCHXCHXAr^{-\cdot}}$$
$$\mathrm{ArCHXCHXAr^{-\cdot} \dashrightarrow ArC{\equiv}CAr}$$
$$\mathrm{ArCHX\cdot + O_2^{-\cdot} \longrightarrow ArCHXOO^-}$$
$$\mathrm{ArCHXOO^- \longrightarrow ArCHO + OX^-}$$
$$\mathrm{ArCHO + ArCHX^- \longrightarrow ArCH(OH)CHXAr}$$

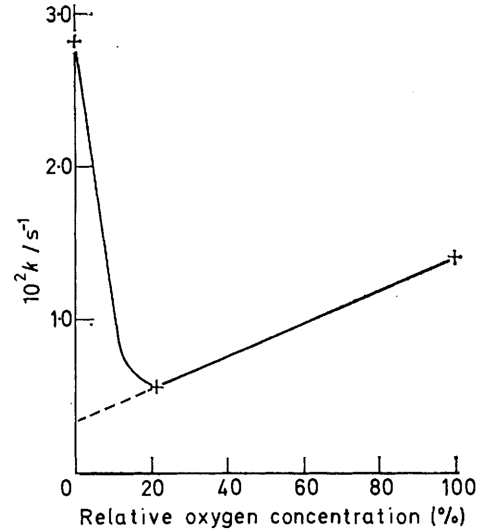


$$\mathrm{ArCH(OH)CHXAr \longrightarrow ArCH\overset{O}{—}CHAr}$$

SCHEME 4

The rate of disappearance of carbanion is then reduced to the rate of radical anion production plus the rate of the direct reaction of carbanion with oxygen. The Figure shows the rates of disappearance of carbanion in Table 2 plotted as a function of oxygen concentration. In the absence of oxygen the high rate is due to the chain reaction. At high relative oxygen concentrations the rate is essentially the reaction of the carbanion with oxygen. Extrapolation of the rates obtained in the presence of oxygen to zero oxygen concentration gives an estimate for the maximum value of the rate of radical anion production of 3×10^{-3} s^{-1}. Since some stilbene is produced from the reaction with air at spectroscopic concentrations (10^{-5}M) the actual rate will be less than this value. This also explains earlier observations [1,7] that the reaction rate was independent of oxygen concentration. At the high concentrations of (I) used (10^{-2}M) oxygen would be unable to compete successfully for the radicals.

Conclusions.—The radical anion chain mechanism for the reaction of (I) and (II) with t-butoxide in t-butyl alcohol can account for all the observations made in the present study. A similar mechanism can also explain previous results for the production of 4,4′-dinitrostilbene in dioxan–water mixtures.[23] Minor products such as bis-(4-nitrophenyl)acetylene and 4,4′-dinitrostilbene oxide probably result from the side reaction involving electron transfer from the carbanion to oxygen. The radical produced can either react with carbanion to give ultimately the acetylene or with oxygen to give the stilbene oxide *via* 4-nitrobenzaldehyde (Scheme 4). It is even possible that the radical chain mechanism might be initiated by the reaction with oxygen. This would account for the increase in rate in the presence of oxygen observed by Closs and Goh.[2] At the high concentrations of (I) used the oxygen (*ca.* 10^{-3}M) present in the solution would be rapidly used up and this could be the explanation of the departure of their kinetics from pseudo-first-order behaviour. It would certainly agree with the observed change in overall order from third to second as the initiation step would then be first order in (I), hydroxide, and oxygen. In any case the hydroxide ion is not such a good electron donor as the t-butoxide ion and it is therefore likely that, in the absence of oxygen, the radical anion mechanism has to compete with the bimolecular displacement mechanism.



Rate of carbanion disappearance as a function of the oxygen content of the atmosphere above it

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