Electron-transfer *versus* Nucleophilic Substitution in the Reactions of α-Halogenated 4-Nitrotoluenes with Base[1]

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A comparative study of the reactions of 4-nitrobenzyl and 4-nitrobenzylidene halides (ArCHXY; Ar = $4\text{-}NO_2C_6H_4^-$; X = H or Halogen; Y = Halogen) with alkali shows that the reaction is sensitive to the nature of the side chain halogen substituent(s) as well as the reaction conditions. In alcoholic alkali, only 4-nitrobenzyl chloride ($ArCH_2Cl$) reacts smoothly *via* the electron transfer (ET)-radical pathway to give mainly dimeric products while the corresponding bromide ($ArCH_2Br$) and iodide ($ArCH_2I$) give exclusively S_N products. The ET pathway is enhanced for these substrates by the application of phase-transfer catalysis. In the case of the 4-nitrobenzylidene dihalides (ArCHXY; X = Y = Cl; X = Cl, Y = Br; X = Y = Br; X = F, Y = Br) it is also shown that although progressive bromine substitution suppresses the ET pathway, application of phase-transfer catalysis minimises competing solvolytic reactions and enhances the radical reaction.

There has been recent increasing interest in electron-transfer processes in organic chemistry. One class of reactions that has attracted considerable attention are substitution reactions previously considered to be polar in nature but for which alternative electron-transfer (ET) pathways have been proposed.[2–7] The rapidly lengthening list of such reactions has spawned an ensuing debate centering on the so-called Polar–ET dichotomy that has been intense and at times controversial.[8] A well established ET mechanism is $S_{RN}1$ (Kornblum,[9] Russell,[10] Bunnett[11]), in which a product of net substitution is obtained *via* a radical-chain mechanism involving as the key step, transfer or photoinjection of an electron into a π-acceptor substituent or orbital of the substrate. We have been interested in the reactivity of nitrobenzylic derivatives, in particular their reactions in basic media. We have previously shown *via* kinetic studies that the reactions of 4-nitrobenzyl- as well as 4-nitrobenzylidene chlorides with hydroxide ion to yield mainly dimeric products proceed *via* a mechanism involving ET as the rate-determining step and not through alternative α-elimination or S_N2 pathways (Scheme 1).[12,13] The key intermediates in the proposed mechanism (a variant of the Kornblum mechanism) are the anion-radicals formed by electron-capture in the rate-determining step. We have also probed the effect of additional ring substituents on the reaction pathway and have found that the nature of the ring substituents can markedly influence the course of the reaction, chlorine substituents enhancing the ET reaction whereas methyl substituents divert the reaction towards solvolysis.[14] We have now extended the study to encompass a wide range of side chain halogen derivatives and the results are now reported.

$$\mathrm{ArCHXY + OH^- \underset{slow}{\overset{fast}{\rightleftharpoons}} Ar\bar{C}XY + H_2O} \qquad (1)$$

$$\mathrm{Ar\bar{C}XY + ArCHXY \longrightarrow Ar\dot{C}XY + ArCHXY^{\bullet -}} \qquad (2)$$

$$\mathrm{ArCHXY^{\bullet -} \longrightarrow Ar\dot{C}HX + Y^-} \qquad (3)$$

$$\mathrm{Ar\dot{C}XY + Ar\dot{C}HX \longrightarrow \xrightarrow{OH^-} (\mathit{E}\ and\ \mathit{Z})\text{-}ArCX{=}CXAr} \qquad (4)$$

$$\mathrm{2Ar\dot{C}XY \longrightarrow (ArCXY)_2} \qquad (5)$$

$$\mathrm{2Ar\dot{C}HX \longrightarrow \xrightarrow{OH^-} ArC{\equiv}CAr} \qquad (6)$$

$$\mathrm{Ar\dot{C}HX + ArCHXY \longrightarrow ArCH_2X + Ar\dot{C}XY} \qquad (7)$$

$$\mathrm{ArCH_2X \xrightarrow{ROH} ArCH_2OR} \qquad (8)$$

$$\mathrm{ArCH_2X + ArCH_2OH \longrightarrow ArCH_2OCH_2Ar} \qquad (9)$$

$$\mathrm{Ar = 4\text{-}NO_2\text{–}C_6H_4\text{-}}$$

Scheme 1

Results and Discussion

The reactions of the various nitrobenzylic compounds with hydroxide ion under various conditions were carried out and the results are shown in Table 1. Essentially these reactions gave dimeric products and although some minor differences are noted the general similarity of the products is indicative of a common mechanistic pathway *viz.*, one involving carbanion formation, electron-transfer, and subsequent reactions of the resulting radicals (Scheme 1).

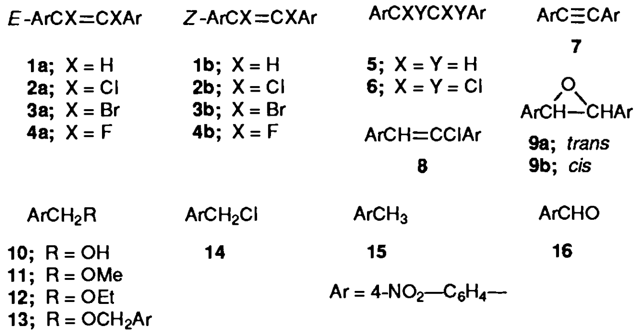
Nevertheless these reactions are sensitive to the nature of the side chain halogen substituents as well as the reaction conditions. In the case of the monohalogenated compounds (4-nitrobenzyl halide series), only the reaction of 4-nitrobenzyl chloride ($ArCH_2Cl$) proceeded smoothly with hydroxide ion in ethanol to furnish mainly dimeric products (**1a**, **1b**, **5**, **7**) *via* the ET pathway whereas in contrast, both 4-nitrobenzyl bromide ($ArCH_2Br$) and 4-nitrobenzyl iodide ($ArCH_2I$) not unexpectedly, reacted with hydroxide ion in ethanol to give the solvolysis product (4-nitrobenzyl ethyl ether, **12**) in quantitative yield. Similar behaviour for the bromide and iodide has been noted previously.[13a] In view of the susceptibility of these more labile halides to nucleophilic attack by the solvent, we reasoned that reactions conducted in two-phase media with phase-transfer catalysis might reduce the competing solvolytic component and allow the ET reaction to proceed. This indeed turned out to be the case. Under these conditions, the reaction of the bromide furnished up to 60% yield of ET derived dimeric products (**1a**, **1b**, **5**, **7**), the other products being bis(4-nitrobenzyl) ether (**13**, 13%) and 4,4′-dinitrostilbene oxide (**9a** and **9b**, 11%). Even the otherwise extremely labile iodide afforded about 41% yield of dimeric products (**1a**, **1b**) while the yields of the dibenzyl ether (**13**) and stilbene oxides (**9a** and **9b**) have increased to 23 and 17% respectively.

The dibenzyl ether **13** is derived from the initial solvolytic product, 4-nitrobenzyl alcohol (**10**). The origin of the stilbene epoxides (**9a** and **9b**) in reactions carried out under nitrogen is

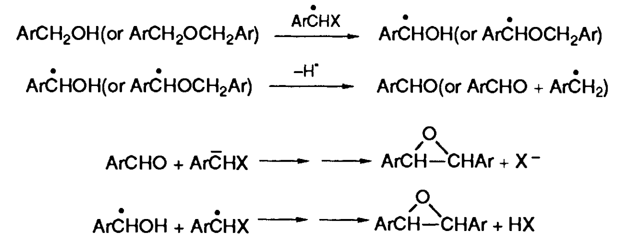
Table 1 Distribution of products in the reaction of 4-nitrobenzyl and 4-nitrobenzylidene halides (ArCHXY) with alkali under various conditions[a]

Substrate (ArCHXY)	Products (%)[b] OH$^-$/EtOH or MeOH[c]	Phase-transfer catalysis
ArCH$_2$Cl[d]	**1a** (61), **1b** (5), **5** (2) **7** (10), **12** (2)	
ArCH$_2$Br	**12** (90)	**1a** (34), **1b** (13), **5** (2), **7** (10), **9a** (4), **9b** (7), **13** (13)
ArCH$_2$I	**12** (99)	**1a** (18), **1b** (23), **9a** (2), **9b** (15), **13** (23)
ArCH$_2$F	*e*	*e*
ArCHCl$_2$		
(a) 95% MeOH:	**2a** (22), **2b** (16), **6** (34), **7** (12), **11** (9), **14** (3)	
(b) 90% EtOH:	**2a** (18), **2b** (12), **6** (34), **7** (8), **8** (10), *f*	
ArCHClBr	**2a** (31), **2b** (30), **7** (34), **14** (1)	
ArCHBr$_2$	**3a** (17), **3b** (13), **7** (16), **12** (12)	**3a** (25), **3b** (24), **7** (28)
ArCHFBr	**16** (90)	**4a** (27), **4b** (25), *g*

[a] All reactions were carried out under nitrogen to 90–99% completion. [b] Yields were based on ArCHXY. [c] Unless otherwise stated, reactions were carried out in EtOH. [d] Reaction carried out in 90% EtOH. [e] Extremely unreactive. [f] **1b** also detected. [g] Other minor products also isolated but were not characterised.



less clear and has remained a puzzling aspect of the reactivity of these derivatives in basic media.[13b,15] The formation of the epoxides has been attributed to the known rapid reaction between 4-nitrobenzaldehyde and 4-nitrobenzyl carbanion.[16] However the origin of the intermediate aldehyde has remained unclear. In the present study it can be seen that epoxide formation is invariably accompanied by that of bis(4-nitrobenzyl) ether. On going from 4-nitrobenzyl bromide to 4-nitrobenzyl iodide the increase in the proportion of the epoxides is accompanied by a corresponding increase in the proportion of the bibenzyl ether which is in turn derived from the alcohol. This result coupled with the earlier observation that added 4-nitrobenzyl alcohol increases the yield of the epoxide in the similar reaction of the related 4-nitrobenzyl sulfonium derivative[13b] suggest that a likely precursor of the epoxide is 4-nitrobenzyl alcohol. The epoxide could be formed either *via* the intermediate aldehyde derived homolytically from the alcohol or the dibenzyl ether or alternatively *via* cross coupling of the benzyl radical derived from 4-nitrobenzyl alcohol and the radical $\mathrm{Ar\dot{C}HX}$ followed by elimination of HX (Scheme 2).



Scheme 2

In any case, we have shown that for the reactions of the monohalogenated compounds with hydroxide ion in ethanol, ET reactions proceed smoothly only in the case of the chloride, while for the bromide and iodide the competing S_N2 pathway predominates to the virtual exclusion of the radical reaction. In these cases, the ET reaction is enhanced at the expense of the solvolysis component when the reaction is carried out under phase-transfer catalysis. The fluoride is notably anomalous being virtually inert both in ethanol as well as in a two-phase medium. The reactions of a series of 4-nitrobenzylidene dihalides were also investigated and the results are shown in Table 1. It can be seen that for the dihalogenated derivatives, on going from ArCHCl$_2$ to ArCHClBr, substitution by the larger bromine atom does not markedly change the nature of the products, dimeric products still predominate although the rate of reaction has decreased (the relative reactivity of ArCHCl$_2$, ArCHClBr, ArCHBr$_2$ in ethanol is in the order: ArCHCl$_2$ > ArCHClBr > ArCHBr$_2$). The nature of the products for the reaction of ArCHClBr clearly shows that bromide ion is preferentially lost from the radical anion $\mathrm{ArCHClBr}^{\bullet -}$ (step 3, Scheme 1) although EPR studies at low temperature indicate that loss of chloride ion also occurs to some extent (see following paper). The products also indicate preferential elimination of HBr over HCl from the intermediate compound ArCHClCClBrAr (step 4, Scheme 1) which is not unexpected based on bond strength considerations. Further bromine substitution however (as in ArCHBr$_2$) produced a more marked effect, decreasing further the reactivity as well as the proportion of radical derived products. The reduced reactivity of ArCHBr$_2$ is less likely to be a result of steric hindrance to electron transfer since this would be expected to occur at the unhindered nitroaromatic face of the reactants. A possible cause of the effect of bromine substitution on the reactivity of ArCHBr$_2$ could be due to the increase in the reduction potential caused by the reduced electronegativity of bromine. As before, application of phase transfer catalysis has a beneficial effect on the ET-radical reaction; the same reaction carried out in a two-phase medium in the presence of a phase transfer catalyst raises the yield of the dimeric products from about 50 to *ca.* 90%. A noteworthy feature of the reaction of the dihalogenated derivatives is the formation of 4-nitrobenzyl halide (ArCH$_2$X) or its solvolysis derivative (ArCH$_2$OR) which is accounted for as arising from hydrogen donation of ArCHXY to the radical $\mathrm{Ar\dot{C}HX}$ (step 7, Scheme 1).[12,14] Although the products are essentially similar when comparing the reaction of ArCHCl$_2$, ArCHClBr and ArCHBr$_2$, one notable difference is the absence of the tetrahalogenated dimer (ArCXYCXYAr) for the reaction of ArCHClBr and ArCHBr$_2$. This result is not new and has been observed previously in the reactions of nuclear substituted derivatives.[14] For example whereas the reaction of 3-chloro-4-nitrobenzylidene dichloride furnishes the tetrachloroethane dimer Ar′CCl$_2$CCl$_2$Ar′, similar reaction of the 2-chloro-4-nitro-derivative does not. One possible reason could be that in these reactions the dimer has undergone further reaction such as hydrolysis or reduction; alternatively since the tetrahalogenated dimer is not detected for substrates in which either the ring has *ortho* substitution or where the benzylic halogen is one or more bromine, the highly substituted dimer is probably not formed due to steric reasons. In the case of the α-fluoro-α-bromo derivative (ArCHFBr) the dichotomous behaviour under

Table 2

ArCHXY	Yield (%)	M.p. (°C)	δ(C*H*XY)
$ArCH_2F$	72	38 (lit.,[19] 37.5–38)	5.51 (d, *J* 47)[a]
$ArCH_2I$	66	128–130 (lit.,[20] 127–128)	4.48[a]
$ArCHCl_2$	76	42 (lit.,[12] 46)	6.70[b]
$ArCHBr_2$	60	80–81 (lit.,[21] 82)	6.67[a]
ArCHClBr	97	54–55 (lit.,[21] 53)	6.72[b]
ArCHFBr	90	*c*, *d*	7.4 (d, *J* 48.7)[a]

[a] $CDCl_3$ solutions. [b] CCl_4 solutions. [c] B.p. 110–112° at 5 mmHg. [d] EIMS, *m*/*z* 154 (M^+ – Br, 100%).

different reactions was even more pronounced. The α-fluoro-α-bromo compound was extremely susceptible to solvolysis and its reaction in alcoholic base gave exclusively S_N products in quantitative yield while reaction in a two-phase medium results in the isolation of up to *ca.* 50% of radical derived dimeric products. In conclusion the present results have provided a clearer overall picture for these reactions with respect to the way in which changes in structural features of the substrates and the reaction conditions affect the reactivity and have also demonstrated the utility of phase transfer catalysis in enhancing the ET or radical pathway. We have also carried out EPR studies (see following paper) to probe the electron transfer step and have shown that the various 4-nitrobenzyl and 4-nitrobenzylidene halides can capture electrons to form anion radicals which subsequently dissociate to the corresponding radicals.

Experimental

General.—Melting points were determined on a Leitz Wetzler melting apparatus and were uncorrected. ^1H NMR spectra were recorded on a Hitachi–Perkin-Elmer R 20B instrument at 60 MHz or a JEOL FX 100 spectrometer at 100 MHz in CCl_4 or $CDCl_3$ solutions with Me_4Si as internal standard. Mass spectra were obtained on an AEI MS 3074 spectrometer. Solvents were deoxygenated by boiling under nitrogen and transfers of solutions were by syringes. All reactions were carried out in deoxygenated vessels under nitrogen. Product mixtures were separated by column chromatography over silica gel or Florisil. The column was eluted with light petroleum (b.p. 60–80 °C), toluene, chloroform and finally methanol. Fractions eluted were examined by TLC and by NMR spectroscopy. Further resolution of partially separated mixtures of dimeric products was achieved by repeated fractional crystallisation. The product yields were estimated by a combination of weighing and by NMR spectroscopy. *J*-Values are given in Hz.

Materials.—4-Nitrobenzyl chloride and 4-nitrobenzyl bromide were commercial samples and were recrystallised before use. 4-Nitrobenzyl fluoride was prepared from the reaction of 4-nitrobenzyl bromide and anhydrous KF in benzene in the presence of 18-Crown-6.[17] 4-Nitrobenzyl iodide was prepared from 4-nitrobenzyl alcohol and trimethylsilyl iodide.[18] 4-Nitrobenzylidene dichloride was prepared from 4-nitrobenzaldehyde as described previously.[12] 4-Nitrobenzylidene dibromide, α-bromo-α-chloro-4-nitrotoluene and α-bromo-α-fluoro-4-nitrotoluene were prepared by standard free radical bromination of 4-nitrobenzyl bromide, 4-nitrobenzyl chloride and 4-nitrobenzyl fluoride respectively. The preparation of the compounds are summarised in Table 2.

Reactions of ArCHXY *with Hydroxide Ion.—General Procedure.* The procedure is illustrated by the reaction of 4-nitrobenzylidene dibromide. 4-Nitrobenzylidene dibromide (0.354 g, 1.2 mmol) was dissolved in deoxygenated ethanol (10.88 cm^3) under nitrogen. Potassium hydroxide (1.12 cm^3, 3.2 mol dm^{-3}) in ethanol was added and the reaction mixture was kept at *ca.* 28 °C for 150 min (95% conversion). The reaction mixture was acidified by concentrated hydrochloric acid and cooled in ice. The precipitated products were filtered off on a sintered funnel and washed with cold water. Extraction of the filtrate with chloroform afforded a further crop of products. Chromatography of the product mixture as described above followed by crystallisation gave **3a**, **3b**, **7** and **12**. The same reaction was carried out in a two-phase medium as follows. 4-Nitrobenzylidene dibromide (0.360 g, 1.2 mmol) and a catalytic amount (0.066 g) of the phase-transfer catalyst, benzyltriethylammonium chloride was dissolved in deoxygenated dichloromethane (12 cm^3) and potassium hydroxide solution (12 cm^3, 50% w/v) was then added. The reaction mixture was then kept under nitrogen with vigorous stirring for 60 min (92% conversion). The organic phase was then separated and the aqueous phase was extracted with dichloromethane. The combined organic extract was then washed with water, dried (anhydrous Na_2SO_4) and the solvent evaporated off to furnish the crude product mixture. Chromatography of the mixture gave **3a**, **3b** and **7**.

(*E*)-α,α′-dibromo-4,4′-dinitrostilbene (**3a**) crystallised from benzene as almost colourless rods, m.p. 249–250 °C; δ_H(100 MHz, $CDCl_3$) 7.71 (4 H, d, *J* 9, H-2, H-6, H-2′, H-6′), 8.32 (4 H, d, *J* 9, H-3, H-5, H-3′, H-5′). The EI-mass spectrum showed molecular ion characteristic of a dibromo-compound at *m*/*z* 426 (M^+, 11%), 428 (M^+ + 2, 21), 430 (M^+ + 4, 10) and a base peak at 268 (M^+ – 2Br, 100).

(*Z*)-α,α′-dibromo-4,4′-dinitrostilbene (**3b**) crystallised from benzene as almost colourless rods, m.p. 181–182 °C; δ_H(100 MHz, $CDCl_3$) 7.36 (4 H, d, *J* 9, H-2, H-6, H-2′, H-6′), 8.05 (4 H, d, *J* 9, H-3, H-5, H-3′, H-5′). The EI-mass spectrum also showed molecular ion peaks at *m*/*z* 426 (M^+, 35%), 428 (M^+ + 2, 67), 430 (M^+ + 4, 33) and a base peak at 268 (M^+ – 2Br, 100).

The reaction of α-bromo-α-fluoro-4-nitrotoluene with potassium hydroxide in a two-phase medium gave **4a** and **4b**.

(*E*)-α,α-difluoro-4,4′-dinitrostilbene (**4a**) crystallised from benzene as almost colourless rods, m.p. 242–244 °C; δ_H(100 MHz, $CDCl_3$) 7.99 (4 H, d, *J* 9, H-2, H-6, H-2′, H-6′), 8.34 (4 H, d, *J* 9, H-3, H-5, H-3′, H-5′); *m*/*z* 306 (M^+, 100%), 276 (11), 214 (40) and 201 (48).

(*Z*)-α,α-difluoro-4,4′-dinitrostilbene (**4b**) crystallised from benzene as almost colourless rods, m.p. 173–175 °C; δ_H(100 MHz, $CDCl_3$) 7.53 (4 H, d, *J* 9, H-2, H-6, H-2′, H-6′), 8.20 (4 H, d, *J* 9, H-3, H-5, H-3′, H-5′); *m*/*z* 306 (M^+, 100%), 276 (9), 214 (39) and 201 (38).

The products from the other reactions have been previously characterised[12,13,22] and were readily identified based on their melting points and spectral data. The yields are shown in Table 1.

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