Notes

Base-Catalyzed Elimination Reactions of 4-Nitrobenzyl Fluoride

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Numerous studies of the reactions of 4-nitrobenzyl chloride and various derivatives thereof with alkali in mixed aqueous solvents have so far failed to determine unequivocally the mechanism of formation of 4,4′-dinitrostilbene (or derivatives thereof) under these conditions.[1–4] The reactions of the corresponding bromide and iodide analogs are reported to yield bis(4-nitrobenzyl) ether[5] but we are unaware of any similar studies of 4-nitrobenzyl fluoride, except the study of its reaction with sodium ethoxide in ethanol, in which an unidentified, high-melting product was obtained,[6] possibly the stilbene. In view of the considerable product sensitivity of these base-catalyzed reactions to the halide ion, it is of interest to study the reaction of 4-nitrobenzyl fluoride in an effort to provide evidence contributing toward a unifying, and acceptable, mechanistic scheme for these reactions. Accordingly we report here some results for reactions of the fluoride, together with product analyses for reactions of all four halides in the presence of *p*-dinitrobenzene. This reagent is well known as both a radical trap and an acceptor of one electron from a carbanion,[7] the latter role causing reactions to proceed via radical anion intermediates. Thus, these studies should indicate the probability, or otherwise, of the occurrence of a radical mechanism.

Reaction of 4-nitrobenzyl fluoride with excess sodium hydroxide in carefully purified aqueous dioxane 50% (v/v) under air gave *cis*- (40%) and *trans*-4,4′-dinitrostilbene epoxide (40%), ca. 5% *trans*-4,4′-dinitrostilbene, and traces of 4-nitrobenzyl alcohol and several other unidentified products. A similar reaction under nitrogen gave *cis*- (ca. 2%) and *trans*-4,4′-dinitrostilbene (20%), bis(4-nitrobenzyl) ether (24%), and a tar containing at least four other components (see Table I). These products may be contrasted with the *cis*- and *trans*-4,4′-dinitrostilbene obtained from the chloride and bis(4-nitrobenzyl) ether reported[5,8] from the bromide or iodide under air. The products from reactions of 4-nitrobenzyl fluoride thus differ markedly from those of the other halides and imply that the reaction proceeds via a different pathway or via more than one pathway. A possible alternative mechanism involves radical anion intermediates even though no product arising from the dimerization of 4-nitrobenzyl radicals was found. Thus, initial formation of the conjugate base, followed by electron transfer to either a neutral reactant molecule or to oxygen (eq 1–3), could initiate these reactions.

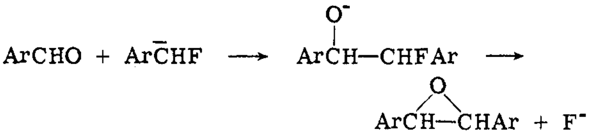
$$\mathrm{ArCH_2F} + {}^{-}\mathrm{OH} \rightleftharpoons \mathrm{Ar\bar{C}HF} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{Ar\bar{C}HF} + \mathrm{O_2} \longrightarrow \mathrm{ArCHF}\cdot + \mathrm{O_2}\cdot^{-} \qquad (2)$$

$$\mathrm{Ar\bar{C}HF} + \mathrm{ArCH_2F} \longrightarrow \mathrm{Ar\dot{C}HF} + \mathrm{ArCH_2F}\cdot^{-} \qquad (3)$$

$$\mathrm{ArCHF}\cdot + \mathrm{O_2} \longrightarrow \mathrm{ArCHFO_2}\cdot \xrightarrow{\mathrm{ArCH_2F}} \mathrm{ArCHFO_2H} + \mathrm{ArCHF}\cdot \qquad (4)$$

$$\mathrm{ArCHFO_2H} + {}^{-}\mathrm{OH} \xrightarrow{-\mathrm{H_2O}} \mathrm{ArCHFO_2}^{-} \longrightarrow \mathrm{ArCHO} + \frac{1}{2}\mathrm{O_2} + \mathrm{F}^{-} \qquad (5)$$



$$\mathrm{ArCHO} + \mathrm{Ar\bar{C}HF} \longrightarrow \mathrm{Ar}\overset{\mathrm{O^-}}{\overset{|}{\mathrm{C}}}\mathrm{H{-}CHFAr} \longrightarrow \mathrm{ArCH{-}CHAr\ (epoxide,\ O\ bridging)} + \mathrm{F}^{-} \qquad (6)$$

$$\mathrm{Ar} = 4\text{-}\mathrm{O_2NC_6H_4}$$

If reaction of the fluoride proceeds via radical anion intermediates, then the addition of a radical-trapping agent, e.g., *p*-dinitrobenzene, should cause the reaction rate to decrease and competing reaction pathways to become evident (cf. the effect of *o*-dinitrobenzene on base-catalyzed elimination from 4-nitrobenzyldimethylsulfonium ion[9]). The similar addition of such a compound to the bromide or iodide should allow some reaction to occur via a radical anion pathway as a result of electron transfer from the α-halo carbanion to the added nitroaromatic[10] to give the stilbene and the corresponding epoxides, viz.

Table I
Percentage Yields of Products from Base-Catalyzed Reactions of 4-Nitrobenzyl Halides in Aqueous Dioxane (50% v/v)[d]

Registry no.	$4\text{-}O_2NC_6H_5CH_2X$ Product	X = F[a]		X = Cl		X = Br		X = I		X = F[c]	
		N_2	Air	N_2	Air	N_2	Air	N_2	Air	N_2	Air
619-93-2 (cis) 736-31-2 (trans)	4,4′-Dinitrostilbene (*cis*- and *trans*-)	22	5	43	26	33	17	28	12	26	13
14688-37-0	*cis*-4,4′-Dinitrostilbene epoxide		40		20		29		23		*b*
968-01-4	*trans*-4,4′-Dinitrostilbene epoxide		40		21		32		25		*b*
56679-04-0	Bis(4-nitrobenzyl) ether	24		5		6		14		52	47
619-73-8	4-Nitrobenzyl alcohol		*b*	9	*b*	13	*b*	16	*b*	15	21
2735-14-0	4,4′-Dinitrotolane	*b*		5		5		5			

[a] Reactions in the absence of *p*-dinitrobenzene. [aryl halide] = 1 × 10^{-2} *M*; [base] = 3 × 10^{-2} *M*. [b] Trace product. [c] [Aryl halide] = 1 × 10^{-2} *M*; [base] = 3 × 10^{-2} *M*. [d] [Aryl halide] = 1 × 10^{-2} *M*; [base] = 1 × 10^{-1} *M*; [*p*-dinitrobenzene] = 1 × 10^{-2} *M*.

$$\mathrm{Ar\bar{C}HX} + \mathrm{ArNO_2} \longrightarrow \mathrm{ArCHX}\cdot + \mathrm{ArNO_2}\cdot^- \quad (7)$$

$$\mathrm{ArCH_2X} + \mathrm{ArNO_2}\cdot^- \longrightarrow \mathrm{ArCH_2X}\cdot^- + \mathrm{ArNO_2} \quad (8)$$

$$\mathrm{ArCH_2X}\cdot^- \longrightarrow \mathrm{X^-} + \mathrm{ArCH_2}\cdot \xrightarrow{\mathrm{Ar\bar{C}HX}} \mathrm{ArCH_2CHXAr}\cdot^- \quad (9)$$

$$\mathrm{ArCH_2CHXAr}\cdot^- + \mathrm{ArNO_2} \longrightarrow \mathrm{ArCH_2CHXAr} + \mathrm{ArNO_2}\cdot^- \quad (10)$$

$$\mathrm{ArCH_2CHXAr} + {}^-\mathrm{OH} \longrightarrow \mathrm{ArCH{=\!=}CHAr} + \mathrm{H_2O} + \mathrm{X^-} \quad (11)$$

$$\mathrm{X} = \mathrm{Cl, Br, or\ I}$$

The results of reactions in the presence of *p*-dinitrobenzene are shown in Table I, from which the change in products obtained is immediately evident. Under nitrogen, 4,4′-dinitrostilbene is obtained from reactions of all four halides together with small amounts of 4-nitrobenzyl alcohol and 4,4′-dinitrotolane.[2] Low yields of bis(4-nitrobenzyl) ether are obtained from all compounds except the fluoride from which a large amount of this product is formed. Reactions under air gave large amounts of the *cis*- and *trans*-4,4′-dinitrostilbene epoxides but decreased amounts of 4,4′-dinitrostilbene from the chloride, bromide, and iodide.

The epoxide presumably arises via 4-nitrobenzaldehyde (eq 5 and 6). No evidence of 4,4′-dinitrobenzyl was obtained, suggesting that 4,4′-dinitrostilbene is only formed by oxidation of this intermediate if this oxidation is 100% efficient (cf. base-catalyzed oxidation of 4-nitrotoluene[10]). It is of interest to note that formation of the epoxides apparently occurs *only* at the surface of the solution.

The increasing strength of the carbon–halogen bond with decreasing atomic weight of the halogen increases the stability of the corresponding α-halo carbanions and shifts the equilibrium of eq 1 to the right. Reaction via the SN2 pathway, which involves attack on neutral reactant molecules, is thus progressively disfavored on going from iodine through to fluorine, as is reaction via the α-ElcB mechanism, which requires carbon–halogen bond breakage. Although the formation of radical anions from 4-nitrobenzyl and 4-nitrocumyl chlorides has been observed in the presence of 2-nitro-2-propyl carbanions, etc,[11] no evidence of reaction of 4-nitrobenzyl chloride via the radical anion is obtained except in the presence of *p*-dinitrobenzene. SN2 reaction via an ion pair intermediate[12] thus seems preferable to the α-ElcB mechanism for the chloride, whereas the poorer leaving group in the fluoride results in reaction via the radical anion mechanism. These results are thus in good accord with our conclusions from kinetic, etc., studies of derivatives of 4-nitrobenzyl chloride,[3,4] i.e., that reaction via a radical mechanism in the absence of radical initiators (e.g., peroxides) is unlikely.

Experimental Section

4-Nitrobenzyl fluoride (1.0877 g) was dissolved in dioxane (300 ml), sodium hydroxide solution (300 ml, 0.022 *N*) was added, and the reaction mixture was kept thermostatted at 35°C for 1 month. Yellow needles were precipitated and, after isolation, were shown to be *trans*-4,4′-dinitrostilbene oxide (40% based on substrate). The remaining solution was then acidified with concentrated hydrochloric acid and freeze dried. *cis*-4,4′-Dinitrostilbene epoxide (40%) and *trans*-4,4′-dinitrostilbene (5%) were isolated by preparative TLC using benzene as eluent. All compounds were identified by NMR, mass spectrometry, melting point, and mixture melting point with authentic samples.

Reactions of 4-nitrobenzyl chloride, bromide, and iodide with sodium hydroxide in the presence of *p*-dinitrobenzene in aqueous dioxane, under air or nitrogen, were perforn[illegible] at room temperature, and products were analyzed after 4–5 hr, [illegible] 95% of the added *p*-dinitrobenzene was recovered unchanged.

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Registry No.—4-Nitrobenzyl fluoride, 500-11-8; sodium hydroxide, 1310-73-2; 4-nitrobenzyl chloride, 100-14-1; 4-nitrobenzyl bromide, 100-11-8; 4-nitrobenzyl iodide, 3145-86-6.

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[8] In agreement with other workers[2] we have also obtained some alcohol from reactions of the bromide and iodide.

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The *p*-Nitrobenzyl System. IV.[1] Base-Induced Transformations in *p*-Nitrobenzyl Chloride, Bromide, Iodide, Tosylate, and Sulfonium Salts[2-4]

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As a part of a reinvestigation of the mechanisms of formation of *p,p′*-dinitrostilbene (**2**) from *p*-nitrobenzyl chloride (**1**),[5] we wish to report the products of base-induced reactions in several *p*-nitrobenzyl compounds. It has been repeatedly mentioned in the recent literature[6] that the product of reacting **1** with hydroxide ion in aqueous dioxane (eq 1) is almost exclusively *trans*-**2**. In view of doubts of this information,[7] and in an attempt to elucidate the mechanism of this transformation, we carried out, in addition to kinetic and isotope effect measurements[4] to be published separately, a product analysis of the reactions of hydroxide ion with **1** and with *p*-nitrobenzyl bromide (**3**), iodide (**4**), and tosylate (**5**) in 50% aqueous dioxane. For comparative purposes,[8] we also reinvestigated the products of reacting *p*-nitrobenzyldimethylsulfonium bromide (**6**) and tosylate (**7**) with sodium hydroxide in aqueous solution. The results are shown in Tables I–III. It is quite evident from inspection of Table I that the reputed[5] *almost quantitative* yield of *trans*-**2** from the reaction of **1** with sodium hydroxide in 50% aqueous dioxane is in error. The reaction given in eq 1 yields a yellowish precipitate whose weight corresponds to 98% of that expected for a quantitative yield of **2**; however, TLC and its visible and uv spectra show that it contains the geometrical isomers of both **2** and *p,p′*-dinitrostilbene oxide (**8**) as well as smaller amounts of other compounds (Table I). On recrystallization of the crude product from nitrobenzene in the presence of a crystal of

$$\underset{\mathbf{1}}{\mathrm{ArCH_2Cl}} + \mathrm{OH^-} \longrightarrow \underset{\mathbf{2}}{\mathrm{ArCH{=\!=}CHAr}} \qquad (1)$$

$$\mathrm{Ar} = p\text{-}\mathrm{NO_2C_6H_4}$$