х

А

$$\operatorname{ArCHX} + \operatorname{ArNO}_2 \longrightarrow \operatorname{ArCHX} + \operatorname{ArNO}_2$$
 (7)

$$\operatorname{ArCH}_{2}X + \operatorname{ArNO}_{2} \stackrel{\bullet}{\longrightarrow} \operatorname{ArCH}_{2}X \stackrel{\bullet}{\longrightarrow} + \operatorname{ArNO}_{2}$$
 (8)

$$\operatorname{ArCH}_{2} X^{\bullet} \longrightarrow X^{\bullet} + \operatorname{ArCH}_{2} \bullet \xrightarrow{\operatorname{ArCH} X} \operatorname{ArCH}_{2} \operatorname{CHXAr}^{\bullet}$$
(9)

 $ArCH_2CHXAr \cdot + ArNO_2$ 

$$rCH_{3}CHXAr + OH \longrightarrow ArCH=CHAr + H_{3}O + X$$

(11)

 $ArCH_CHXAr + ArNO$ 

(10)

$$=$$
 CI, 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.<sup>2</sup> 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<sup>10</sup>). 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  $\alpha$ -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  $\alpha$ -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 2nitro-2-propyl carbanions, etc,<sup>11</sup> 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<sup>12</sup> thus seems preferable to the  $\alpha$ -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,<sup>3,4</sup> 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 1 at room tempera-95% of the added ture, and products were analyzed after 4-5 hr, p-dinitrobenzene was recovered unchanged.

Notes

Acknowledgment. We are grateful to the National Research Council of Canada for financial support, and to a reviewer for most valuable comments concerning this work.

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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The p-Nitrobenzyl System. IV.<sup>1</sup> Base-Induced Transformations in p-Nitrobenzyl Chloride, Bromide, Iodide, Tosylate, and Sulfonium Salts<sup>2-4</sup>

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# Received June 30, 1975

As a part of a reinvestigation of the mechanisms of formation of p,p'-dinitrostilbene (2) from p-nitrobenzyl chloride (1)<sup>5</sup> we wish to report the products of base-induced reactions in several *p*-nitrobenzyl compounds. It has been repeatedly mentioned in the recent literature<sup>6</sup> that the product of reacting 1 with hydroxide ion in aqueous dioxane (eq 1) is almost exclusively trans-2. In view of doubts

$$ArCH_{2}Cl + OH^{-} \rightarrow ArCH = CHAr$$
(1)  

$$1 \qquad 2$$
  

$$Ar = p \cdot NO_{2}C_{2}H_{2}$$

of this information,<sup>7</sup> and in an attempt to elucidate the mechanism of this transformation, we carried out, in addition to kinetic and isotope effect measurements<sup>4</sup> 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,<sup>8</sup> 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<sup>5</sup> 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

Table IProducts and Yields of the Reaction of p-Nitrobenzyl Chloride with Sodium Hydroxide in<br/>Aqueous Dioxane (50% Water) at 25°

Entry no.	Reactants, M			Yields, %					
	[ArCH2C1]	[NaOH]	Conditions	2a, b	8a, b	16 <sup>c</sup>	12 0	Others	
1	0.01	0.10	Degassed	52 <sup>d</sup>	43 <sup>e</sup>	3	Trace	<b>17°</b> and $p$ -nitrotolane, <sup><i>a</i></sup> trace	
2	0.02	0.10	Oxygen		88 <sup>f</sup>	5	2	p-Nitrobenzoic acid, <sup>a</sup> 4	
3	0.01	0.10	p-DNB, 0.01 M	16	22	19	2	p,p'-Dinitrobibenzyl, <sup>a,c</sup> 11, <b>17</b> <sup>c</sup>	
4	0.01	0.10	Nitroxide, 0.001 M degassed	41	35	12	1	<i>p</i> -Nitrotolane, <sup><i>a</i></sup> trace	
5	0.01	0.10	Nitroxide, 0.005 <i>M</i>		34	49	6		

<sup>a</sup> Detected by TLC. <sup>b</sup> Quantitated by uv. <sup>c</sup> Determined by VPC. <sup>d</sup> cis-2, 27.8%; trans-2, 24.2%. <sup>e</sup> cis-8, 24.5%; trans-8, 18.5%. <sup>l</sup> cis-8, 51%; trans-8, 37%.

Table IIProducts and Yields of the Reactions of p-Nitrobenzyl Dimethylsulfonium Tosylate and Bromide,0.01 M, with Sodium Hydroxide, 0.1 M, in Water at 60°

Fata.	Anion of sulfonium salt	Yield	ls, %		
no.		2 <sup><i>a</i>,<i>b</i></sup>	8 a, b	Reaction conditions	
6	OTs <sup>-</sup>	31	52	No precautions to exclude air	
7°	OTs <sup>-</sup>	3	54	Saturated with $O_2$	
8	Br-	37	43	No precautions to exclude air	
9	Br-	4	59	Saturated with $O_2$	

<sup>a</sup> Detected by TLC. <sup>b</sup> Quantitated by uv. <sup>c</sup> p-Nitrobenzyl alcohol (11%) and p-nitrotoluene (3%) were also detected.

iodine to isomerize cis-2 to trans-2,<sup>8</sup> only trans-2 is obtained. This is due to the fact that the other major product, viz. 8, is fairly soluble in nitrobenzene and remains in solution while only pure trans-2 crystallizes out. We tested this by mixing authentic samples of 2 and 8, dissolving in hot nitrobenzene, and cooling for crystallization. The crystalline material thus obtained was pure by TLC (silica), had undepressed melting point when mixed with pure trans-2, and had uv, NMR, and ir spectral characteristics identical with those of pure trans-2.

It is puzzling that the epoxide 8 is produced in thoroughly degassed solutions. Its formation may be accounted for by the reaction scheme shown in eq 2–6. The production of

$$ArCH_2Cl + OH^- \rightleftharpoons ArCHCl + H_2O \qquad (2)$$

$$Ar\bar{C}HCl + ArCH_2Cl \longrightarrow Ar\bar{C}HCl + ArCH_2Cl^{-}$$
(3)  
10 11

$$\operatorname{Ar\dot{C}HCl}$$
 +  $\operatorname{H}_{2}O \longrightarrow \operatorname{ArC}(OH)\operatorname{HCl}$  +  $\operatorname{H}_{\cdot}$  (4)

$$\operatorname{ArC}(OH)\operatorname{HCl} + OH^{-} \longrightarrow \operatorname{ArCHO} + \operatorname{Cl}^{-} + \operatorname{H}_{2}O$$
 (5)

ArCHO + ArCHCl 
$$\rightarrow$$
 ArCH $-$ CHAr + Cl<sup>-</sup> (6)  
8

the carbanion 9 in the reaction medium has been proven by deuterium labeling.<sup>5,9</sup> The reaction of a radical, 10, with water (eq 4) to abstract a hydroxyl radical may seem strange; however, in the virtual absence of reduced products (Table I) eq 4 is necessary to account for the observed epoxide. An example of a similar hydroxyl abstraction is afforded by the oxidation of isobutyraldehyde by Fremy's salt in basic solution.<sup>10</sup> The hydrogen atom generated in eq 4 is presumably captured by unreacted 1 to give a transient radical anion<sup>11</sup> (HArCH<sub>2</sub>Cl<sup>-</sup>) which reacts with hydroxide

Table IIIProducts and Yields of the Reactions ofp-Nitrobenzyl Bromide, Iodide, and Tosylate withSodium Hydroxide<sup>a</sup> in 50% Aqueous Dioxane at 25°

<b>T</b> 4	N24-1	Yields, %				
no.	compd <sup>b</sup>	20	8 <sup>c</sup>	16 <sup>d</sup>	Other <sup>d</sup>	
10	Bromide	~1	10	67	18, 5; 12 and 17, traces	
11	Iodide	Trace	20	76	12, 3	
12	Tosylate	$\sim 4$	20	52	12, 2; 17, trace	
a []	NaOH = 0.	1 M. <sup>b</sup> [A	ArCH	$_{2}X1 =$	= $0.01 \ M.$ <sup>c</sup> Determined by	
TLĊ.	<sup>d</sup> Determine	d by VPC		•		

ion to give another radical anion, 11 in eq 3. The interception of the carbanion 9 by  $p_{-n}$  itrobenzaldebyde (12) to give

tion of the carbanion 9 by p-nitrobenzaldehyde (12) to give 8 (eq 6) is well documented.<sup>5</sup>

The possibility of intervention of radical anions in this system has been entertained previously.<sup>11</sup> We tested this possibility by conducting the reaction of 1 with hydroxide ion in the presence of *p*-dinitrobenzene (*p*-DNB), which is known to be a good electron acceptor, particularly from radical anions.<sup>12</sup> and in the presence of oxygen is reported to react with *p*-nitrobenzyl radical to give 12.<sup>13</sup> The presence of  $O_2$  inhibits completely the formation of 2 but enhances the formation of 8, while *p*-DNB lowers the yields of both 2 and 8 to 16 and 22%, respectively (Table I). It is quite probable that the fates of the radical 10 and the radical anion 11 of eq 3 follow the scheme represented by eq 7–13.

$$ArCH_2Cl^- + O_2 \longrightarrow ArCH_2Cl + O_2^-$$
(7)  
11 1

$$Ar\dot{C}HCl + O_2 \longrightarrow ArCH(O_2)Cl$$
(8)  
10

$$\operatorname{ArCH}(O_2)Cl + \operatorname{ArCHCl} \longrightarrow \operatorname{ArCH}(O_2)Cl + 10$$
 (9)

$$ArCH(O_2^{-})Cl + H_2O \longrightarrow ArCH(O_2H)Cl + OH^{-}$$
(10)  
$$ArCH(O_2H)Cl + ArCHCl^{-} \longrightarrow$$

$$ArCH(O^{-})Cl + ArCH(OH)Cl$$
 (11)

$$ArCH(O^{-})Cl \longrightarrow ArCHO + Cl^{-}$$
 (12)  
12

$$ArCH(OH)Cl + OH^{-} \rightarrow 12 + Cl^{-} + H_{*}O$$
 (13)

The above scheme serves to illustrate several points. The radical anion 11, which may be invoked in stilbene formation,<sup>11</sup> is diverted back to 1 (eq 7). The radical 10 which, in the present scheme, is ultimately responsible for the production of the epoxide 8 via the aldehyde 12 (eq 6), is regenerated in what may be regarded as chain-propagation steps (eq 8 and 9). It is evident from eq 2, 3, 7, 8, and 9 that oxygen would divert 11 to give ultimately 8. In the absence of oxygen it is possible that 11 is responsible for the production of 2 as indicated in the following scheme, eq 14-17.

$$ArCH_2Cl^- \longrightarrow ArCH_2 + Cl^-$$
(14)  
13

$$\operatorname{Ar\dot{C}H}_{2} + \operatorname{Ar\ddot{C}HCl} \longrightarrow \operatorname{ArCH}_{2}\operatorname{CHClAr}^{-}$$
 (15)  
14

$$ArCH_2CHClAr^- + OH^- \longrightarrow$$
$$ArCH = CHAr^- + H_2O + Cl^- (16)$$

$$ArCH = CHAr \cdot + 1 \longrightarrow ArCH = CHAr + ArCH_2Cl^{-}$$
(17)

Alternatively, 14 may react with 1 to give 15 which undergoes a  $\beta$ -elimination to 2 (eq 18, 19).

$$ArCH_{2}CHClAr \cdot^{-} + ArCH_{2}Cl \longrightarrow$$

$$ArCH_{2}CHClAr + ArCH_{2}Cl \cdot^{-} \quad (18)$$
15

 $ArCH_2CHClAr + OH^- \rightarrow$ 

$$ArCH = CHAr + H_2O + Cl^{-} (19)$$

To test the presence of free radicals, the reaction between 1 and hydroxide ion in 50% aqueous dioxane was carried out in the presence of di-tert-butyl nitroxide, which is known to be a radical scavenger.<sup>14</sup> With added nitroxide, the yield of 2 is lowered while the amount of p-nitrobenzyl alcohol (16) is increased (Table I). This may reflect the scavenging of 13 by the nitroxide.

For comparison purposes, the products and yields of the reaction of the sulfonium salts 6 and 7 with hydroxide ion in aqueous solution are reported in Table II. Here, too, the products which were once thought to be exclusively 2 are actually mixtures of 2 and 8 as well as 16 and p-nitrotoluene (17) when no precautions to exclude oxygen are taken.

In Table III are reported the products and yields of the reactions of 3, 4, and 5 with sodium hydroxide in 50% aqueous dioxane. Previously, 3 and 4 were reported to give p,p'-dinitrobibenzyl ether (18) in quantitative yield.<sup>15</sup>

In summary, we wish first to call attention to the complexity of base-induced transformations of p-nitrobenzyl compounds and second to correct some of the errors which are perpetually relayed in the literature. We wish also to emphasize that although the present work suggests that radicals and radical anions may be involved in the 1 to 2 transformation, neither the carbene mechanism nor the alkylation-dehydrohalogenation mechanism can be excluded. Indeed, the three mechanisms may be operative simultaneously. We will report on the pros and cons of each of these mechanisms in the light of kinetic and isotope effect data.

#### **Experimental Section**

Qualitative analysis of the reaction products was done by TLC. Silica plates with a fluorescent indicator (Brinkmann silica gel HF-254) were used and were developed with benzene; standards were run alongside the unknown mixtures. VPC was used to quantitate the readily volatile components of products (Varian Aerograph 600-D with a flame ionization detector; 5% SE-30 6 ft  $\times$ 0.125 in. column). Calibration curves, using trans-stilbene as an internal standard, were prepared for 1, 12, 16, 17, and p-DNB. Spectroscopic analyses (uv and visible on a Cary 14) were performed in DMF for the quantitation of the dinitrostilbenes<sup>16</sup> [trans-2, 368 nm (4.577); cis-2, 320 nm (4.193)] and the dinitrostilbene oxides [trans-8, 291 nm (4.371); cis-8, 277 nm (4.264)]. Mixtures of cis- and trans-2 exhibited one maximum between 368 and 320 nm.<sup>17</sup> The amounts of the four components, cis- and trans-2 and cis- and trans-8, were determined by solving simultaneous equations for the absorbances at 380, 340, 290, and 270 nm

$$A_{380} = 32300c_1 + 5350c_2 + 266c_3$$
  

$$A_{340} = 25200c_1 + 15000c_2 + 1840c_3 + 935c_4$$
  

$$A_{290} = 5700c_1 + 11750c_2 + 23500c_3 + 1600c_4$$
  

$$A_{270} = 4200c_1 + 8190c_2 + 14400c_3 + 17600c_4$$

where  $c_1$ ,  $c_2$ ,  $c_3$ , and  $c_4$  refer to the concentrations in DMF of trans- and cis-2 and trans- and cis-8, respectively.

Materials. The compounds used in this study were either commercially available and purified before using or prepared and purified by known procedures. The following compounds were used as chromatographic standards. Their melting points and spectral characteristics were in agreement with the literature: cis- and trans-2,<sup>16</sup> cis- and trans-8,<sup>18</sup> ArCH<sub>2</sub>CH<sub>2</sub>Ar,<sup>19</sup> ArCH<sub>2</sub>OCH<sub>2</sub>Ar,<sup>15</sup> ArC=CAr,<sup>20</sup> 12, 16, and 17.

Product Studies. All aqueous dioxane solutions were prepared from purified and freshly distilled dioxane and used immediately. Studies that involved degassed solutions were done on a vacuum line. Those studies involving the effect of  $O_2$  were performed by saturating the solutions with  $O_2$  and keeping the reaction mixture under an O<sub>2</sub> atmosphere. All experiments were conducted in 50% aqueous dioxane (v/v) except those with the sulfonium salts, where water was used as the solvent.

In a typical experiment, 50 ml of a 0.02 M solution of 1 in dioxane and 50 ml of a 0.20 M NaOH solution were degassed separately by a series of freeze-thaw cycles and then mixed under vacuum. After 24 hr, the reaction mixture was opened to atmospheric pressure, neutralized with dilute HCl, diluted with an equal volume of water, and stored in a refrigerator for 24 hr. The precipitate was isolated by filtration and dried; 0.132 of a yellow solid was obtained. This was analyzed by TLC and uv. The yields of 2 and 8 are given in Table I. The precipitate also contained a trace spot with the same  $R_f$  value as p,p'-dinitrotolane. A sample of this compound obtained by preparative TLC had m/e 268. The filtrate was extracted with chloroform. The organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent removed on a rotary evaporator; the remaining solid (5 mg) was analyzed by TLC and shown to be 16, with traces of 12 and 17.

Registry No.-1, 100-14-1; cis-2, 619-93-2; trans-2, 736-31-2; 3, 100-11-8; 4, 3145-86-6; 5, 1153-45-3; 6, 14182-26-4; 7, 19824-23-8; cis-8, 14688-37-0; trans-8, 968-01-4; 12, 555-16-8; 16, 619-73-8; sodium hydroxide, 1310-73-2; p-nitrotoluene, 99-99-0.

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   This research was partially supported by the National Science Founda-tion is the form of a Traineschin to B H D.
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## **Reductive Deoxygenation of Esters with** Trichlorosilane<sup>1</sup>

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# Received June 30, 1975

Trichlorosilane has been shown to be an efficient reagent for reducing simple aliphatic esters to the corresponding ethers under free-radical conditions.<sup>2</sup> We recently demonstrated the applicability of the reagent to the reduction of more complex bicyclic lactones and also the existence of significant selectivity when additional ester groupings were present.<sup>3</sup> We now wish to report that under the appropriate conditions trichlorosilane can be an effective reagent for the reductive deoxygenation of esters of nonprimary aliphatic alcohols.



In general we find that for the reaction of a given ester 1 with trichlorosilane, two products, 2 and 3, are formed competitively. Ether 2 is the result of a "normal" reaction with HSiCl<sub>3</sub> while 3 is the product of reductive deoxygenation. The relative amounts of 2 and 3 are most profoundly affected by the nature of R'. As shown in Scheme I for the acetates of several alcohols, irradiation with excess HSiCl<sub>3</sub> yields largely 2 for a primary acetate, exclusively 3 for a tertiary acetate, and a mixture of 2 and 3 for a secondary acetate.4,5 These results are consistent with a reaction mechanism which involves radical 16 as a common intermediate for the formation of 2 and 3, with the proportion of 16 which undergoes reductive deoxygenation being influenced by the stability of radical .R'. Thus tertiary acetates give the highest proportion of reductive deoxygenation and primary acetates the lowest.

Table I Reaction of 1-Adamantyl Esters with HSiCl,

Ester	HSiCl <sub>3</sub> /17 <sup>a</sup>	THF/17 <sup>b</sup>	% reaction	18/19 <i>c</i>
17a <sup>d</sup>	8		100	$42^{f}/58^{g}$
17a	4		100	30/70
17a	4	<b>24</b>	100	18/82
17a	4	72	87	6/94
17a	2	72	58	2/98
17b <sup>e</sup>	8		100	$12^{h}/88$
17b	4		100	3/97
17b	8	29	7	1/99

<sup>a</sup> Moles of HSiCl<sub>3</sub> per mole of ester. <sup>b</sup> Moles of THF per mole of ester. <sup>c</sup> Determined by GLC analysis. <sup>d</sup> Registry no., 19066-22-9. eRegistry no., 56830-70-7. fRegistry no., 6221-75-6. & Registry no., 281-23-2. hRegistry no., 56830-71-8.



In an effort to determine if a judicious choice of reaction conditions would render the method preparatively useful in instances where .R' was of intermediate stability (i.e., secondary esters), several experiments were performed with esters of 1-adamantanol. The tertiary 1-adamantyl radical has been shown to be slightly more stable than a normal secondary radical,<sup>6</sup> and thus 1-adamantyl esters should provide a sensitive probe of the results of changes in reaction conditions. It was expected that one could most effectively maximize reductive deoxygenation by retarding the bimolecular second step of the ether-forming pathway (path A). For instance, a decrease in the HSiCl<sub>3</sub> concentration should retard path A to the benefit of path B. In addition, an increase in the steric bulk of the ester (pivalates vs. acetates) should have a similar effect. The results summarized in Table I are in general accord with these predictions. It is seen that either decreasing the amount of

