and epoxides 7-oxabicyclo[4.1.0]heptane (**7b**), 13-oxabicyclo-[10.1.0]tridecane (**8b**) were commercial products (Aldrich) and were purified by reported methods. 1,2-Epoxydodecane [**9b**; bp 99–101 °C (4 mm), lit.[14] bp 106–109 °C (6 mm)], prepared by method B, gave spectra identical with samples of the same compound prepared by given procedures.[8,14] Both (*E*)- and (*Z*)-3-phenyloxiranecarboxylic acids **3b** and **4b** have been described.

**4,5-Epoxy-2-hexenoic acid (5b)** was obtained by following method A[2,3] and was recrystallization from $CCl_4/n$-hexane: mp 81–83 °C; IR ($CS_2$) 2930, 2670, 2500, 1697, 1654, 1292, 965, 825 cm$^{-1}$; $^1H$ NMR ($CDCl_3$) δ 11.07 (br s, 1 H), 6.84 (dd, *J* = 16.0, 6.5 Hz, 1 H), 6.12 (d, *J* = 16.0 Hz, 1 H), 3.22 (dd, *J* = 6.5, 1.5 Hz, 1 H), 2.98 (dq, *J* = 5.0, 1.5 Hz, 1 H), 1.4 (d, *J* = 5.0 Hz, 3 H).

Anal. Calcd for $C_6H_8O_3$: C, 56.24; H, 6.29. Found: C, 56.20; H, 6.14.

**5,6-Epoxy-2-hexanone (6b)** was also obtained by following method A: bp 52 °C (0.5 mm); IR ($CHCl_3$) 2995, 1712, 1400, 1360, 1160, 908, 804, 830, 750 cm$^{-1}$; $^1H$ NMR ($CDCl_3$) δ 2.78–3.02 (m, 1 H), 2.33–2.72 (m, 4 H), 2.09 (s, 3 H), 1.65–1.92 (m, 2 H); mass spectrum (50 eV), *m/e* (relative intensity) 114 (5), 86 (4), 85 (4), 82 (6), 72 (9), 58 (4), 55 (15), 54 (12), 53 (4), 44 (9), 43 (100), 42 (4), 39 (12).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.15; H, 8.77. Found: C, 63.28; H, 9.03.

**Epoxidation Procedures.** In the epoxidation of water-soluble olefins (method A), a freshly prepared solution of potassium peroxomonosulfate (24 mmol) in water[15] is added dropwise (during 2–4 h) to a mixture of the alkene (10 mmol) and acetone (0.13 mol) in water at ca. 2 °C. Before the addition is started, the pH is adjusted to 7.5, and it is maintained at this value during the reaction by additions of 0.5 N KOH by use of a pH stat.[2] The reaction mixture is then acidified (at 2 °C) to pH ca. 3 (5% HCl) and extracted with $Et_2O$. The ether extracts are dried ($MgSO_4$), and the solvent is removed in vacuo, affording the crude epoxide. This is then purified by standard methods.[2,3] In an experiment typical of two-phase epoxidations (method B) a solution of potassium peroxomonosulfate (12 mmol) in water (30 mL)[15] is added dropwise (30 min) to a well-stirred biphasic mixture of benzene (50 mL) and buffered (pH 7.5, 0.05 M phosphate buffer) water (20 mL) kept at 6–8 °C and containing cyclododecene (**8a**; 0.85 g, 5.1 mmol), acetone (4 mL), and 18-crown-6 (0.3 g, 1 mmol) as the phase-transfer catalyst. During the addition the pH is monitored and kept constant by using a pH-stat (0.5 N KOH). The mixture is allowed to stand at 8–10 °C for 3 h with stirring, the benzene layer is then separated, and the aqueous phase is extracted with benzene (10 mL). The combined benzene extracts are dried ($MgSO_4$), and after removal of the solvent in vacuo the residue is purified by column chromatography (silica gel, *n*-hexane–$Et_2O$, 4:1), affording 0.79 g (4.34 mmol, 85% yield) of epoxide **8b** [bp 100–102 °C (0.2 mm), lit.[16] bp 116–117 °C (4.7 mm)] having spectra identical with those of a purified commercial sample.

**Registry No.** **3a**, 140-10-3; **3b**, 1566-68-3; **4a**, 102-94-3; **4b**, 73610-79-4; **5a**, 110-44-1; **5b**, 74923-21-0; **6a**, 109-49-9; **6b**, 74877-18-2; **7a**, 110-83-8; **7b**, 286-20-4; (*E*)-**8a**, 1486-75-5; (*Z*)-**8a**, 1129-89-1; *cis*-**8b**, 1502-29-0; *trans*-**8b**, 4683-60-7; **9a**, 112-41-4; **9b**, 2855-19-8.

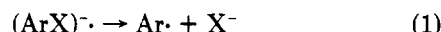## $S_{RN}1$ Mechanism in Bifunctional Systems[1]

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Since the $S_{RN}1$ mechanism of nucleophilic aromatic substitution of unactivated substrates was discovered,[2] it has been found that this reaction has a wide scope with regard to both the substrates and the nucleophiles that participate.[3,4] The most important steps of this mechanism are shown in Scheme I.[3]
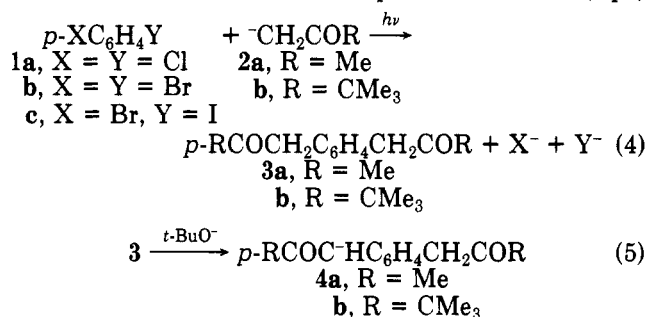
### Scheme I

$$(ArX)^{-\cdot} \rightarrow Ar\cdot + X^- \qquad (1)$$

$$Ar\cdot + Nu^- \rightarrow (ArNu)^{-\cdot} \qquad (2)$$

$$(ArNu)^{-\cdot} + ArX \rightarrow ArNu + (ArX)^{-\cdot} \qquad (3)$$

The fact that such a variety of substrates and nucleophiles is suitable for this reaction, giving in many cases an excellent yield of substitution product, prompted us to explore the possibility of using this reaction to obtain polymers.[5] Two different approaches were used: (1) the reaction of an aromatic substrate bearing two leaving groups and a nucleophile having more than one nucleophilic center was studied; (2) the reaction of a substrate having both the leaving group and the nucleophilic center within the same molecule was also studied.

### Results and Discussion

**Method 1.** *p*-Dihalobenzenes (**1**) were allowed to react with ketone enolate ions **2** under photostimulation[6] (eq 4)

$$p\text{-}XC_6H_4Y \quad + \quad {}^-CH_2COR \xrightarrow{h\nu}$$

**1a**, X = Y = Cl    **2a**, R = Me
**b**, X = Y = Br     **b**, R = CMe$_3$
**c**, X = Br, Y = I

$$p\text{-}RCOCH_2C_6H_4CH_2COR + X^- + Y^- \quad (4)$$
**3a**, R = Me
**b**, R = CMe$_3$

$$3 \xrightarrow{t\text{-}BuO^-} p\text{-}RCOC^-HC_6H_4CH_2COR \quad (5)$$
**4a**, R = Me
**b**, R = CMe$_3$

with an excess of potassium *tert*-butoxide to ionize the disubstitution product formed (eq 5). The anion **4** was expected to act as a nucleophile that could react further with aryl radicals to produce an oligomeric and/or polymeric product.

In the photostimulated reaction of **1a** with a large excess of **2a** or **2b**, the chloride ion was eliminated to the extent of 83 and 93%, respectively, and a 65% yield of **3b** was isolated (see Experimental Section). In the photostimulated reaction of **1a** with **2a** or **2b** and potassium *tert*-butoxide in a ratio 1:1:4, the yield of chloride ion was 25–50% (theoretical 100% considering two chlorine atoms per molecule of **1a**). In the dark there is no reaction (Table I).

The yield of chloride ion indicates that the photostimulated reaction does not proceed to completion, since

(14) Emmons, W. D.; Pagano, A. S. *J. Am. Chem. Soc.* **1955**, *77*, 89.
(15) As a 0.04 M standard solution (iodometric titer) of potassium peroxomonosulfate obtained by dissolving Oxone (Du Pont Co.) and EDTANa$_2$ (ca. 4 × 10$^{-4}$ M, to prevent trace-metal-catalyzed peroxide decomposition) in doubly distilled water. Excess oxidant is used due to the competing peroxide autodecomposition.[2]
(16) Itakura, J.; Tanaka, H.; Ito, H. *Bull. Chem. Soc. Jpn.* **1964**, *42*, 1604.

(1) Research supported in part by the Consejo Nacional de Investigaciones Cientificas y Técnicas, Argentina.
(2) Kim J. K.; Bunnett, J. F. *J. Am. Chem. Soc.* **1970**, *92*, 7463.
(3) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.
(4) Wolfe, J. F.; Carver, D. R. *Org. Prep. Proced.*, **1978**, *10*, 225.
(5) Our goal was to find if the $S_{RN}1$ mechanism could be used for the synthesis of polymers and not to study the intrinsic properties of them.
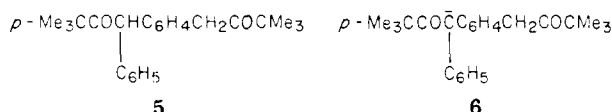(6) Rossi, R. A.; Bunnett, J. F. *J. Org. Chem.* **1973**, *38*, 1407.

Table I. Photostimulated Reactions of *p*-Dihalobenzenes with Ketone Enolate Ions in Liquid Ammonia

| expt | substr (mol) | ketone (mol) | amt t-BuONa,[a] mol | irradiation time, min | halide ion, yield % | product isolated,[b] g |
|------|--------------|--------------|---------------------|------------------------|---------------------|-------------------------|
| 1 | 1a (0.012) | 2a (0.012) | 0.048 | 240 | 50 | 0.719 |
| 2 | 1a (0.008) | 2a (0.044) | 0.048 | 120[c] | 1 | |
| 3 | 1a (0.007) | 2a (0.040) | 0.044 | 180 | 83 | 0.550 |
| 4 | 1a (0.006) | 2b (0.036) | 0.036 | 240 | 93 | 1.059 |
| 5 | 1a (0.021) | 2b (0.021) | 0.063 | 180 | 25 | 0.950 |
| 6 | $C_6H_5Cl$ (0.010) | d (0.001) | 0.008 | 240 | 85 | 0.300 |
| 7 | 1b (0.008) | 2b (0.013) | 0.064 | 300 | 49 | 0.830 |
| 8 | 1a (0.011) | 2a (0.011) | 0.043 | 240 | 55 (Br⁻), 61 (I⁻) | 0.674[e] |

[a] This is the initial concentration of *t*-BuONa without considering the acid-base reaction with the ketone. [b] See Experimental Section. [c] Dark reaction. [d] 1,4-Bis(3,3-dimethyl-2-oxobutyl)benzene. [e] 26% of 1c was recovered.

there was **1a** unreacted. In all runs made, the reaction mixtures were clear solutions at the beginning, but under irradiation they become dark green, and a solid formed. The insolubility of the product together with the darkening of the reaction solution may be the cause of the low reactivity.

In the photostimulated reaction of **3b** as nucleophile, with an excess of chlorobenzene and potassium *tert*-butoxide, there was formed 83% of the theoretical amount of chloride ion, and the product isolated was the ketone **5**.
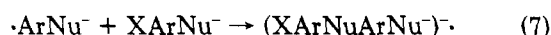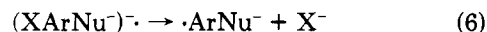
$$p\text{-Me}_3\text{CCOCHC}_6\text{H}_4\text{CH}_2\text{COCMe}_3 \quad\quad p\text{-Me}_3\text{CCOC}\bar{\text{C}}\text{C}_6\text{H}_4\text{CH}_2\text{COCMe}_3$$

$$\underset{\text{5}}{\overset{|}{\underset{\text{C}_6\text{H}_5}{}}} \quad\quad\quad\quad\quad \underset{\text{6}}{\overset{|}{\underset{\text{C}_6\text{H}_5}{}}}$$

This result shows that **4b** is a nucleophile toward phenyl radicals, whereas the anion formed under these basic conditions, **6**, does not react further with aryl radicals. It has been shown before that 1,1-diphenylacetone enolate ion does not react with halobenzenes by photostimulation in liquid ammonia.[7]

The order of the leaving-group mobility in photostimulated reactions of halobenzenes with ketone enolate ions is I > Br > Cl > F;[6] however, the amount of halide ions eliminated in reactions of **1b** with **2b** was almost the same as that with **1a** and **2b**. In the photostimulated reaction of **1c** with **2a** a 51–55% yield of bromide ions and a 57–61% yield of iodide ions were found. The fact that the yield of halide ion liberated is almost independent of the aryl halide used indicates that the low reactivity is due to the insolubility of the highly substituted product together with the formation of structures like **6** that are unreactive toward aryl radicals.

It is known that the photostimulated reaction of the thiophenoxide ion with dihalobenzenes gives the disubstitution product;[8] therefore, the system of *p*-dihalobenzene and the dianion of *p*-dimercaptobenzene was thought to be a suitable one. Unfortunately this dianion was insoluble in liquid ammonia, and little reaction occurred in the photostimulated reaction with *p*-dibromobenzene (15% yield).
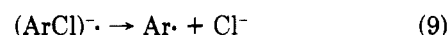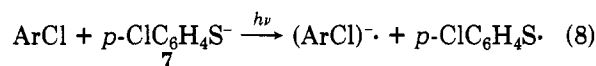
**Method 2.** In this approach the main steps are shown in eq 6 and 7.

$$(\text{XArNu}^-)^{-\cdot} \rightarrow \cdot\text{ArNu}^- + \text{X}^- \quad\quad (6)$$

$$\cdot\text{ArNu}^- + \text{XArNu}^- \rightarrow (\text{XArNuArNu}^-)^{-\cdot} \quad (7)$$

When a solution of *p*-chlorothiophenoxide ion **7** was irradiated in liquid ammonia, a yellow solid appeared. After 4 h of irradiation, a 20–37% yield of chloride ion had

formed, and a small amount of a yellow solid was present which was insoluble in most common solvents.

One possibility for the low yield of the reaction is that the electron transfer in the initiation step is slow, perhaps due the negative charge of the substrate. When the reaction was carried out in the presence of 10 mol% of chlorobenzene or 1-chloronaphthalene, which can act as initiators as shown in eq 8–11, there was not an increase in the yield of products. These results suggest not only that the initiation step is slow but also that the propagation steps are probably not efficient as well.

$$\text{ArCl} + \underset{\text{7}}{p\text{-ClC}_6\text{H}_4\text{S}^-} \xrightarrow{h\nu} (\text{ArCl})^{-\cdot} + p\text{-ClC}_6\text{H}_4\text{S}\cdot \quad (8)$$

$$(\text{ArCl})^{-\cdot} \rightarrow \text{Ar}\cdot + \text{Cl}^- \quad\quad (9)$$

$$\text{Ar}\cdot + 7 \rightarrow (\text{ArSC}_6\text{H}_4\text{Cl})^{-\cdot} \quad\quad (10)$$

$$(\text{ArSC}_6\text{H}_4\text{Cl})^{-\cdot} \rightarrow \text{ArSC}_6\text{H}_4\cdot + \text{Cl}^- \quad (11)$$

A low yield was also obtained in the photostimulated reaction of **7** in Me₂SO and in Me₂SO with ferric nitrate as catalyst.[9] We suspect that the low reactivity is mainly due to the fact that there is a negative charge conjugated with the ring, which makes it a poor electron acceptor and therefore unable to initiate the reaction.
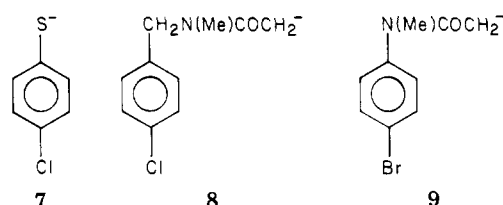


This suggestion is confirmed by the experiment that follows. It is known that the enolate ion of N,N-disubstituted amides reacts with haloarenes by the $S_{RN}1$ mechanism in liquid ammonia.[10] When a solution of N-(*p*-chlorobenzyl)-N-methylacetamide enolate ion (**8**) in ammonia was irradiated, an 80% yield of chloride ion was found. The solid formed in these reactions was almost insoluble in all common solvents, except in Me₂SO. In the dark there was no reaction. The solid product could not be fully identified, but its high melting point, its low solubility, and the high yield of chloride ion suggest that there was a coupling of several molecules of substrate.

The difference between **7** and **8** is that the last one has the leaving group and the nucleophilic center separated by an $sp^3$ carbon atom, where it does not interfere with the extra electron of the radical anion intermediate (Scheme II).

(7) Bunnett, J. F.; Sunberg, J. E. *Chem. Pharm. Bull.* **1975**, *23*, 2620.
(8) Bunnett, J. F.; Creary, X., *J. Org. Chem.*, **1974**, *39*, 3611.

(9) Scamehorn, R. G.; Bunnett, J. F. *J. Org. Chem.* **1977**, *42*, 1449.
(10) Rossi, R. A.; Alonso, R. A. *J. Org. Chem.* **1980**, *45*, 1239.

Table II. Photostimulated Reactions of *p*-Chlorothiophenoxide Ion

| expt | amt $p$-ClC$_6$H$_4$SH, mmol | amt $t$-BuONa, mmol | irradiation time, min | solvent (mL) | halide ion yield, % | product isolated,[a] g |
|---|---|---|---|---|---|---|
| 9 | 6.8 | 6.8 | 240 | NH$_3$ (200) | 29 | 0.32 |
| 10 | 7.1 | 8.8 | 240[b] | NH$_3$ (200) | | |
| 11[c] | 11.1 | 11.2 | 180 | NH$_3$ (220) | 18 | d |
| 12[e] | 8.9 | 8.9 | 180 | NH$_3$ (200) | 15 | d |
| 13 | 7.1 | 8.9[f] | 240 | Me$_2$SO (50) | 30 | 0.48 |
| 14 | 7.8 | 9.2[f] | 240[b] | Me$_2$SO (50) | 1 | |
| 15 | 7.1 | 8.9[f] | 240 | Me$_2$SO[g] (50) | 36 | d |

[a] Product insoluble in most common solvents; mp > 250 °C.  [b] Dark reaction.  [c] 10 mmol % of chlorobenzene was added.  [d] Not determined.  [e] 10 mmol % of 1-chloronaphthalene was added.  [f] CH$_3$ONa.  [g] 10 mmol % of Fe(NO$_3$)$_3$ was added.

**Scheme II[a]**



$$10 + 8 \longrightarrow$$
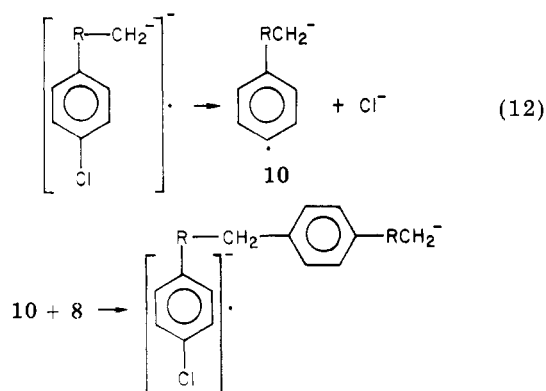
[a] R = CH$_2$N(Me)CO.

We found that the photostimulated reaction of **9** in ammonia gave only an 11% yield of bromide ion, despite the fact that bromine is a better leaving group than chlorine. This is further evidence showing that the interaction of the leaving group and the nucleophilic center through the π system is an important factor in determining a decrease of the reactivity.

When the above reaction was run with added chlorobenzene (1:5 molar ratio of chlorobenzene and **9**), we found that all the chlorobenzene had reacted, together with 53% of **9**. We can observe that now there is 5 times more reaction. These results show that when the system is completely conjugated its reactivity is low. It can, however, be increased by entrainment,[11] namely, by adding a more reactive substrate. In this particular case, a neutral molecule with a poor leaving group is a better substrate than one bearing a negative charge conjugated with a better leaving group.

## Experimental Section

**General Methods.** NMR spectra were recorded on a Varian T-60 nuclear magnetic resonance spectrometer, and all spectra are recorded in parts per million relative to Me$_4$Si ($\delta$). Potentiometric titrations were carried out with a Seybold digital pH meter, Model GTE, using a combined silver–calomel electrode. Liquid ammonia was dried over sodium metal and distilled under nitrogen into the reaction flask. All melting points are uncorrected. Reagents were all commercially available materials and were purified by standard procedures. Me$_2$SO was dried, vacuum distilled under nitrogen, and stored over molecular sieves. *N*-(*p*-Chlorobenzyl)acetamide was prepared from *p*-chlorobenzylamine and acetic anhydride: 70% yield; mp 100–102 °C (from CCl$_4$); NMR (CCl$_4$) $\delta$ 1.80 (3 H, s), 4.25 (2 H, d), 6.25 (1 H, s), 7.20 (4 H, m). *N*-Methyl-*N*-(*p*-chlorobenzyl)acetamide was obtained by reaction of *N*-(*p*-chlorobenzyl)acetamide with MeI in Me$_2$SO with KOH by a procedure already described:[12] NMR

Table III. Photostimulated Reactions of Halophenyl-*N*,*N*-disubstituted Amide Enolate Anions in Liquid Ammonia

| expt | substr (mmol) | irradiation time, min | halide ion yield, % | product isolated, g |
|---|---|---|---|---|
| 16 | 8 (2.56) | 180 | 80 | 0.10[a] |
| 17 | 8 (3.05) | 60[b] | 1 | |
| 18 | 9 (4.69) | 180 | 11 | c |
| 19 | 9[d] (5.11) | 180 | 53[e] | c |

[a] The product isolated was soluble in Me$_2$SO and insoluble in most common solvents; mp 180–200 °C.  [b] Dark reaction.  [c] Not determined.  [d] 20 mmol of chlorobenzene was added.  [e] 100% of the chlorobenzene has reacted.

(CCl$_4$) $\delta$ 2.00 (3 H, s), 2.81 (3 H, s), 4.40 (2 H, s), 7.10 (4 H, br s).

**Photostimulated Reaction of Ketone Enolate Anions.** Into a three-necked, 500-mL, round-bottomed flask equipped with a cold-finger condenser, a nitrogen inlet, and a magnetic stirrer was condensed 200–250 mL of dry ammonia. To the ammonia was added sodium metal and then *tert*-butyl alcohol to form sodium *tert*-butoxide with FeCl$_3$ as catalyst.[13] The ketone was then added followed by the *p*-dihalobenzene. The resulting mixture was irradiated with two 250-W UV lamps (350 nm, water refrigerated, Philips, Model HTP). After the time indicated in Table I, the reactions were quenched with water. Ether was added (ca. 100 mL), and the ammonia was allowed to evaporate. Water was then added, and the residue insoluble in water and in ether was filtered and washed with water and then with ether. In the water the halide liberated was potentiometrically titrated, and the analyses of the products were carried out as follows. Experiment 1: the product isolated from this reaction (0.719 g) was partially soluble in acetone and weighed 0.569 g, mp 85–95 °C. The residue insoluble in acetone weighed 0.110 g, mp >250 °C. Experiment 3: the oil obtained (0.550 g) was column chromatographed on silica gel. It was not possible to isolate a pure fraction. By NMR analysis, however, the compound was mainly 1,4-bis(2-oxopropyl)benzene. Experiment 4: the solid isolated from this reaction was recrystallized in ethanol, giving 1,4-bis(3,3-dimethyl-2-oxobutyl)benzene: 1.068 g (65% yield); mp 97–100 °C. A pure fraction was obtained by recrystallization: mp 101–101.5 °C; NMR (CCl$_4$) $\delta$ 1.21 (9 H, s), 3.70 (4 H, s), 7.0 (4 H, s).

**Photostimulated Reactions of *p*-Chlorothiophenoxide Ion.** Experiment 9: the procedure was similar to those already described. To a solution of *t*-BuONa in liquid ammonia was added *p*-chlorothiophenol, and the mixture was then irradiated. After the reaction was quenched with water, the ammonia was allowed to evaporate; the residue (0.32 g) was insoluble in NaOH solution (10%), water, ethanol, acetone, ether, benzene, and Me$_2$SO; mp >250 °C. Experiment 13: to 50 mL of Me$_2$SO under nitrogen were added MeONa and *p*-chlorothiophenol, and then the mixture was irradiated. After the time indicated in Table II, the reaction was quenched with water (100 mL), and the solid which formed

(11) Swartz, J. E.; Bunnett, J. F. *J. Org. Chem.* 1977, *42*, 1449.

(12) Isele, C. L.; Lëttringhaus, A. *Synthesis*, 1971, 266.
(13) Rossi, R. A.; de Rossi, R. H. *J. Org. Chem.* 1974, *39*, 866.

was filtered, washed with NaOH (10%), water, and all common solvents, including Me$_2$SO, and weighed: 0.48 g; mp >250 °C.

**Photostimulated Reactions of Halophenyl *N,N*-Disubstituted Amide Enolate Anions.** To an equimolecular amount of amide ions in liquid ammonia was added the substrate, and after the time indicated in Table III, the reaction was quenched with water. The residue obtained was insoluble in most common solvents but was soluble in Me$_2$SO and was precipitated by addition of water, giving a fine powder, mp 180–200 °C.

**Registry No. 1a**, 106-46-7; **1b**, 106-37-6; **1c**, 589-87-7; **2a**, 24262-31-5; **2b**, 64723-95-1; **3b**, 74824-50-3; **5**, 74824-46-7; **7**, 35337-68-9; **8**, 74824-47-8; **9**, 74824-48-9; *N*-(*p*-chlorobenzyl)acetamide, 57058-33-0; *p*-chlorobenzylamine, 104-86-9; *N*-methyl-*N*-(*p*-chlorophenyl)acetamide, 10219-10-0; 1,4-bis[(2-propenyl)oxy]benzene, 42237-99-0; 1,4-bis[(3,3-dimethyl-2-butenyl)oxy]benzene, 74824-49-0; *p*-chlorothiophenol, 106-54-7; chlorobenzene, 108-90-7.

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## Removal of Peroxide Impurities by Zeolites

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The literature[1] provides a large number of chemical methods, mainly of a reductive nature, for the removal of peroxides from reagents or solvents, including treatment with alkalies, sodium sulfite, ferrous sulfate, stannous chloride, lead dioxide, zinc and acid, sodium and alcohol, lithium aluminum hydride, and triphenylphosphine. A disadvantage of these methods is the time required, as additional purification by distillation and/or drying is necessary. Moreover, in the case of tetrahydrofuran containing a high concentration of peroxides, the application of some of these methods can be dangerous.[2,3]

Relatively little attention has been paid to the removal of peroxides by selective adsorption. It has been reported that the peroxide content can be reduced by passing the reagent/solvent down an alumina column.[4] We observed, as part of an investigation of the zeolite-catalyzed hydrobromination of alkenes,[5] that peroxide impurities of the alkene compound were selectively adsorbed by zeolites. the extent of adsorption was found to depend on the type of zeolite; with zeolite NaX a fast and essentially complete adsorption was observed. A close examination of the literature revealed that the use of NaX pellets has been suggested for the removal of moderate quantities of peroxides from tetrahydrofuran, but no quantitative data were presented.[6]

Since with NaX side reactions are not expeted to occur due to its weak acidity and/or the absence of catalytically active cations, the use of NaX was investigated in more detail.[7] For comparison experiments were performed with

basic alumina. Typical peroxide-containing solvents like tetrahydrofuran and diisopropyl ether and reagents known to be susceptible to hydroperoxide formation like cyclohexene and 1-octene were used as test substrates. The peroxide oxygen content was quantitatively determined by a photometric ferric thiocyanate method.[8]

Table I shows the results obtained when the reagents were treated with the adsorbent in a slurry technique. With zeolite NaX a strong reduction of the peroxide content of tetrahydrofuran and diisopropyl ether was obtained, whereas cyclohexene and 1-octene became nearly peroxide free. Gas-chromatographic analysis showed that no isomerization of 1-octene occurred. It may be mentioned that drying tetrahydrofuran with zeolite NaA pellets also resulted in some reduction of the peroxide content, showing outer surface adsorption on the zeolite pellet.

For basic alumina a similar order for the removal of peroxides was observed as with NaX. Here good results were obtained for cyclohexene and 1-octene, but only if physically adsorbed water was removed by calcination at 250 °C. For the ethereal solvents the application of a slurry technique using alumina seems less suitable. Therefore, some experiments were performed where these solvents were passed down a column of adsorbent.

When NaX is used in a column technique (see Figure 1) an efficient removal of peroxides was observed. Though not shown in the figure, for tetrahydrofuran (peroxide content 177 $\mu$mol/L) a breakthrough was observed after 400 mL, showing an effective use of adsorbent of 0.6% w/v. Initially alumina also gives good results when applied in a column, but its adsorption capacity is much smaller than that of NaX.

The reduction of the peroxide content with NaX may be caused by selective adsorption and/or by decomposition of the peroxides. Some experiments were performed in which an equal volume of methanol or ethanol was subsequently added to the slurry to desorb the adsorbed species in order to find out which phenomenon predominates with NaX, using a slurry technique. It appeared that in this way the greater part of the peroxides was recovered by desorption, showing that the removal of peroxides by NaX is mainly caused by physical adsorption into the zeolite.

It is known that certain zeolites induce decomposition[9-13] of peroxides. An exploratory series of experiments were performed with zeolite Co(II)X as the adsorbent in order to see whether such decomposition improves the purification of peroxide-contaminated solvents. Slightly improved peroxide removal was obtained, as shown by the data in Table II. With 1-octene traces of 2-octenes were observed after treatment with CoX, showing the isomerization activity of CoX. In contrast to NaX, recovery of the removed peroxides upon addition of methanol or ethanol was very low, showing that with CoX adsorption of the peroxides is followed by a decomposition of the adsorbed species. For instance, cyclohexene $\alpha$-hydroperoxide was found to yield 2-cyclohexene-1-ol and 2-cyclohexen-1-one upon treatment with CoX. Both decomposition products adsorb selectively with respect to cyclohexene into zeolite CoX.[14]

(1) R. D. Mair and R. T. Hall, "Organic Peroxides", Vol. II, D. Swern, Ed., Wiley, New York, 1971, p 541.
(2) R. Halonbrenner and W. Kläui, *Chem. Eng. News*, **56**, 2 (1978).
(3) H. E. Baumgarten, "Organic Syntheses", Collect. Vol. V, Wiley, New York, 1973, p 976.
(4) W. Dasler and C. D. Bauer, *Ind. Eng. Chem., Anal. Ed.*, **18**, 52 (1946).
(5) Th. M. Wortel, S. Rozendaal, and H. van Bekkum, *Recl. Trav. Chim. Pays-Bas*, **98**, 505 (1979).
(6) N. Rabjahn, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, 1963, p 474.
(7) Th. M. Wortel, Ph.D. Thesis, Delft University of Technology, 1979.

(8) G. H. Smith, *J. Sci. Food Agric.*, **3**, 26 (1952).
(9) S. E. Rapichinskaya and G. A. Blokh, *Izv. Vyssh. Uchebn. Zaved., Tekhnol. Legk. Prom.*, **57** (1965); *Chem. Abstr.*, **64**, 2257 (1966).
(10) J. Richly, *J. Polym. Sci., Part B*, **7**, 843 (1969).
(11) J. Richly, *J. Polym. Sci., Part C*, **40**, 133 (1973).
(12) K. H. Bergk and F. Wolf, *Z. Chem.*, **15**, 152 (1975).
(13) K. H. Bergk, F. Wolf, and B. Walter, *J. Prakt. Chem.*, **321**, 529 (1979).