

- (15) H. M. Rosenberg and M. P. Serve, *J. Org. Chem.*, **36**, 3015 (1971).
 (16) K. A. Muszkat and E. Fischer, *J. Chem. Soc. B*, 662 (1967).
 (17) J. Bendig, M. Beyermann, and D. Kreysig, *Tetrahedron Lett.*, 3659 (1977).
 (18) For tentative stereochemical assignments, see Experimental Section.
 (19) W. H. Laarhoven and R. J. F. Nivard, *Recl. Trav. Chim. Pays-Bas*, **84**, 1478 (1965).
 (20) M. L. Hallensleben, *Eur. Polym. J.*, **9**, 227 (1973).
 (21) Assuming an approximately constant energy gap between π and π^* orbitals, the electron affinity will increase with increasing ionization potential.
 (22) R. Dietz and M. E. Peover, *Disc. Faraday Soc.*, **45**, 154 (1968).
 (23) (a) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970); (b) W. Klöpffer in "Organic Molecular Photophysics", J. B. Birks, Ed., Wiley-Interscience, London, 1973, Chapter 7.
 (24) (a) S. Ander, H. Blume, G. Heinrich, and D. Schulte-Frohlinde, *Chem. Commun.*, 745 (1968); (b) H. Kellawi and D. R. Rosseinsky, *J. Chem. Soc. A*, 1207 (1969).
 (25) Y. Shirota, J. Nagata, and H. Mikawa, *Chem. Lett.*, 49 (1972).
 (26) (a) M. Itoh, T. Mimura, H. Usui, and T. Okamoto, *J. Am. Chem. Soc.*, **95**, 4388 (1973); (b) M. Itoh and T. Mimura, *Chem. Phys. Lett.*, **24**, 551 (1974); (c) M. Irie, S. Tomimoto, and K. Hayashi, *J. Phys. Chem.*, **76**, 1419 (1972).
 (27) D. R. Arnold, *Adv. Photochem.*, **6**, 301 (1968).
 (28) S. Farid, S. E. Hartman, J. C. Doty, and J. L. R. Williams, *J. Am. Chem. Soc.*, **97**, 3697 (1975).
 (29) (a) H. Beens and A. Weller, *Chem. Phys. Lett.*, **2**, 140 (1968); (b) J. Saltiel, D. E. Townsend, B. D. Watson, and P. Shannon, *J. Am. Chem. Soc.*, **97**, 5688 (1975); (c) K. H. Grellmann and U. Scukow, *Chem. Phys. Lett.*, **32**, 250 (1975).
 (30) (a) H. Ohta, D. Creed, P. H. Wine, R. A. Caldwell, and L. A. Melton, *J. Am. Chem. Soc.*, **98**, 2002 (1976); (b) R. A. Caldwell and L. Smith, *ibid.*, **96**, 2994 (1974); (c) R. A. Caldwell, D. Creed, and H. Ohta, *ibid.*, **97**, 3246 (1975); (d) D. Creed, R. A. Caldwell, H. Ohta, and D. C. DeMarco, *ibid.*, **99**, 277 (1977).
 (31) C. Pac and H. Sakurai, *Chem. Lett.*, 1067 (1976).
 (32) (a) N. C. Yang, D. M. Shold, and B. Kim, *J. Am. Chem. Soc.*, **98**, 6587 (1976); (b) J. Saltiel, D. E. Townsend, B. D. Watson, P. Shannon, and S. L. Finson, *ibid.*, **99**, 884 (1977).
 (33) R. O. Campbell and R. S. H. Liu, *Mol. Photochem.*, **6**, 207 (1974).
 (34) P. P. Wells and H. Morrison, *J. Am. Chem. Soc.*, **97**, 154 (1975).
 (35) J. H. Bowie, D. H. Williams, P. Madsen, G. Schroll, and S. O. Lawesson, *Tetrahedron*, **23**, 305 (1967).
 (36) R. Stoermer and F. Bacher, *Chem. Ber.*, **55**, 1860 (1922).

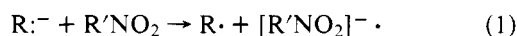
Electron Transfer Processes. 20. Conversion to *p,p'*-Dinitrostilbene and Other Examples of the $S_{RN}1$ Substitution Reactions of *p*-Nitrobenzyl Derivatives

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Abstract: The following reactions have been demonstrated to proceed by electron-transfer mechanisms and to involve intermediate radicals and radical anions: (a) the coupling of the anion of 2-nitropropane with *N*-(*p*-nitrobenzyl)pyridinium chloride to form 2-nitro-2-methyl-1-(*p*-nitrophenyl)propane; (b) the coupling of the anion of 2-nitropropane with *p*-nitro- α,α -dimethylbenzyl phenyl sulfoxide or sulfone to yield 2-nitro-3-(*p*-nitrophenyl)-2,3-dimethylbutane; (c) the base-catalyzed coupling of *p*-nitrobenzyl chloride or dimethyl-*p*-nitrobenzylsulfonium bromide to give *p,p'*-dinitrostilbene; (d) the substitution reaction of thiophenoxide ion with *p*-nitro- α,α -dimethylbenzyl phenyl sulfoxide or sulfone to yield *p*-nitro- α,α -dimethylbenzyl phenyl sulfide.

It is recognized that numerous reactions of *p*-nitrobenzyl derivatives proceed by free-radical and/or radical-anion intermediates. It has been demonstrated by ESR spectroscopy that a wide variety of carbanions will transfer an electron to nitrobenzenes or nitroalkanes:¹⁻³



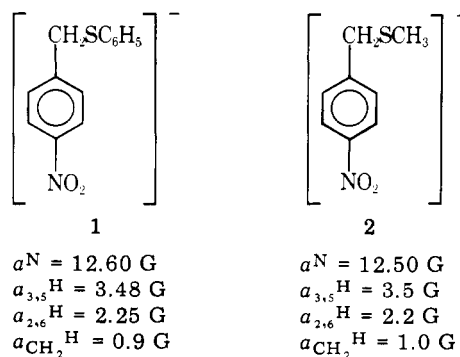
Reaction 1 has been shown to be involved in the spontaneous disproportionation of *p*-nitrotoluene,²⁻⁴ in the autoxidation of 2-nitropropane or *p*-nitrotoluene in basic solutions,^{5,6} in the oxidation of fluorene anion catalyzed by nitroaromatics,⁷ in the C-alkylation of the anion of 2-nitropropane by 2-halo-2-nitropropanes,⁸ *p*-nitrobenzyl chloride,⁸⁻⁹ *p*-nitrobenzyl dimethyl sulfonium salts,⁸ *p*-nitro- α,α -dimethylbenzyl chloride,¹⁰ α,β -dinitrocumene,¹¹ *p*-nitrobenzyl pentachlorobenzoate,⁹ and undoubtedly trimethyl-*p*-nitrobenzylammonium salts,⁸⁻¹² in the oxidative dimerization by nitroaromatics or 2-chloro-2-nitropropane of the anions of indoxyl,¹³ 1,3-dithianes,^{14,15} diphenylacetonitrile¹⁵ or ω,ω -di(methylmercapto)acetophenone,¹⁵ and other benzylic or allylic anions.¹⁵

We now report some other examples of a radical chain process involving the *p*-nitrobenzyl moiety including (a) the base-catalyzed reaction of *p*-nitrobenzyl sulfonium salts or *p*-nitrobenzyl chloride to yield the *p,p'*-dinitrostilbene, (b) the substitution reactions of *N*-(*p*-nitrobenzyl)pyridinium chloride and *p*-nitro- α,α -dimethylbenzyl phenyl sulfoxide and sulfone with the anions of 2-nitropropane or thiophenol.

Results and Discussion

Reaction of *p*-Nitrobenzyl Chloride with Mercaptide Ion.

The reaction on thiophenoxide or methyl mercaptide¹⁶ ions with *p*-nitrobenzyl chloride in ethanol yields the corresponding *p*-nitrobenzyl sulfides (in 97 and 68% yields, respectively). When the reactions of *p*-nitrobenzyl chloride are performed in an ESR cell the signals of the radical anions of *p*-nitrobenzyl phenyl sulfide (**1**) and *p*-nitrobenzyl methyl sulfide (**2**) are



readily detected. Radical ions **1** and **2** are also formed when the performed sulfides are treated with the mercaptide ions in ethanol. The reaction of thiophenoxide ion with *p*-nitrobenzyl chloride at 0 °C in ethanol was not significantly retarded by 10 mol % of *p*-dinitrobenzene or significantly accelerated by

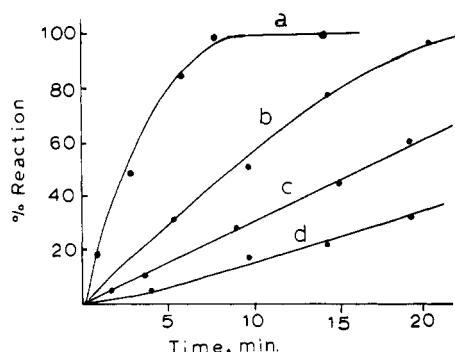


Figure 1. Reaction of 0.01 M NaSCH₃ with 0.01 M *p*-nitrobenzyl chloride in ethanol at 0 °C under nitrogen: (a) reactions illuminated with a sunlamp in Pyrex; (b) reactions in ordinary fluorescent lighting; (c) reactions in dark; (d) reactions in presence of 10 mol % of *p*-dinitrobenzene and ordinary fluorescent lighting.

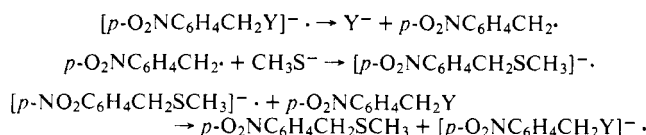
Table I. Percent Yield of *p,p'*-Dinitrostilbene in the Reaction of 0.09 M *p*-Nitrobenzyl Chloride with 0.6 M Sodium Ethoxide in Ethanol, Reaction Time = 7 min

conditions	27 °C	-6 °C
dark	35	0
fluorescent light ^a	62	35
sunlamp	70	44
10% <i>m</i> -dinitrobenzene ^a	28	trace
10% <i>p</i> -dinitrobenzene ^a	15	0

^a Ordinary laboratory lighting.

illumination with a sunlamp. We conclude that this reaction is occurring nearly exclusively by an ionic (S_N2) pathway. The reaction of *p*-nitrobenzyl chloride with methyl mercaptide ion in ethanol is accompanied by 2–3% of *p,p'*-dinitrobenzyl, a product suggestive of radical intermediates. The reaction at 0 °C is retarded by 10 mol % of *p*-dinitrobenzene and accelerated by illumination. However, the retardation and acceleration are not dramatic (Figure 1). We conclude that the S_{RN}1 process¹⁷ (Y = Cl) (Scheme I) and the S_N2 substitution reaction are occurring simultaneously.

Scheme I



Reaction of *p*-Nitrobenzyl Chloride with Ethoxide Ion. *p*-Nitrobenzyl chloride reacts in the presence of ethoxide ion to give a 75–80% yield of the *p,p'*-dinitrostilbene in 10–15 min at room temperature.^{18,19} An α -elimination (carbene) mechanism (α -E₁cB) has been proposed for this^{20,21} and similar processes.^{22,23} However, products of the reaction of the carbene with the solvent are not found and attempts to trap *p*-nitrocarbene under the reaction conditions are unsuccessful.^{24,25}

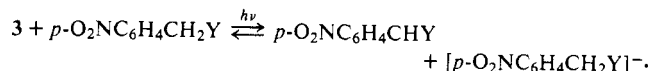
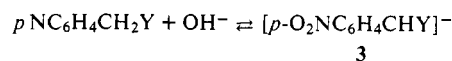
Table I presents experimental evidence highly suggestive of a radical chain process for this coupling–elimination reaction.

The most reasonable radical-chain mechanism which will explain these results is outlined in Scheme II. The data of Table I does not demand that this mechanism is the only one operating at elevated temperatures, and indeed at 27 °C perhaps a competing ionic displacement–elimination mechanism is occurring, as proven by Hauser in the formation of stilbene from benzyl chloride and sodium amide,²⁶ and favored for the reaction of trinitrobenzyl chloride with sodium hydroxide²⁷ and for the coupling reaction of bis(4-nitrophenyl)methyl

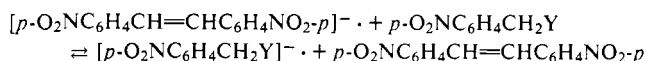
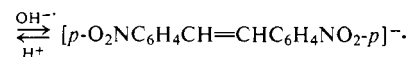
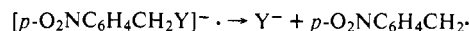
chloride and α -phenyl-4-nitrobenzyl chloride with sodium hydroxide in aqueous dioxane.²⁸

Scheme II (Y = Cl)

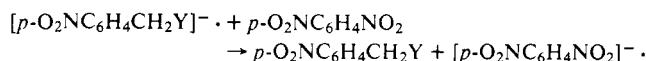
initiation



propagation

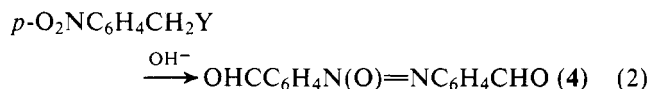


inhibition



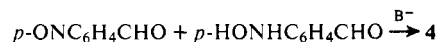
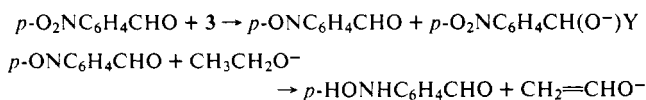
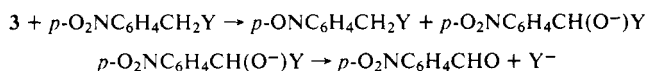
Reaction of Dimethyl-*p*-nitrobenzylsulfonium Bromide with Hydroxide Ion in Ethanol. Coupling to give *p,p'*-dinitrostilbene has been indicated to be a carbenoid process.^{22,23} However, such a mechanism is completely inconsistent with our results, at least in ethanol at 60–65 °C. It is known that this reaction is accelerated by light but this in itself does not distinguish between a carbenoid and free-radical pathway.^{8,22,31} However, if *p*-dinitrobenzene (0.015 M) is added to deoxygenated solutions of the sulfonium salt (0.1 M) in 95% ethanol containing 0.3 M sodium hydroxide, the yield of the stilbene in 15 min is decreased from 75–80 to 0%. Scheme II is thus strongly indicated.

Reaction of *N*-(*p*-Nitrobenzyl)pyridinium Chloride with Hydroxide Ion. Reaction of the pyridinium salt with hydroxide ion in 90% aqueous ethanol yields *p*-azoxybenzaldehyde (4) as the predominant product,³² a reaction similar to that observed for *p*-nitrobenzylthioacetic acid.³³ We found that the reaction



Y = pyridinium, occurs in the presence or absence of oxygen and was not affected by irradiation (sunlamp) or by the presence of *p*-dinitrobenzene. Scheme II does not operate with Y = pyridinium. Instead, conversion of the substrate to *p*-nitrosobenzaldehyde and *p*-hydroxylaminobenzaldehyde appears to be occurring by Scheme III.

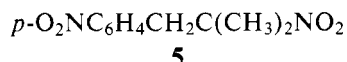
Scheme III (Y = pyridinium ions)



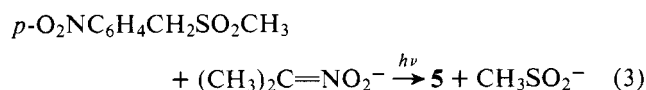
The condensation of nitrosobenzenes and phenylhydroxylamines to azoxybenzenes proceeds via nitrosobenzene radical anions under some conditions³⁴ and apparently the coupling of these radical ions is sufficiently fast that oxygen or *p*-dinitrobenzene do not significantly interfere with this process.

We have found that in basic ethanol solutions that *p*-nitrobenzyl methyl or phenyl sulfides will react with oxygen to yield a mixture of **4**, *p*-nitrobenzaldehyde, and the disulfide. In independent experiments it was shown that *p*-nitrobenzaldehyde does not spontaneously yield **4** in the presence of base or base plus mercaptan. The autoxidation of the *p*-nitrobenzyl sulfides in basic solution apparently yields initially *p*-nitrobenzaldehyde from which the last three steps of Scheme III can follow with $Y = SR$.

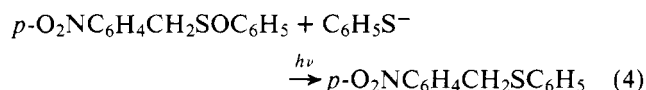
Further Examples of the Reaction of the Anion of 2-Nitropropane with *p*-Nitrobenzyl Derivatives. Potentially *p*-nitrobenzyl sulfides, sulfoxides, and sulfones can enter into Scheme I with the leaving group $Y = RS^-$, RSO^- , RSO_2^- , although the stability observed for **1** and **2** argues against such processes occurring readily for the sulfides. *p*-Nitrobenzyl nitrile, sulfide, sulfoxide, or sulfone can all be recovered from basic alcoholic solutions after irradiation in the absence of oxygen. In the presence of the anion of 2-nitropropane and irradiation for 24 h, the methyl or phenyl sulfides or sulfoxide failed to yield any of the coupling product (**5**) expected from Scheme I. *p*-Ni-



trobenzyl methyl sulfone did give a low yield (32%) of **5** upon irradiation (24 h):

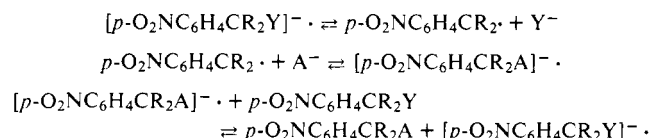


In apparently a similar reaction *p*-nitrobenzyl phenyl sulfoxide when irradiated in the presence of thiophenoxide anion yielded the sulfide in 20% yield (reaction 4). However, oxygen-transfer reactions cannot be excluded.

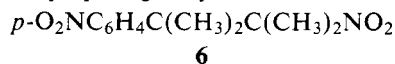


In the presence of the anion of 2-nitropropane *N*-(*p*-nitrobenzyl)pyridinium salts are converted to **5** in good yield in a reaction which is quenched completely by *p*-dinitrobenzene and which shows pronounced photochemical acceleration. Reaction Scheme IV is undoubtedly involved ($R = H$; $Y = \text{pyridinium ion}$; $A = 2\text{-nitro-2-propyl}$).

Scheme IV

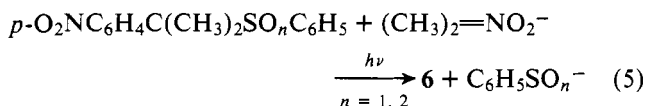


The failure of *p*-nitrobenzyl sulfoxide or sulfone to enter readily into Scheme IV may be connected with the presence of acidic benzylic hydrogen atoms. Thus, we have observed that the *p*-nitro- α,α -dimethylbenzyl phenyl sulfoxide and sulfone will react with phenyl mercaptide ion (20-h irradiation) to yield 45 and 60% of the sulfide (Scheme IV, $R = \text{CH}_3$; $X = \text{C}_6\text{H}_5\text{SO}$ or $\text{C}_6\text{H}_5\text{SO}_2$; $A = \text{C}_6\text{H}_5\text{S}$) while under similar conditions the anion of 2-nitropropane gives yields of **6** of 50 and 60% from



the sulfoxide and sulfone (Scheme IV, $R = \text{CH}_3$; $X = \text{C}_6\text{H}_5\text{SO}$ or $\text{C}_6\text{H}_5\text{SO}_2$; $A = (\text{CH}_3)_2\text{C}=\text{NO}_2$). The reactions were ac-

companied by *p,p'*-dinitrodimethyl (up to 10%) as well as considerable amounts of 2,3-dimethyl-2,3-dinitrobutane or diphenyl disulfide. No reaction of the *p*-nitro- α,α -dimethylbenzyl phenyl sulfide with the anions of 2-nitropropane was observed (reaction 5, $n = 0$).



The *S_{RN}1* substitution of the sulfone group has also been observed in reactions of aliphatic α -nitro sulfones ($R_2\text{C}(\text{NO}_2)\text{SO}_2\text{Ar}$) with the anions of nitroalkanes.³⁵

Experimental Section

Preparation of Sulfides. *p*-Nitrobenzyl chloride (41 mmol) in 100 mL of ethanol was added under nitrogen to a solution of 120 mmol of benzenethiol in 100 mL of ethanol in which 0.12 g-atom of sodium had been dissolved.³⁶ *p*-Nitrobenzyl phenyl sulfide, mp 74–75 °C (lit.³⁶ mp 79 °C), was isolated after stirring for 30 min by acidification followed by ether extraction in 97% yield: ¹H NMR (CDCl_3) δ 4.15 (s, 2), 7.25 (m, 7), 8.05 (d, 2). The same procedure was used for the preparation of *p*-nitro- α,α -dimethylbenzyl phenyl sulfide¹⁰ in 86% yield; ¹H NMR (CDCl_3) δ 1.75 (s, 6), 7.3 (m, 7), 8.1 (d, 2); mass spectrum (70 eV) m/e 273 (M^+). To *p*-nitrobenzyl chloride (74 mmol) in 200 mL of ethanol under nitrogen was added 45 mL of a 2.5 M solution (140 mmol) of sodium and methyl mercaptan in ethanol.³⁷ *p*-Nitrobenzyl methyl sulfide was isolated after 10 min of stirring by acidification and ether extraction in 68% yield: mp 70 °C (lit.¹⁶ mp 70–72 °C); ¹H NMR (CDCl_3) δ 1.79 (s, 3), 3.47 (s, 2), 7.1 (d, 2), 7.9 (d, 2); mass spectrum (70 eV) m/e 183 (M^+).

Preparation of Sulfoxides.^{38,39} To the appropriate sulfide (100 mmol) dissolved in 50 mL of chloroform at –10 °C was added 1 equiv of *m*-chloroperbenzoic acid (83% assay) in 50 mL of chloroform. After standing for 24 h at –20 °C the benzoic acid was removed by filtration and the chloroform washed with aqueous sodium bicarbonate and water. The chloroform was evaporated under reduced pressure to leave the sulfoxides in high purity in yields of 90–95%.

Phenyl *p*-nitrobenzyl sulfoxide had a mp of 153–155 °C (lit.⁴⁰ mp 161–162 °C); ¹H NMR (CDCl_3) δ 4.2 (AB quartet); IR 1045 cm^{-1} . Phenyl α,α -dimethyl *p*-nitrobenzyl sulfoxide gave an IR absorption at 1025 cm^{-1} ; ¹H NMR (CDCl_3) δ 1.6 (d, 6), 7.5 (m, 7), 8.2 (d, 2). The sulfoxide could be oxidized to the known sulfone⁴² by 30% hydrogen peroxide in aqueous acetic acid. Methyl *p*-nitrobenzyl sulfoxide, mp 101–102 °C (lit.⁴¹ mp 108 °C), had an AB quartet at δ 4.1 and IR absorption at 1030 cm^{-1} .

Preparation of Sulfones. Phenyl *p*-nitrophenyl sulfide was dissolved in glacial acetic acid and an excess of aqueous hydrogen peroxide (30% assay) added. After 45 min of reflux the reaction mixture was added to twice its volume of water and extracted with chloroform. The chloroform solution was dried by molecular sieves and evaporated under reduced pressure to give a quantitative yield of phenyl *p*-nitrobenzyl sulfone, mp 202–203 °C (lit.⁴⁰ mp 209 °C), with a ¹H NMR singlet at δ 4.5, IR 1100, 1350 cm^{-1} . In a similar fashion methyl *p*-nitrobenzyl sulfone, mp 159–163 °C (lit.⁴³ mp 160–165 °C), was prepared. An alternate procedure applicable to phenyl *p*-nitro- α,α -dimethylbenzyl sulfides involved the addition of the sulfide to a mixture of acetic acid (60%)–water (40%) acidified to 3 M with sulfuric acid. An excess of aqueous hydrogen peroxide (30%) was added dropwise over 15 min and the mixture refluxed for 24 h before dilution with water and chloroform extraction to yield the sulfone,⁴² mp 82–84 °C, in 80% yield: ¹H NMR δ 1.9 (s, 6), 7.6 (m, 7), 8.1 (d, 2); mass spectrum (70 eV) m/e 304 (M^+).

Coupling Reactions with the Anion of 2-Nitropropane. A solution (50 mL, 0.2 M) of an α -substituted *p*-nitrotoluene in DMF was deoxygenated by a stream of nitrogen for 10 min. A separately deoxygenated solution of lithium ethoxide and 2-nitropropane (50 mL, 0.5 M) in DMF was injected by syringe through a rubber septum into the first solution. Temperatures were controlled by immersing the reaction flask in a thermostat. Irradiation was provided by a 275-W sunlamp 12 in. from the reaction vessel. After a reaction time of 15 h the reaction mixture was acidified with 200 mL of 0.03 N sulfuric acid and the precipitate extracted with chloroform (*p*-nitrobenzyl phenyl sulfoxide or sulfone, 4-nitro- α,α -dimethylbenzyl sulfoxide or

sulfone) or ether (*p*-nitrobenzyl phenyl and methyl sulfides, *p*-nitrobenzyl methyl sulfone) to yield **5**⁴⁴ or **6**.^{10,42}

N-(*p*-Nitrobenzyl)pyridinium chloride⁴⁵ was reacted with the lithium salt of 2-nitropropane in ethanol by a previously described procedure.⁸ The reaction required 8 h for completion in the absence of illumination but only 2 h when illuminated. There was no reaction in the presence of 0.002 M *p*-dinitrobenzene.

Reactions of α -Substituted *p*-Nitrotoluenes with Mercaptide Anions.

To *p*-nitrobenzyl chloride in ethanol (25 mL, 0.02 M, deoxygenated by dry nitrogen) was added by syringe 25 mL of a deoxygenated 0.02 M solution of sodium and methyl mercaptan or benzenethiol in ethanol. The stirred reaction mixture was placed in a thermostat and 5-mL aliquots withdrawn by syringe and added to 20 mL of a 0.0115 M solution of *p*-toluenesulfonic acid. Excess acid was titrated with standard base to the bromophenol blue end point. Irradiation was accomplished by a 275 sunlamp positioned 12 in. from the reaction flask.

Sodium thiophenoxide in ethanol or potassium thiophenoxide in DMF (from potassium *tert*-butoxide and thiophenol) were reacted with *p*-nitrobenzyl phenyl sulfoxide or sulfone and with *p*-nitro- α,α -dimethylbenzyl phenyl sulfoxide or sulfone. In DMF 18 h of sunlamp irradiation produced 30% of the sulfide from *p*-nitrobenzyl phenyl sulfone. In DMF the *p*-nitro- α,α -dimethylbenzyl sulfoxide and sulfone yielded 45 and 60% of *p*-nitro- α,α -dimethylbenzyl phenyl sulfide after 20 h of irradiation.

Treatment of α -Substituted *p*-Nitrotoluenes with Strong Base.

p-Nitrobenzyl phenyl sulfide, sulfoxide, and sulfone could be recovered upon acidification from a DMF solution of potassium *tert*-butoxide under nitrogen. Irradiation by a sunlamp had no effect. *p*-Nitrobenzyl chloride dissolved in ethanol (40 mL, 0.15 M) was deoxygenated by nitrogen and added by syringe to 25 mL of 1.6 M sodium ethoxide in ethanol. All solutions were thermostated. After 7 min the reaction mixture was quenched with 200 mL of dilute sulfuric acid and the precipitate washed with 75 mL of ethyl ether to yield *p,p'*-dinitrostilbene. Dimethyl-*p*-nitrobenzyl sulfonium bromide, mp 111–112 °C (lit.⁴⁶ mp 111–112 °C) (7 mmol), was reacted in 95% ethanol (70 mL) at 60 °C under nitrogen for 18 h with 25 mmol of sodium hydroxide to yield 75–80% of *p,p'*-dinitrostilbene. No stilbene was detected when 1 mmol of *p*-dinitrobenzene was added. Under the above conditions *N*-(*p*-nitrobenzyl)pyridinium chloride yielded *p*-azoxybenzaldehyde, mp 193 °C (lit.³² mp 193–194 °C).

References and Notes

- (1) Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1962**, *84*, 4155.
- (2) Russell, G. A.; Janzen, E. G. *J. Am. Chem. Soc.* **1962**, *84*, 4153.
- (3) Russell, G. A.; Janzen, E. G.; Strom, E. T. *J. Am. Chem. Soc.* **1964**, *86*, 1807.
- (4) Russell, G. A.; Janzen, E. G. *J. Am. Chem. Soc.* **1967**, *89*, 300.
- (5) Russell, G. A. *J. Am. Chem. Soc.* **1953**, *75*, 5011.

- (6) Russell, G. A.; Moye, A. J.; Janzen, E. G.; Mak, S.; Talaty, E. R. *J. Org. Chem.* **1967**, *32*, 137.
- (7) Russell, G. A.; Janzen, E. G.; Bemis, A. G.; Geels, E. J.; Moye, A. J.; Mak, S.; Strom, E. T. *Adv. Chem. Ser.* **1965**, *51*, 112.
- (8) Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 5663. **1968**, *90*, 347.
- (9) Kornblum, N.; Michael, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 5660, 5663.
- (10) Kornblum, N.; Davies, T. M.; Earl, G. W.; Green, G. S.; Holy, N. L.; Kerber, R. C.; Manthey, J. W.; Musser, M. T.; Snow, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 725.
- (11) Kornblum, N.; Davies, T. M.; Earl, G. W.; Green, G. S.; Holy, N. L.; Kerber, R. C.; Manthey, J. W.; Musser, M. T.; Snow, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 5714.
- (12) Shechter, H.; Kaplan, R. B. *J. Am. Chem. Soc.* **1951**, *73*, 1883.
- (13) Russell, G. A.; Kaupp, G. J. *J. Am. Chem. Soc.* **1969**, *91*, 3851.
- (14) Baarschers, W. H.; Loh, T. L. *Tetrahedron Lett.* **1971**, 3483.
- (15) Russell, G. A.; Jawdoski, M.; Makosza, M. *J. Am. Chem. Soc.*, **1979**, *101*, 2355.
- (16) Brand, K.; Kranz, K. W. *J. Prakt. Chem.* **1927**, *115*, 143.
- (17) Kim, J. K.; Bunnett, J. F. *J. Am. Chem. Soc.* **1970**, *92*, 7463, 7464.
- (18) Bischoff, C. A. *Chem. Ber.* **1888**, *21*, 2072.
- (19) Walden, P.; Kernbaum, A. *Chem. Ber.* **1890**, *23*, 1958.
- (20) Hanna, S. B.; Iskander, Y.; Riad, Y. *J. Chem. Soc.* **1961**, 217.
- (21) Soleib, D.; Iskander, Y. *J. Chem. Soc. B* **1967**, 1154.
- (22) Swain, C. G.; Thornton, E. R. *J. Am. Chem. Soc.* **1961**, *83*, 4033.
- (23) Rothberg, I.; Thornton, E. R. *J. Am. Chem. Soc.* **1964**, *86*, 3296, 3302.
- (24) Goh, S. H. *J. Chem. Soc. C* **1971**, 2275.
- (25) Closs, S. L.; Goh, S. H. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2103.
- (26) Hauser, C. R.; Brasen, W. R.; Skell, P. S.; Kantor, S. W.; Broadhag, A. E. *J. Am. Chem. Soc.* **1956**, *78*, 1653. Brasen, W. R.; Kantor, S. W.; Skell, P. S.; Hauser, C. R. *ibid.* **1957**, *79*, 397.
- (27) Shipp, K. G.; Kaplan, L. A. *J. Org. Chem.* **1966**, *31*, 857. Shipp, K. G. *ibid.* **1964**, *29*, 2620.
- (28) Tewfik, R.; Fovad, F. M.; Farrell, P. G. *J. Chem. Soc., Perkin Trans. 2* **1974**, *31*, 1975, 384. A radical coupling mechanism has been discussed by Closs and Goh,^{25,29} but the strong catalytic and inhibitory effects observed in this work and by Hanna³⁰ require a chain mechanism with appreciable kinetic chain length.
- (29) Closs, S. L.; Goh, S. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2473. Goh, S. H.; Kam, T. S. *ibid.* **1978**, 648.
- (30) Hanna, S. B.; Ruehle, P. H. *J. Org. Chem.* **1975**, *40*, 3882.
- (31) Trost, B. M. *J. Am. Chem. Soc.* **1966**, *88*, 1587.
- (32) Hanna, S. B. *Chem. Commun.* **1965**, 487.
- (33) Iskander, Y.; Riad, Y. *J. Chem. Soc.* **1951**, 2084. **1961**, 2397.
- (34) Russell, G. A.; Geels, E. J.; Smentowski, F. S.; Chang, K. Y.; Reynolds, J.; Daupp, G. *J. Am. Chem. Soc.* **1967**, *89*, 3821.
- (35) Zeilstra, J. J.; Engberts, B. J. B. F. N. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 954. Kornblum, N.; Boyd, S. D.; Ono, N. *J. Am. Chem. Soc.* **1974**, *96*, 2580.
- (36) Waldrin, W. R.; Reid, E. E. *J. Am. Chem. Soc.* **1923**, *45*, 2399.
- (37) Plieninger, H. *Chem. Ber.* **1950**, *83*, 264.
- (38) Paquette, L. A. *J. Am. Chem. Soc.* **1964**, *86*, 4085.
- (39) Russell, G. A.; Ochymowycz, L. A. *J. Org. Chem.* **1970**, *35*, 2106.
- (40) Leandri, G.; Mangini, A.; Passerini, R. *J. Chem. Soc.* **1957**, 1386.
- (41) Entwistle, J. D.; Jonstone, R. A. W.; Millard, B. J. *J. Chem. Soc. C* **1967**, 302.
- (42) Kornblum, N.; Earl, G. W.; Holy, N. L.; Manthey, J. W.; Musser, M. T.; Snow, D. H.; Swiger, R. T. *J. Am. Chem. Soc.* **1968**, *90*, 6221.
- (43) Ingold, C. K.; Ingold, E. H.; Shaw, F. R. *J. Chem. Soc.* **1927**, 810.
- (44) Hass, H. B.; Bender, M. L. *J. Am. Chem. Soc.* **1949**, *71*, 1767.
- (45) Williams, J.; Nys, J. *Bull. Soc. Chim. Belg.* **1967**, 506.
- (46) Mamalis, P. *J. Chem. Soc.* **1960**, 4747.