Electron-Transfer Substitution Reactions: Leaving Groups[1]

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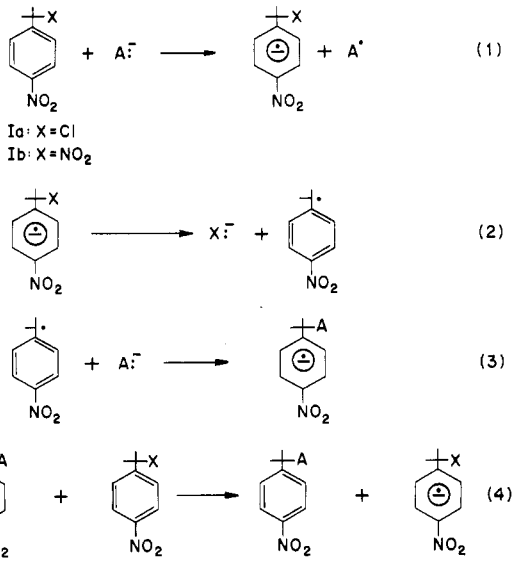
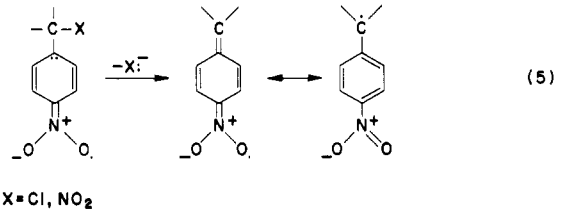
Received August 24, 1987

A number of groups that do not participate in S_N2 displacement processes are able to function as leaving groups in electron-transfer chain reactions at room temperature; such groups include azide, sulfone, ethers, nitro, quaternary ammonium ions, esters, and thioethers. Even carbanions are able to function as leaving groups as can be seen from fragmentation of carbon–carbon bonds.

Nucleophilic substitution at the tertiary carbon of *p*-nitrocumyl chloride (Ia) and α,*p*-dinitrocumene (Ib) via the electron-transfer chain mechanism of eq 1–4 occurs with great ease.[2,3] In contrast, S_N2 displacement of hal-

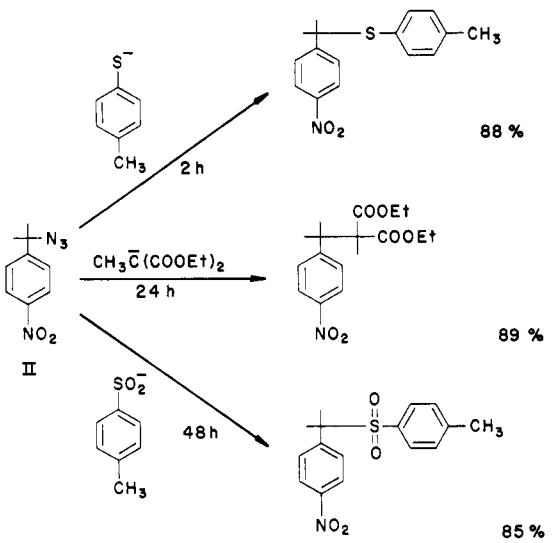


ogen from a tertiary carbon is rarely observed[4] and the S_N2 displacement of a nitro group from a tertiary carbon atom simply does not occur. The mechanism of eq 1–4 provides a simple rationale for this difference. It will be seen that in the second step (eq 2) expulsion of an anion occurs; this is viewed as an intramolecular elimination which produces an olefin—an olefin that also happens to be a free radical (eq 5).[3] If expulsion of chloride, and nitrite, is indeed an



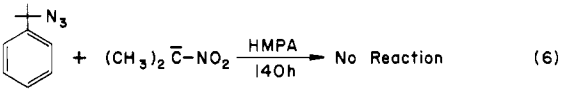
intramolecular elimination, then analogous elimination reactions may be anticipated for other groups which do not function as leaving groups in S_N2 processes. That this

Scheme I

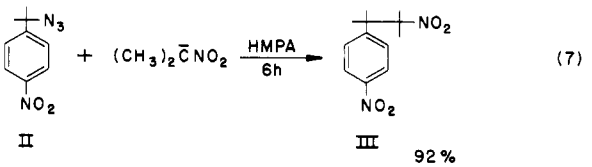


is a fruitful idea becomes clear from the results reported herein.[5]

Azides. The azide group attached to a saturated carbon does not undergo S_N2 displacement when treated with a nucleophile.[6] Thus, it is not surprising that a hexamethylphosphoramide (HMPA) solution of cumyl azide fails to react with the lithium salt of 2-nitropropane even after 140 h at room temperature (eq 6).[7] However, *p*-



nitrocumyl azide (II) reacts completely in 6 h to give a 92% yield of the pure carbon alkylate (eq 7),[7,8] a result which is easy to understand on the basis of the electron-transfer chain mechanism of eq 1–4.



Nor is this an isolated example; even though electron-transfer substitution processes generally proceed less

(1) This is paper 32 in the series "Substitution Reactions which Proceed via Radical Anion Intermediates". For the preceeding paper, see: Kornblum, N.; Wade, P. A. *J. Org. Chem.* **1987**, *52*, 5301.

(2) Kornblum, N.; Davies, T. M.; Earl, G. W.; Greene, G. S.; Holy, N. L.; Kerber, R. C.; Manthey, J. W.; Musser, M. T.; Snow, D. H. *J. Am. Chem. Soc.* **1967**, *89*, 5714.

(3) Kornblum, N.; Cheng, L.; Davies, T. M.; Earl, G. W.; Holy, N. L.; Kerber, R. C.; Kestner, M. M.; Manthey, J. W.; Musser, M. T.; Pinnick, H. W.; Snow, D. H.; Stuchal, F. W.; Swiger, R. T. *J. Org. Chem.* **1987**, *52*, 196.

(4) This is clearly true for α,*p*-dinitrocumene (Ib) and, with very few exceptions, true of *p*-nitrocumyl chloride; see footnote 13 of the review: Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734.

(5) The view that the process of eq 5 is reversible also has merit for it serves to explain numerous facts which would otherwise be anomalous; see: Kornblum, N.; Ackermann, P.; Swiger, R. T. *J. Org. Chem.* **1980**, *45*, 5294.

(6) We have been unable to find any examples of S_N2 displacements of N_3^- from aliphatic azides.

(7) The reaction flask was placed under the light bank—a light source that consisted of two 110-V, 20-W white fluorescent lights mounted horizontally about 12 cm apart.

(8) Even in the dark this reaction gave a 60% yield of III after 6 h.

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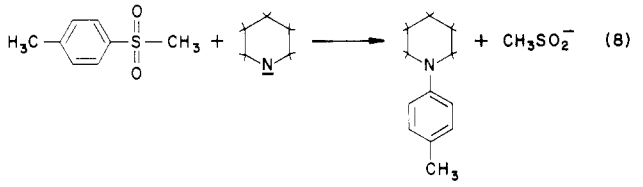
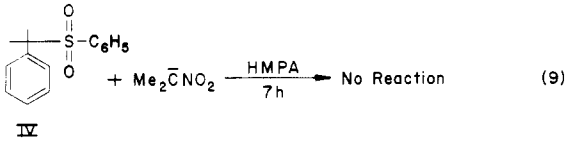
rapidly in dimethyl sulfoxide (Me_2SO) than in HMPA,[3] the azide group of *p*-nitrocumyl azide (II) is displaced by the sodium salts of *p*-thiocresol, methylmalonic ester, and *p*-toluenesulfinic acid in Me_2SO at room temperature[7] to give 85–89% yields of pure products (Scheme I).

Sulfones. A sulfone group attached to an aliphatic carbon atom is not displaced by nucleophiles via the S_N2 mechanism. Thus, di-*n*-octyl sulfone and sodium ethoxide at 200 °C give 1-octene (70% yield) and sodium *n*-octanesulfinate (62% yield).[9] And phenyl benzyl sulfone is cleaved by sodium piperidide in refluxing piperidine to give *N*-phenylpiperidine and sodium phenylmethanesulfinate.[10] Especially significant is the conversion of *p*-tolyl methyl sulfone to *N*-*p*-tolylpiperidine and sodium methanesulfinate by the action of sodium piperidide in refluxing piperidine (eq 8).[10]



(8)

In our hands α-cumyl phenyl sulfone (IV) on treatment at room temperature for 7 h with the lithium salt of 2-nitropropane is quantitatively recovered (eq 9), a failure to react which contrasts with the facile transformation of eq (10); once again we are witnessing the ability of a *p*-nitro



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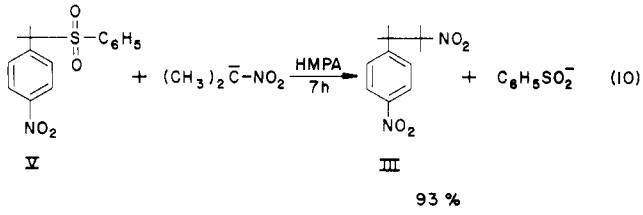
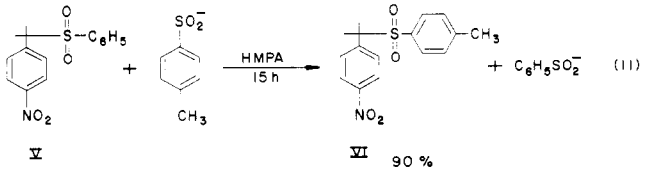


(10)

group to bring about reaction, an ability that derives from the electron-transfer sequence of eq 1–4 in which intramolecular displacement of benzenesulfinate occurs.

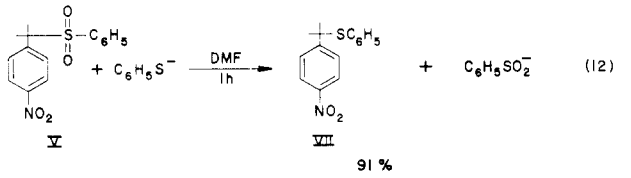
This capability for displacing a sulfone group is possessed by a number of other anions including sulfinate ions. Thus, *p*-nitrocumyl phenyl sulfone (V) when treated with a large excess of sodium *p*-toluenesulfinate, after 15 h at room temperature gives a 90% yield of the *p*-tolyl sulfone VI (eq 11). In contrast, cumyl phenyl sulfone (IV) does not react with sodium *p*-toluenesulfinate.



(11)

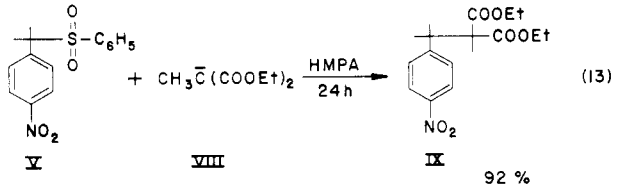
It must also be emphasized that the reaction of eq 11 is reversible. Treatment of VI with a ninefold excess of sodium benzenesulfinate for 15 h gave a product consisting of two-thirds V and one-third VI.

Sodium thiophenoxide also reacts with *p*-nitrocumyl phenyl sulfone (V); in DMF at room temperature the reaction is complete in 1 h and a 91% yield of the tertiary sulfide (VII) is isolated (eq 12). In contrast, cumyl phenyl sulfone (IV) fails to react; after 4 h 92% is recovered.



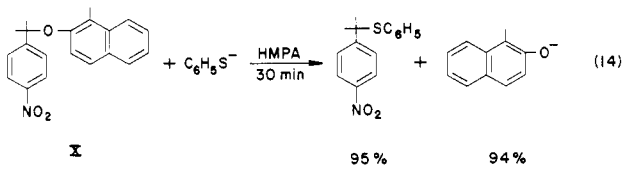
(12)

Finally, an HMPA solution of the sodium salt of diethyl methylmalonate (VIII) displaces benzenesulfinate from *p*-nitrocumyl phenyl sulfone (V); after 24 h at room temperature a 92% yield of pure IX is isolated (eq 13). However, cumyl phenyl sulfone (IV) does not react with the methylmalonate anion (VIII); after a 24-h reaction time 82% is recovered.



(13)

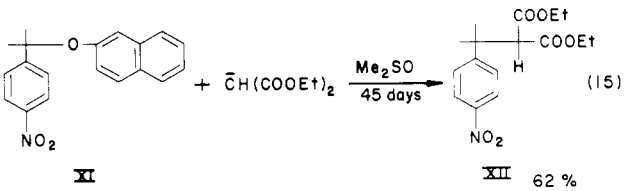
Ethers. The ether linkage is stable toward bases; cleavage of ethers by KOH or NaOH requires temperatures of 200–250 °C, typically for 10–15 h.[11] The fact that the reaction of eq 14 is complete at room temperature[7] in 30 min dramatically illustrates the capability which the



(14)

electron transfer mechanism provides for converting a nonleaving group into one which departs readily.[12] And, it again demonstrates the usefulness of the intramolecular elimination concept of eq 5.

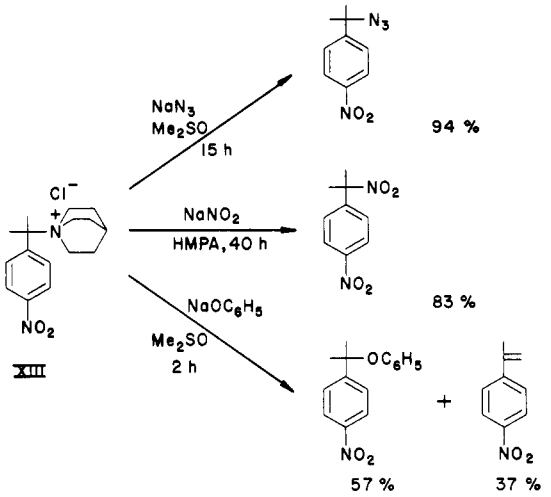
The transformation of eq 15 also takes place at room temperature but is much slower than the thiophenoxide reaction of eq 14. After 45 days[7] a 62% yield of (*p*-nitrocumyl)malonic acid diethyl ester (XII) is isolated along with a 57% yield of β-naphthol.[13,14]



(15)

(9) Fenton, G. W.; Ingold, C. K. *J. Chem. Soc.* **1930**, 705.
(10) Bradley, W. *J. Chem. Soc.* **1938**, 458.
(11) *Methoden der Organischen Chemie* (*Houben*-Weyl), 4th ed.; Thieme: Stuttgart, 1965; Vol. 6, Part 3, p 164.
(12) Even in total darkness the reaction of eq 14 is 25% complete in 30 min.
(13) There is no reaction in the dark after 45 days.
(14) Although thiophenoxide is the most reactive of the nucleophiles employed here,[3] there are three reasons for suggesting that the rate difference between thiophenoxide and malonate ions, while substantial, is almost certainly smaller than appears. The thiophenoxide experiment was conducted in HMPA, a solvent in which electron-transfer substitution proceeds more rapidly than in Me_2SO[3] (the solvent employed in the malonate reaction). Second, the reaction rate in the malonate case was monitored by withdrawing samples and, in the process, small amounts of oxygen (an inhibitor)[3] may well have been introduced. Finally, the illumination employed in the malonate reaction was provided by two 15-W white fluorescent lights, i.e., a less powerful light source than the 20-W lamps used in the thiophenoxide experiment. The significance of this fact is clear when one realizes that in the dark there is no reaction whatsoever between β-naphthyl *p*-nitrocumyl ether (XI) and the sodium salt of diethyl malonate after 45 days.

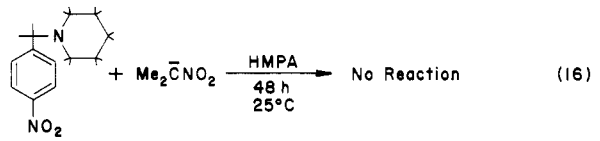
Scheme II



XIII

Quaternary Ammonium Salts. That the 2-nitropropane anion can displace trimethylamine from (*p*-nitrobenzyl)trimethylammonium chloride via the electron-transfer chain mechanism was established in 1966.[15] We have now found that at room temperature azide, nitrite, and phenoxide ions displace quinuclidine from (*p*-nitrocumyl)quinuclidinium chloride (XIII) (Scheme II). The concomitant formation of olefin in the phenoxide case closely parallels what is observed when sodium phenoxide reacts with Ia and Ib—about one-third of the product is the olefin.[3]

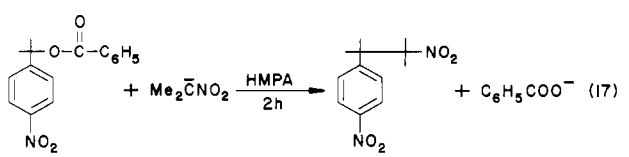
The facility with which quinuclidine is displaced is in sharp contrast to the resistance exhibited by *N*-(*p*-nitrocumyl)piperidine (XIV) to the action of the lithium salt of 2-nitropropane; in HMPA this amine is quantitatively recovered after 48 h[7] (eq 16). For reaction to occur re-



XIV

quires the formation of a very strong base—the piperidide ion—and in a solvent that is not especially hospitable to anions. With quaternary ammonium salts these problems do not exist. We see, then, that not all functions will take on the role of a leaving group—despite the availability of the electron-transfer substitution pathway.

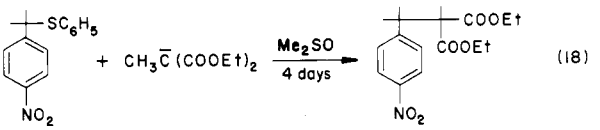
Esters. It has been known for some time that the pentachlorobenzoate ion can function as a leaving group in an electron-transfer reaction.[15] That the benzoate ion also possesses this capability is clear from the fact that *p*-nitrocumyl benzoate (XV) completely reacts with the lithium salt of 2-nitropropane in 2 h to give the carbon alkylate III in ca. 70% yield (eq 17).[16,17]



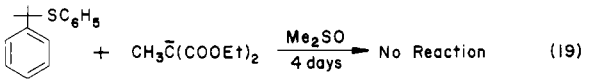
XV III

(15) Kornblum, N.; Michel, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 5660, 5662.

Thioethers. *p*-Nitrocumyl phenyl sulfide (VII) is slowly attacked by the sodium salt of methylmalonic ester (VIII); after 4 days at room temperature the reaction is 80% complete and a 68% yield of the pure product is isolated (eq 18). In contrast, cumyl phenyl sulfide (XVI) under the same conditions does not react at all (eq 19).



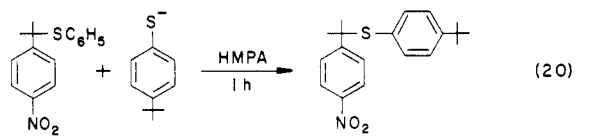
VII VIII



XVI

The reaction of the lithium salt of 2-nitropropane with *p*-nitrocumyl phenyl sulfide (VII) is also slow. In HMPA after 3 days a 28% yield of the carbon alkylate (III) is isolated and 50% of the starting sulfide is recovered. The importance of the *p*-nitro group is again brought home by the fact that after 5 days cumyl phenyl sulfide (XVI) fails to react with the salt of 2-nitropropane.

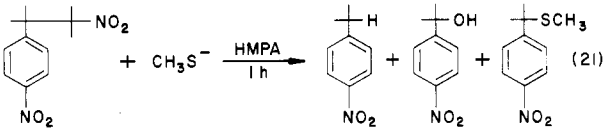
The reaction of *p*-nitrocumyl phenyl sulfide with the sodium salt of *p*-*tert*-butylthiophenol is fast; in HMPA it is complete within an hour and gives an 81% yield of pure (XVII) (eq 20). The same type of transformation is ob-



VII XVII 81 %

served when *p*-nitrocumyl phenyl sulfide (VII) is treated with the sodium salt of *p*-thiocresol; in DMF, after 6 h, a 79% yield of *p*-nitrocumyl *p*-tolyl sulfide is obtained.

Fragmentation of Carbon–Carbon Bonds. No discussion of leaving groups in electron-transfer chain reactions would be complete without drawing attention to the fact that even the carbon–carbon bond is not sacrosanct. For example, compound III when exposed to the sodium salt of methyl mercaptan—a one electron transfer agent—for 1 h at room temperature gives a 69% yield of fragmentation products (eq 21).[18a]



III 18 % 28 % 23 %

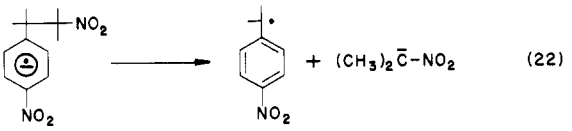
The products of eq 21 arise as a consequence of the reaction of eq 22 (which, it should be noted, is the reverse of the third step of the four-step sequence (eq 1–4)—the

(16) In 1978 it was found that *p*-nitrobenzyl esters of penicillins and cephalosporins are cleaved in 25–35 min at ice-bath temperatures by aqueous sodium sulfide: Lammert, S. R.; Ellis, A. I.; Chauvette, R. R.; Kukolja, S. *J. Org. Chem.* **1978**, *43*, 1243. The authors regard their deblocking procedure as a hydrolysis. It seems quite likely, however, that since Na_2S is a good electron donor,[17] cleavage is really an electron-transfer process in which the carboxylic anion of these antibiotics functions as a leaving group; in other words, alkyl–oxygen fission rather than acyl–oxygen fission is taking place.

(17) Kornblum, N.; Boyd, S. D.; Pinnick, H. W.; Smith, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 4316.

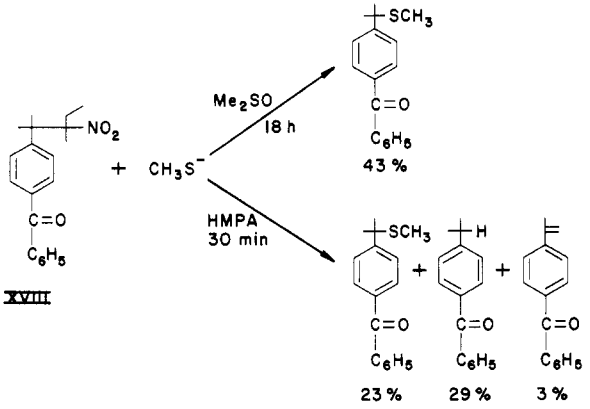
(18) (a) Kornblum, N.; Carlson, S. C.; Smith, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 647. (b) Kornblum, N.; Widmer, J.; Carlson, S. C. *Ibid.* **1979**, *101*, 658.

pathway by which III and other β-arylated nitroparaffins are formed[19]). The fragmentation of eq 22 is doubtless



(22)

facilitated by the relatively high stability of the p-nitrocumyl radical. Other electron-attracting groups also facilitate fragmentation of β-arylated nitroparaffins. Compound XVIII provides a clear demonstration.[18b] These,



and other examples of the fragmentation of β-arylated nitroparaffins[18] effectively lay to rest the assertion[20] that the coupling of p-nitrobenzyl (and p-nitrocumyl) radicals with nitroparaffin salts, i.e., the reaction of eq 3, is an irreversible, kinetically controlled, process.

Inasmuch as fragmentation of β-arylated nitroparaffins under electron-transfer conditions is so facile one wonders how it is that β-arylated nitroparaffins can be prepared from α-nitrocumenes and nitroparaffin salts by an electron-transfer process.[19] The answer is that when nitroparaffin anions react with cumylic radicals carbon–carbon bonds and, also, carbon–oxygen bonds result. Preferential, but by no means exclusive, reversal of the coupling process occurs for the nitronic esters (i.e., the oxygen alkylates) and, eventually, recombination at the carbon of the nitroparaffin anion prevails, i.e., thermodynamic control. In contrast, when radical anions are produced by the action of CH_3S^- on β-arylated nitroparaffins the cumylic radicals produced by fragmentation are scavenged by CH_3S^- to form RH and/or $RSCH_3$. This serves to prevent their recombining with the nitroparaffin anion—the other product of fragmentation. In other words, in the presence of CH_3S^- ions the fragmentation process becomes irreversible.

Experimental Section

Solvents. HMPA, Me_2SO and DMF were purified as described earlier.[3] *Caution*! HMPS should be handled with great care since it has been found to cause cancer in laboratory animals.[21]

Cumyl Azide. Freshly distilled α-methylstyrene [11.8 g; bp 62–63 °C (12 mm)] was cooled to 0 °C and anhydrous HCl was passed in for 7 h. The crude product was diluted with distilled CH_2Cl_2 and treated with a small amount of silicic acid. After filtering and evaporating the solvent the colorless liquid was distilled; 11.9 g (77% yield) of cumyl chloride was obtained: bp 39–41 °C (0.9 mm); n^{20}_D 1.5228; NMR (CCl_4) δ 1.88 (s, 6 H), 7.33 (m, 5 H).

A 100-mL three-necked flash containing 30 mL of HMPA and a magnetic stirrer was fitted with two addition tubes.[19] Sodium azide (1.3 g; 20 mmol) and 395 mg (2.56 mmol) of cumyl chloride were each put into addition tubes and after degassing by the freeze–pump–thaw procedure[19] the reactants were added to the HMPA[7] and the mixture was stirred for 645 h. The resulting colorless solution was poured into 100 mL of ice–water layered with ethyl ether (100 mL); the aqueous phase was further extracted with 2 × 100 mL of ether, and the combined extracts were washed twice with cold 60-mL portions of saturated $NaHCO_3$ and then three times with 60-mL portions of ice–water. After drying ($MgSO_4$) the ether solution was distilled off through a short column. The residue (491 mg) by NMR contained cumyl azide and α-methylstyrene in the ratio 23.3:4.5. Chromatography on acid-washed alumina gave 203 mg of VPC pure cumyl azide. Distillation at 3 mm and a pot temperature of 55 °C gave a colorless liquid: n^{20}_D 1.5215; IR (neat) 2100 cm^{-1} (N_3); NMR (CCl_4) δ 1.57 (s, 6 H), 7.30 (m, 5 H); mass spectrum (75 eV), *m/e* (relative intensity) 161 (3), 119 (100), 91 (31), 77 (38).

Anal. Calcd for $C_9H_{11}N_3$: C, 67.06; H, 6.88; N, 26.07. Found: C, 67.47; 67.56; H, 6.80, 6.91; N, 26.14, 26.21.

Reaction of Cumyl Azide with the Lithium Salt of 2-Nitropropane. Under argon (freeze–pump–thaw technique),[19] a solution of 138 mg (1.45 mmol) of the lithium salt of 2-nitropropane[22] and 95 mg (0.59 mmol) of cumyl azide in 8 mL of HMPA was stirred under the light bank[7] for 140 h. On working up, the crude product (ca. 100 mg) was found by NMR to consist of cumyl azide contaminated with less than 5% of α-methylstyrene. This was confirmed by TLC.

Reactions of *p*-Nitrocumyl Azide. (a) With the Lithium Salt of 2-Nitropropane. Under argon (freeze–pump–thaw technique)[19] 318 mg (3.3 mmol) of the lithium salt of 2-nitropropane[22] and 195 mg (0.95 mmol) of p-nitrocumyl azide in 20 mL of HMPA were allowed to react.[7] After being stirred for 6 h the purple mixture was worked up by pouring into cold water and extracting with benzene. The crude yellow product, 234 mg, was digested for an hour with 6 mL of ethyl ether to give 196 mg of the pure alkylate III; mp 205.5–207 °C. Removal of the ether and recrystallization of the residue from $CHCl_3$–CCl_4 gave an additional 23 mg of III: mp 205–206.5 °C (lit.[3] mp 206–208 °C); total 219 mg (92% yield).

A duplicate reaction employing 183.7 mg (1.95 mmol) of the lithium salt of 2-nitropropane, 170.6 mg (0.83 mmol) of the azide and 20 mL of HMPA was conducted for 6 h in the complete absence of light. The crude product obtained on workup (190 mg) was digested with 10 mL of ethyl ether. This gave 115 mg of III: mp 206–208 °C. Evaporation of the ether left 75 mg of material, which, by column chromatography, was separated into 57 mg of the starting azide and 12 mg of III. The total yield of III was 126 mg (60%) and the recovery of p-nitrocumyl azide was 34%.

(b) With the Sodium Salt of *p*-Thiocresol. Under argon (freeze–pump–thaw technique)[19] a solution of 0.91 g (6.25 mmol) of the sodium salt of p-thiocresol and 0.517 g (2.5 mmol) of p-nitrocumyl azide in 25 mL of Me_2SO was stirred for 2 h.[7] The deep brown solution was poured into ice–water and extracted with ethyl ether, and the ether solution was washed with water and dried (Na_2SO_4). Removal of the ether left a yellow liquid (0.8 g) whose NMR was that of the almost pure thioether. TLC showed the presence of p-thiocresol and the absence of starting p-nitrocumyl azide. Chromatography over silica gel using benzene–hexane (1:1) gave pale yellow crystals of p-nitrocumyl p-tolyl sulfide, 0.63 g (88% yield), mp 47–48 °C. Recrystallization from hexane gave pale yellow crystals, mp 47–48 °C: NMR ($CDCl_3$) δ 1.7 (s, 6 H), 2.3 (s, 3 H), 7.0 (s, 4 H), 7.5 (d, 2 H), 8.12 (d, 2 H).

Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.87. Found: C, 67.04; H, 6.10; N, 4.63.

(c) With the Sodium Salt of Diethyl Methylmalonate (VIII). Under nitrogen,[19] NaH (0.17 g, 7 mmol) and 1.11 g (6.39 mmol) of diethyl methylmalonate were added to 25 mL of deoxygenated Me_2SO. After the NaH had reacted 0.448 g (2.1 mmol) of p-nitrocumyl azide was introduced, and the solution was stirred

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for 24 h.[7] The crude product obtained on working up was a yellow liquid (0.9 g) whose NMR and TLC showed that none of the azide was present. Heating at 50 °C (1 mm) for 2 h removed the diethyl methylmalonate; the residue, in benzene, was plug filtered through silica gel. In thii way pure IX was obtained as a pale yellow liquid (0.65 g; 89% yield): NMR ($CDCl_3$) δ 1.18 (t, 6 H), 1.42 (s, 3 H), 1.64 (s, 6 H), 4.20 (q, 4 H), 7.62 (d, 2 H), 8.10 (d, 2 H).

Anal. Calcd for $C_{17}H_{23}NO_6$: C, 60.53; H, 6.83; N, 4.15. Found: C, 60.65; H, 6.88; N, 4.20.

(d) With Sodium *p*-Toluenesulfinate. Under argon,[19] sodium *p*-toluenesulfinate (0.94 g; 5.2 mmol) and *p*-nitrocumyl azide (0.547 g; 2.6 mmol) were dissolved in 20 mL of deoxygenated Me_2SO, and the yellow solution was stirred for 48 h.[7] It was then poured into ice–water and extracted with benzene. The benzene phase was washed with water and dried (Na_2SO_4); on removing the benzene 0.81 g of a white solid remained. Recrystallization from benzene–hexane afforded white crystals (0.72 g; 85% yield) of *p*-nitrocumyl *p*-tolyl sulfone, mp 200–201 °C; a mixed mp with authentic sulfone[23] was undepressed and the NMR spectrum was identical with that of authentic *p*-nitrocumyl *p*-tolyl sulfone.

***p*-Aminocumyl Phenyl Sulfone.** Catalytic reduction of *p*-nitrocumyl phenyl sulfone[23] over platinum oxide in absolute ethanol at 1 atm of pressure gave the amine, pale yellow crystals, mp 181.5–183 °C, in 80% yield: IR (KBr) 1135 and 1270 (SO_2), 3400 (NH_2) cm^{-1}; NMR ($CDCl_3$) δ 1.76 (s, 6 H), 6.55–6.65 (m, 2 H), 7.12–7.45 (m, 7 H).

Anal. Calcd for $C_{15}H_{17}NO_2S$: C, 65.42; H, 6.22; N, 5.08. Found: C, 65.32; H, 6.44; N, 4.95.

Cumyl Phenyl Sulfone. *p*-Aminocumyl phenyl sulfone (0.3 g, 1.09 mmol) was treated with 12 mL of ice-cold 50% aqueous H_3PO_2 and $NaNO_2$ (0.125 g, 1.79 mmol), and the stirred mixture was maintained at 0–5 °C for 16 h. On workup 0.26 g of a pale yellow solid was obtained; on recrystallization from hexane this gave 0.22 g (78% yield) of crystals, mp 90–91 °C: IR (KBr) 1140 and 1280 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 1.82 (s, 6 H), 7.36–7.42 (m, 10 H).

Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19. Found: C, 69.21; H, 6.37.

Reaction of Cumyl Phenyl Sulfone with the Lithium Salt of 2-Nitropropane. Under argon,[19] a solution of 124 mg (1.31 mmol) of the lithium salt of 2-nitropropane[22] and 63.2 mg (0.243 mmol) of cumyl phenyl sulfone in 10 mL of HMPA was stirred[7] for 7 h. On workup the product 61.2 mg (97% recovery) of white crystals had mp 90–91 °C and an NMR spectrum identical with that of the pure sulfone.

Reactions of *p*-Nitrocumyl Phenyl Sulfone. (a) With the Lithium Salt of 2-Nitropropane. Under argon (freeze–pump–thaw technique)[19] 503 mg (5.3 mmol) of the lithium salt of 2-nitropropane[22] and 286 mg (0.935 mmol) of the sulfone in 20 mL of HMPA were allowed to react[7] for 7 h. The crude product obtained on workup was recrystallized from $CHCl_3$–CCl_4; this gave 221 mg (0.875 mmol; 93% yield) of the dinitro compound III, mp 206–207.5 °C. Analytically pure III has mp 206–208 °C.[3] The NMR spectrum was identical with that of authentic material.

A duplicate reaction conducted for 6 h gave a 73% yield of III and a 19% recovery of *p*-nitrocumyl phenyl sulfone. In contrast, a second duplicate reaction conducted in total darkness for 6 h gave only a 25% yield of III and a 74% recovery of the sulfone. Thus there is a small, but real, light effect.

(b) With Sodium *p*-Toluenesulfinate. Under argon,[19] 260 mg (1.46 mmol) of sodium *p*-toluenesulfinate and 51.7 mg (0.169 mmol) of *p*-nitrocumyl phenyl sulfone were added to 12 mL of HMPA. After being stirred for 15 h[7] the originally light yellow solution had become brownish yellow. It was poured into water and extracted with benzene; the benzene phase, after being washed with water, was dried ($MgSO_4$), and then, the benzene was removed. The pale yellow residue, 52.8 mg, mp 201–202.5 °C, was chromatographed on silica gel using benzene as the solvent. This gave 49 mg (90% yield) of *p*-nitrocumyl *p*-tolyl sulfone, white crystals, mp 202–203 °C; a mixture with an authentic sample[23] was undepressed, and the NMR spectrum was identical with that of the authentic sample.

A duplicate experiment employing 15 mL of HMPA, sodium *p*-toluenesulfinate (0.32 g, 1.8 mmol), and cumyl phenyl sulfone (0.069 g, 0.27 mmol) after 15 h[7] gave 0.066 g (96% recovery) of the pure starting cumyl phenyl sulfone, mp 89.5–90.5 °C.

Clear evidence for the reversibility of the reaction of eq 11 was provided by an experiment in which 47.2 mg (0.148 mmol) of *p*-nitrocumyl *p*-tolyl sulfone (VI) was treated with 229 mg (1.4 mmol) of sodium benzenesulfinate in 12 mL of HMPA under argon (freeze–pump–thaw technique)[19] for 15 h.[7] The resulting brown-yellow solution on workup yielded a crystalline product whose NMR spectrum showed that it consisted of 67% of *p*-nitrocumyl phenyl sulfone (V) and 33% of the starting *p*-tolyl sulfone VI.

(c) With Sodium Thiophenoxide. Under argon (freeze–pump–thaw technique)[19] 1.0 g (7.8 mmol) of sodium thiophenoxide[24] and 0.6 g (1.9 mmol) of *p*-nitrocumyl phenyl sulfone in 25 mL of DMF were allowed to react.[7] The dark red-brown solution was stirred for 1 h and then poured into ice–water and extracted with ethyl ether. The ether solution was washed with water, with 10% NaOH, and, finally, with water and then dried (Na_2SO_4). Removal of the ether left a yellow liquid (0.65 g) which was chromatographed on silica gel using hexane as the eluent and, finally, hexane–benzene (1:1). In this way 0.49 g (91% yield) of *p*-nitrocumyl phenyl sulfide (VII) was obtained, mp 51–52 °C. A mixed mp with authentic sulfide[3] was undepressed, and the NMR spectrum was identical with that of the authentic sample.

A duplicate experiment in which cumyl phenyl sulfone (IV) (0.5 g, 1.9 mmol), sodium thiophenoxide (1 g, 7.6 mmol), and 25 mL of DMF were employed was allowed to proceed for 4 h.[7] The crude pale yellow product (0.56 g) by NMR consisted of the starting sulfone and some thiophenol. Washing with hexane gave white crystals (0.46 g, 92% recovery), mp 90–91 °C.

(d) With the Sodium Salt of Diethyl Methylmalonate (VIII). Under nitrogen,[19] NaH (0.246 g, 10 mmol) and 1.585 g (9.1 mmol) of diethyl methylmalonate were added to 25 mL of deoxygenated HMPA. After the hydrogen evolution had ceased 0.6 g (1.9 mmol) of *p*-nitrocumyl phenyl sulfone was introduced. The resulting yellow solution was stirred for 24 h[7] by which time the color had become deep blue-green. The crude product obtained on workup was a yellow liquid (1 g), whose NMR was that of IX contaminated with diethyl methylmalonate. It was heated to 50–55 °C (1 mm) for 3 h and then plug filtered through silica gel by using benzene. A pale yellow liquid was isolated (0.61 g, 92% yield), whose NMR spectrum was identical with that of analytically pure IX (vide supra) and which by TLC was pure.

A duplicate experiment employing cumyl phenyl sulfone (IV), 0.56 g (2.1 mmol) NaH (0.279 g, 11.6 mmol), diethyl methylmalonate (1.84 g, 10.5 mmol), and 20 mL of HMPA was carried out under N_2 for 24 h.[7] The crude product by TLC and NMR consisted solely of IV and diethyl methylmalonate; after removal of the malonic ester 0.46 g (82% recovery) of pure cumyl phenyl sulfone, mp 90–91 °C was obtained.

Reactions of β-Naphthyl Ethers. (a) With Sodium Thiophenoxide. Under argon (freeze–pump–thaw procedure)[19] a red solution of 290 mg (2.2 mmol) of sodium thiophenoxide[24] and 329 mg (1.025 mmol) of *p*-nitrocumyl 1-methyl-2-naphthyl ether[3] (X) in 20 mL of HMPA was stirred for 30 min.[7] Workup gave 431 mg of a light yellow solid, which was chromatographed on neutral alumina; elution with hexane, benzene–hexane (1:2), and, finally, benzene gave 271 mg (95% yield) of *p*-nitrocumyl phenyl sulfide (VII), mp 51–52 °C (lit.[3] mp 52–53 °C), whose NMR spectrum is that of the pure sulfide.[3] This was followed by 152 mg (94% yield) of 1-methyl-2-naphthol, mp 107–108 °C (lit.[25] mp 109–110 °C). The mp of a mixture with authentic 1-methyl-2-naphthol of mp 108.5–109.5 °C was 108–108.5 °C, and the NMR spectrum was identical with that of authentic 1-methyl-2-naphthol.[26]

A duplicate of this experiment was carried out in complete darkness by using 271 mg (2.03 mmol) of sodium thiophenoxide,

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348 mg (1.08 mmol) of X, and 20 mL of HMPA. Chromatography of the crude product (396 mg) gave 221 mg of the pure starting ether X and another 34 mg in interfractions with *p*-nitrocumyl phenyl sulfide (VII) for a total recovery of 255 mg (73%) of X. Pure *p*-nitrocumyl phenyl sulfide (VII) (12 mg) was isolated, and this, plus 61 mg in interfractions with the starting ether X, makes a total of 73 mg of VII (25% yield). In addition, 42 mg of pure 1-methyl-2-naphthol (26% yield) was isolated. Thus, the reaction proceeds in the dark but at a slower rate than in the light.

(b) With the Sodium Salt of Diethyl Malonate. Under a positive pressure of argon 2.730 g (15 mmol) of diethyl sodiomalonate was dissolved in 40 mL of deoxygenated Me_2SO. To this was added 2.154 g (7 mmol) of *p*-nitrocumyl 2-naphthyl ether (XI) in 30 mL of deoxygenated Me_2SO. The reaction was run with magnetic stirring, under argon, and under two 15-W white fluorescent lights. After 45 days the reaction mixture was worked up. The crude product, an oil, was chromatographed on a silica gel column to give 1.393 g (62% yield) of (*p*-nitrocumyl)malonic acid diethyl ester (XII), a pale yellow oil whose NMR spectrum was identical with that of an analyzed sample.[3] In addition, 0.577 g (57% yield) of pure 2-naphthol was isolated and 0.568 g (25%) of the starting *p*-nitrocumyl 2-naphthyl ether was recovered. In addition, 0.101 g (0.61 mmol) of *p*-nitrocumene and 0.052 g (0.29 mmol) of *p*-nitrocumyl alcohol were isolated.

A duplicate reaction in the dark resulted in a quantitative recovery of unreacted *p*-nitrocumyl 2-naphthyl ether after 45 days.

***p*-Nitrocumyl 2-Naphthyl Ether (XI).** This compound was prepared in the same way as *p*-nitrocumyl 1-methyl-2-naphthyl ether[3] by using 2 mol of sodium 2-naphthoxide to 1 mol of α,p-dinitrocumene. For analysis it was recrystallized from petroleum ether, mp 68.5–69.5 °C.

Anal. Calcd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56; M_r 307. Found: C, 74.10; H, 5.72; N, 4.89; M_r 296.

Reactions of (*p*-Nitrocumyl)quinuclidinium Chloride. (a) With Sodium Azide. Under argon (freeze–pump–thaw technique)[19] a solution of 0.31 g (1.0 mmol) of the quinuclidinium salt and 0.13 g (2.0 mmol) of sodium azide[3] in 10 mL of Me_2SO was stirred for 15 h.[7] The reaction mixture was poured into cold 3% hydrochloric acid and extracted with benzene. The benzene extracts were washed with water and dried ($MgSO_4$) and the benzene removed. A pale yellow oil (0.194 g, 94% yield) was obtained whose NMR spectrum was that of pure *p*-nitrocumyl azide.[3]

(b) With Sodium Nitrite. Under argon[19] a solution of 1.24 g (3.99 mmol) of (*p*-nitrocumyl)quinuclidinium chloride and 0.30 g (4.35 mmol) of sodium nitrite in 20 mL of HMPA was stirred for 40 h[7] and then worked up by pouring into 3% hydrochloric acid layered with benzene. The benzene extracts were washed with water and dried ($MgSO_4$) and the benzene removed. The residue was chromatographed on acid-washed alumina by using benzene–hexane mixtures for elution; this gave 0.693 g (83% yield) of pure α,p-dinitrocumene; white crystals, mp 67–67.5 °C (lit.[3] mp 69–70 °C). The NMR spectrum was identical with that of authentic α,p-dinitrocumene.

The reaction is slower in Me_2SO; a duplicate experiment in Me_2SO gave 0.596 g (71% yield) of pure α,p-dinitrocumene after a 90-h reaction time.

(c) With Sodium Phenoxide. Under argon[19] a solution of 0.31 g (1.0 mmol) of the quinuclidinium salt and 0.23 g (2.0 mmol) of sodium phenoxide[27] in 10 mL of Me_2SO was allowed to react for 2 h.[7] The product was poured into dilute aqueous sodium hydroxide layered with benzene. The aqueous phase was extracted with benzene and the extracts combined, washed with water, and dried ($MgSO_4$). Removal of the benzene gave 0.205 g of an oil; by NMR the yield of *p*-nitrocumyl phenyl ether[27] was 57% and that of *p*-nitro-α-methylstyrene 37%.

Reaction of *N*-(*p*-Nitrocumyl)piperidine (XIV) with the Lithium Salt of 2-Nitropropane. A deoxygenated solution,[19] containing 2.38 g (25 mmol) of lithium 2-nitropropanate and 1.2368 g (5.0 mmol) of *N*-(*p*-nitrocumyl)piperidine dissolved in 100 mL of HMPA, was prepared. The yellow solution was stirred in the light bank[7] for 48 h and then poured into 1 L of 3% aqueous HCl layered with 300 mL of benzene. The benzene phase was separated, and the aqueous layer was extracted with two further 300-mL portions of benzene. The combined benzene layers were washed with water, dried ($MgSO_4$), filtered, and concentrated to give a yellow oil (0.8769 g), which by NMR consisted of aliphatic compounds, presumably derived from the nitroparaffin salt.

The aqueous acidic phase was made basic (pH >10) with 200 mL of 15% aqueous NaOH. Organic products were extracted into benzene, washed with H_2O, and dried. Removal of the benzene gave 1.154 g (94% recovery) of *N*-(*p*-nitrocumyl)piperidine as a yellow solid, mp 44–47 °C; the analytically pure compound has mp 47–48 °C.[28] The NMR spectrum of the recovered compound was that of the pure starting material. In a duplicate experiment, run for 24 h, the only product found (by NMR) was, again, the starting material.

Preparation of *p*-Nitrocumyl Benzoate.[29] The method of Brewster and Ciotti[30] was employed for the conversion of *p*-nitrocumyl alcohol[23] to its benzoate. The crude product was chromatographed on acid-washed alumina by using hexane, hexane–benzene mixtures, and, finally, benzene for elution, mp 82–82.5 °C. For analysis a sample was recrystallized from hexane: white needles, mp 82.5–83 °C; NMR ($CDCl_3$) δ 1.88 (s, 6 H), 7.3–7.7 (m, 5 H), 7.9–8.3 (m, 4 H).

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91; M_r 285. Found: C, 67.26; H, 5.46; N, 4.67; M_r 282.

Reaction of *p*-Nitrocumyl Benzoate with the Lithium Salt of 2-Nitropropane.[29] Under argon (freeze–pump–thaw procedure)[19] a solution of *p*-nitrocumyl benzoate (0.28 g, 1.0 mmol) and the lithium salt of 2-nitropropane (0.19 g, 2.0 mmol) in 20 mL of HMPA was allowed to react for 2 h.[7] The reaction mixture was worked up by pouring into 200 mL of water and extracting with benzene. The benzene solution was washed with water and dried ($MgSO_4$) and the benzene removed. The 0.25 g of a white solid so obtained, on digestion with ethyl ether, gave 158 mg (62% yield) of the carbon alkylate III, mp 204–206 °C (lit.[3] mp 206–208 °C). The NMR spectrum was identical with that of authentic III.[3] NMR analysis of the material which had been leached out by the ethyl ether showed that none of the starting benzoate ester remained and that an additional 15–20% of the carbon alkylate III was present along with ca. 10% of *p*-nitrocumyl alcohol.

Preparation of Cumyl Phenyl Sulfide (XVI). At room temperature 11 g (100 mmol) of thiophenol was added to a well-stirred solution of 50 mL of H_2O and 50 mL of 96% H_2SO_4. Then, over a period of 1 h, a solution of α-methylstyrene (11.8 g, 100 mmol) in 50 mL of THF was added dropwise; stirring at room temperature was continued for an additional 30 min. The resulting mixture was poured into 400 mL of ice–water and extracted with benzene. The benzene phase was washed with H_2O, with 5% aqueous NaOH, and with H_2O and then dried ($MgSO_4$). A pale yellow liquid remained after removal of the benzene; on distillation at 1 mm a middle cut, bp 148 °C, of colorless cumyl phenyl sulfide (14.2 g, 65% yield) was obtained: NMR ($CDCl_3$) δ 1.68 (s, 6 H), 7.18–7.45 (m, 10 H); IR ($CDCl_3$) 3020, 2975, 1110 cm^{-1}. Anal. Calcd for $C_{15}H_{16}S$: C, 78.89; H, 7.06. Found: C, 78.80; H, 7.19.

Reactions of *p*-Nitrocumyl Phenyl Sulfide (VII). (a) With the Sodium Salt of Diethyl Methylmalonate (VIII). Under argon,[19] NaH (0.22 g, 9.4 mmol) and diethyl methylmalonate (1.56 g, 9 mmol) were added to 25 mL of Me_2SO. When gas evolution ceased, 0.5 g (1.8 mmol) of VII was introduced, and the resulting yellow solution was stirred for 4 days.[7] By NMR the 0.8 g of yellow liquid obtained on workup contained ca. 20% of the starting sulfide. Chromatography on silica gel using benzene–hexane (1:1) and then benzene gave 0.5 g of a yellow liquid, which was heated at 50 °C (1 mm) until all the diethyl methylmalonate was removed. The residual 0.41 g (68% yield) had the same NMR as the analytical sample of [(*p*-nitrocumyl)methyl]malonic acid diethyl ester (vide supra).

A duplicate of this experiment in which cumyl phenyl sulfide (XVI) (0.446 g, 1.9 mmol), diethyl methylmalonate (1.65 g, 9.5 mmol), NaH (0.252 g, 10 mmol), and 25 mL of Me_2SO were employed was conducted for 4 days.[7] The crude product (0.5 g) by NMR was found to consist of the starting cumyl phenyl sulfide

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(29) This experiment was carried out by Dr. R. T. Swiger.

(30) Brewster, J. H.; Ciotti, C. J. *J. Am. Chem. Soc.* **1955**, *77*, 6214.

(XVI) and the methylmalonic ester. Heating at 50 °C and 1 mm removed the diethyl methylmalonate and, on distilling the residual liquid at 146–148 °C (1 mm), 0.32 g (72% recovery) of colorless cumyl phenyl sulfide was obtained. Its NMR spectrum was identical with that of the starting material.

(b) With the Lithium Salt of 2-Nitropropane. Under argon,[19] 850 mg (9 mmol) of the lithium salt of 2-nitropropane and 500 mg (1.8 mmol) of *p*-nitrocumyl phenyl sulfide were dissolved in 15 mL of HMPA. The red solution was stirred for 72 h[7] and then worked up as usual. This gave 0.6 g of an orange-brown crude product, which was digested with warm absolute ethanol, cooled, filtered, and washed with cold ethanol. The almost white, ethanol insoluble solid is the carbon alkylate III: 0.11 g (27% yield); mp 204–206 °C (lit.[3] mp 206–208 °C).

Evaporation of the ethanol left 0.48 g of a residue, which was loaded onto a silica gel column and eluted with hexane and then with hexane–benzene (1:1). In this way an additional 30 mg of III was obtained, for a total yield of 0.14 g (28%). In addition, 245 mg (50%) of the starting *p*-nitrocumyl phenyl sulfide (VII), mp 50–52 °C, was recovered.

A duplicate of this experiment was carried out by using 0.469 g (2 mmol) of cumyl phenyl sulfide (XVI), 0.95 g (10 mmol) of the lithium salt of 2-nitropropane and 20 mL of HMPA. After 5 days the usual workup gave 0.4 g of a crude material, which, by NMR, was devoid of any product. On distillation at 145–148 °C (1 mm) 0.33 g (70% recovery) was obtained; the NMR spectrum of this colorless liquid was identical with that of the starting cumyl phenyl sulfide.

(c) With the Sodium Salt of *p*-*tert*-Butylthiophenol. Under argon,[19] sodium *p*-*tert*-butylphenyl sulfide (3.3 g, 18 mmol) and 0.5 g (1.8 mmol) of *p*-nitrocumyl phenyl sulfide (VII) were placed in 35 mL of HMPA. The deep purple solution was stirred for 1 h[7] and then poured into ice–water, which was extracted with benzene, and the benzene phase, after washing with water, 10% NaOH, and water, was dried (Na_2SO_4). Removal of the solvent left a yellow solid (0.64 g), which by NMR and TLC was free of VII. Recrystallization from absolute ethanol gave colorless crystals of *p*-nitrocumyl *p*-*tert*-butylphenyl sulfide (0.48 g, 81% yield), mp 81–82 °C: NMR ($CDCl_3$) δ 1.28 (s, 9 H), 1.72 (s, 6 H), 7.1–7.3 (m, 4 H), 7.55 (d, 2 H), 8.15 (d, 2 H). Anal. Calcd for $C_{19}H_{23}NO_2S$: C, 69.26; H, 7.03; N, 4.25. Found: C, 69.21; H, 6.89; N, 4.16.

(d) With the Sodium Salt of *p*-Thiocresol. In DMF (20 mL) 2.6 g (18 mmol) of the sodium salt of *p*-thiocresol reacted with *p*-nitrocumyl phenyl sulfide (0.5 g, 1.8 mmol) in 6 h[7] when the procedure of the preceeding experiment was followed. Workup in the usual way gave 0.42 g (79% yield) of *p*-nitrocumyl *p*-tolyl sulfide, mp 47–48 °C. The analytical sample (vide supra) has mp 47–48 °C, and the NMR spectra of the two samples are identical.

Acknowledgment. These studies were supported by grants from The National Science Foundation, the donors of the Petroleum Research Fund, administered by The American Chemical Society, Eli Lilly and Company, and the Hoffmann-La Roche Foundation.

Registry No. Ib, 3276-35-5; I (X = SC_6H_4-*p*-CH_3), 113109-56-1; I (X = OC_6H_5), 113109-58-3; I (X = H), 1817-47-6; I (X = OH), 22357-57-9; I (X = SCH_3), 113109-61-8; II, 105639-48-3; III, 14851-03-7; III$^{\bullet-}$, 113109-62-9; IV, 53439-66-0; V, 70951-74-5; VI, 75506-57-9; VII, 15013-24-8; VIII·Na^+, 18424-77-6; IX, 113109-57-2; X, 14851-08-2; XI, 113109-64-1; XII, 14851-05-9; XIII, 105639-51-8; XIV, 105639-50-7; XV, 113109-59-4; XVI, 4148-93-0; XVII, 113109-60-7; XVIII, 65253-42-1; $(CH_3)_2C^-NO_2Li^+$, 3958-63-2; $C_6H_5SO_2Na$, 873-55-2; C_6H_5SNa, 930-69-8; $Na^+CH^-(COOEt)_2$, 996-82-7; NaN_3, 26628-22-8; $NaNO_2$, 7632-00-0; $NaOC_6H_5$, 139-02-6; C_6H_5COOLi, 553-54-8; CH_3SNa, 5188-07-8; C_6H_5SH, 108-98-5; cumyl azide, 32366-26-0; sodium *p*-thiocresolate, 10486-08-5; sodium *p*-toluenesulfinate, 824-79-3; sodium 1-methyl-2-naphtholate, 14851-07-1; β-naphthol, 135-19-3; α-methyl-*p*-nitrostyrene, 1830-68-8; sodium *p*-*tert*-butylthiophenoxide, 54166-35-7; *p*-nitrocumyl radical, 80866-17-7; *p*-benzoylcumyl methyl sulfide, 69719-15-9; *p*-benzoylcumene, 18864-76-1; *p*-benzoyl-α-methylstyrene, 103384-71-0; α-methylstyrene, 98-83-9; cumyl chloride, 934-53-2; *p*-aminocumyl phenyl sulfone, 113109-63-0.

Methyl Viologen Reactions. 5. Rates and Mechanism of Cation-Radical Formation in Aqueous Base[1]

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Received May 8, 1987

Initial rates for methyl viologen cation-radical ($MV^{\bullet+}$) formation from methyl viologen (MV^{2+}) in aqueous base have been obtained by spectrophotometry at 604 nm and 24 °C. From rate runs at various reactant concentrations, the order in MV^{2+} was found to be 2 and the order in base was 1 (or in a few sets of runs somewhat larger). The rate constant k_0 based on the third-order rate law is 1.46×10^{-4} M^{-2} s^{-1} in H_2O; in D_2O the constant is 2.48×10^{-3} M^{-2} s^{-1}.

Introduction

Methyl viologen ion MV^{2+} (also known as Paraquat)[2] has been the focus of numerous studies. (For list of symbols used, see Glossary at the beginning of the Results Section.) In recent years it has been used as a herbicide;[3] there has been widespread interest in its potential in solar energy collection and storage systems,[4] and it serves as a biological redox indicator in photosynthetic research.[5] Several comprehensive reviews of the chemistry of MV^{2+} and related compounds are available.[6]

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(2) Paraquat is the trade name for the dichloride salt of MV^{2+}.

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