Electron-Transfer Chain-Substitution Reactions of Ambident Anions[1]

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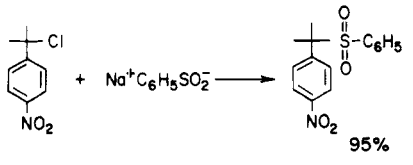
A simple explanation is proposed for the fact that electron-transfer chain-substitution reactions involving ambident anions give only one of the two possible products and experimental evidence which supports this hypothesis is presented.

Equations 1–5 illustrate an important characteristic of electron-transfer chain-substitution reactions involving ambident anions—only one of the two possible isomeric products is isolated.[1,2] Why this is so is the concern of this paper.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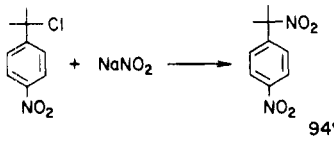
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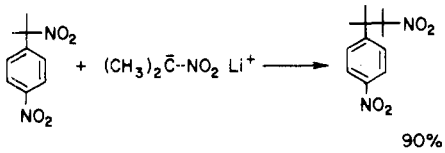
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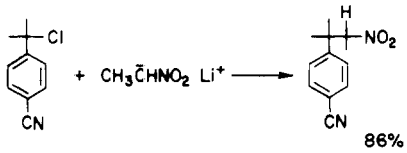
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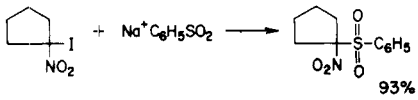
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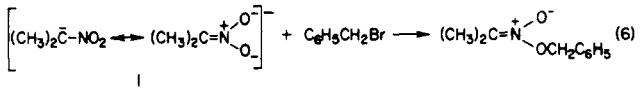
In discussing this question it is useful to remember that treatment of a nitroparaffin salt with an alkyl halide ordinarily results in oxygen alkylation, whereas Michael additions routinely give the carbon alkylate. Oxygen alkylation of a nitroparaffin salt is a simple S_N2 displacement,[2,3] a single-stage irreversible process subject to kinetic control, e.g., as in eq 6. In contrast, the Michael reaction is a multistage process which is subject to thermodynamic control (eq 7).[4]

With this as a starting point it is possible to propose a simple explanation for the fact that electron-transfer chain reactions of ambident anions give but one of the two possible products. This becomes apparent when the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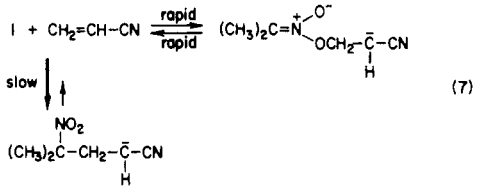
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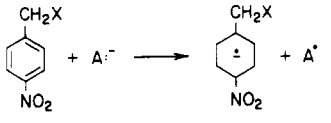
mechanism of electron-transfer substitution is recalled (eq 8–11).[2] The third step of this sequence (eq 10), addition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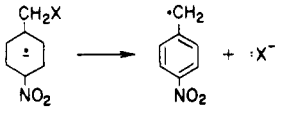
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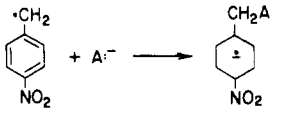
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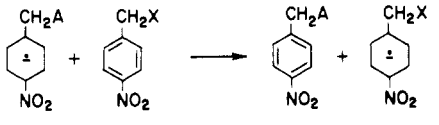
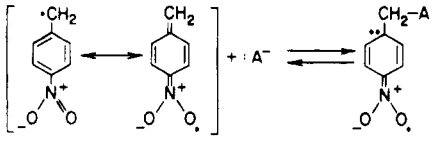

(11)

of the nucleophile to the radical to give a radical anion, is regarded as the first stage of a Michael-type addition; i.e., eq 10 can be written as eq 10′. As with other Michael reactions the process of eq 10(10′) ought to be rapidly reversible and, thus, subject to thermodynamic control.


(10′)

A direct test of this hypothesis can be achieved by exposing the isomeric compounds which are *not* isolated from reactions employing ambident anions (e.g., those of eq 1–5) to the corresponding nucleophiles. This should result in rapid isomerization. The oxygen alkylates of nitroparaffin

(1) This is paper 24 in the series "Substitution Reactions Which Proceed via Radical Anion Intermediates". For the preceding paper, see N. Kornblum and M. J. Fifolt, *J. Org. Chem.*, 45, 360 (1980).
(2) N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, 14, 734 (1975).
(3) N. Kornblum, P. Pink, and K. V. Yorka, *J. Am. Chem. Soc.*, 83, 2779 (1961).
(4) So far as we are aware this rationale for the reactions of nitroparaffin salts has never been published.

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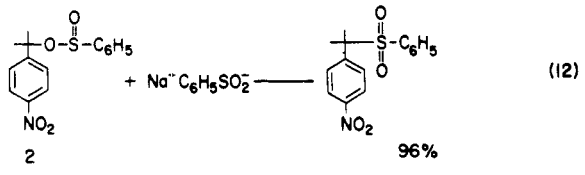
salts are attractive candidates for such a test but, unfortunately, they are unstable when derived from primary or secondary halides[2] and those derived from tertiary halides are not known. Consequently, we directed our attention to sulfinate esters, i.e., the isomers of sulfones (cf. eq 1).[5] These studies, as will be seen from the sequel, provide strong support for the proposed explanation.

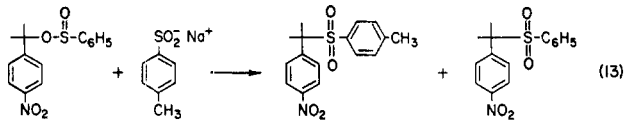
The first set of experiments involves *p*-nitrocumyl benzenesulfinate (2). Treatment of this ester with sodium benzenesulfinate under the reaction conditions used for the transformation of eq 1 resulted in rapid and quantitative isomerization to the sulfone (eq 12). The inter-



(12)

2 96%

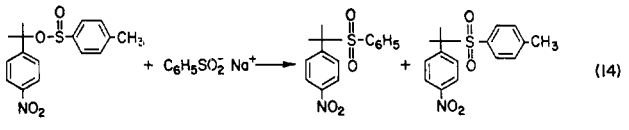
molecular nature of this process was demonstrated by the use of sodium *p*-toluenesulfinate. As before, a rapid reaction occurred but now two sulfones were produced (eq 13). When 2 mol of the sodium salt per mole of ester was



(13)

employed the product was ca. 80% *p*-tolyl sulfone and ca. 20% phenyl sulfone. With 10 mol of sodium *p*-toluenesulfinate for each mole of ester the proportion of *p*-tolyl sulfone in the product rose to ca. 95% and pure *p*-nitrocumyl *p*-tolyl sulfone was isolated in 81% yield. The reaction of eq 13 is a chain process. That this is so is clear from the fact that it is completely inhibited by 10 mol% di-*tert*-butyl nitroxide.[6]

These findings were confirmed and extended by a second set of experiments employing *p*-nitrocumyl *p*-toluenesulfinate (3). The reaction of eq 14 occurred rapidly

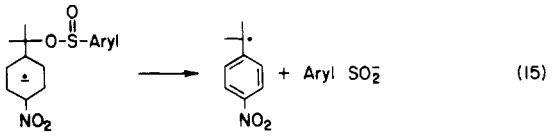


(14)

3

and was complete within 15 min at room temperature. The mixture of sulfones, isolated in quantitative yield, consisted of the phenyl sulfone and the *p*-tolyl sulfone in proportions ranging from 70:30 to 89:11 as a function of the amount of sodium benzenesulfinate used. This reaction does not take place in the dark; it is inhibited by a catalytic amount of di-*tert*-butyl nitroxide[6] and is also inhibited by *m*-dinitrobenzene.[7]

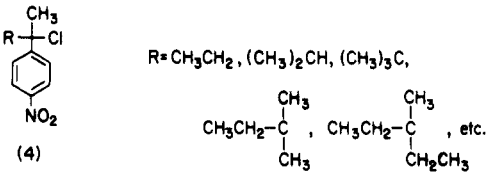
In view of these characteristics there can be little doubt that the reactions of eq 13 and 14 are electron-transfer chain processes in which radical anions and free radicals are intermediates—in other words that they proceed via the mechanistic sequence of eq 8–11. The speed with which these *p*-nitrocumyl sulfinate esters are converted to sulfones by the electron-transfer mechanism, and the near certainty that the radical anions of these esters are less stable than the esters themselves, makes it reasonable to presume that the decomposition of radical anions of *p*-nitrocumyl sulfinate esters according to eq 15 is very



(15)

rapid. Thus, in the reaction of *p*-nitrocumyl chloride with a sulfinate salt, e.g., the process of eq 1, even if most of the initial product corresponding to eq 10 (10′) were the radical anion of the sulfinate ester the facility with which the reaction reverses (eq 15) guarantees that this radical anion will be short lived. And, of course, any *p*-nitrocumyl sulfinate ester which is formed from the sulfinate ester radical anion will, as we have seen, quickly be transformed into sulfone. Manifestly these ideas are applicable to the electron-transfer chain reactions of other ambident anions and, thus, the fact that in such processes only one product is obtained becomes intelligible.

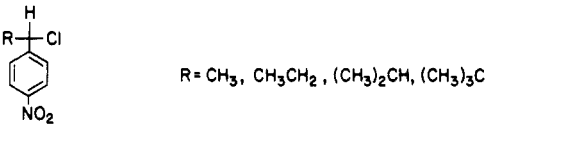
These ideas also provide a basis for discussing related problems. The ease with which substitution occurs at a tertiary carbon under very mild conditions shows that electron-transfer chain substitution is, in contrast to S_N2 displacements, rather insensitive to steric hindrance.[2] This insensitivity is even more dramatic when it is realized that with benzenesulfinate ion, nitroparaffin anions, and nitrite ion, covalency is established at the more hindered of the two available positions—even though substitution is occurring at a highly hindered carbon atom. But clearly if a homologous series of halides such as 4 is allowed to react



(4)

with an ambident anion, e.g., the anion of 2-nitropropane, a point will eventually be reached where the steric problem becomes overriding. At that juncture the carbon alkylate will no longer be the thermodynamically stable product and it is conceivable that the nitronic ester will then be produced.

While such reactions of the series of tertiary halides 4 have not been investigated, the homologous series of secondary chlorides (5) has been employed by Norris and



(5)

Randles as a probe for the study of steric effects in electron-transfer chain substitutions.[8a] Unfortunately, this system has built-in ambiguities which effectively preclude the obtaining of meaningful results. Since these are not

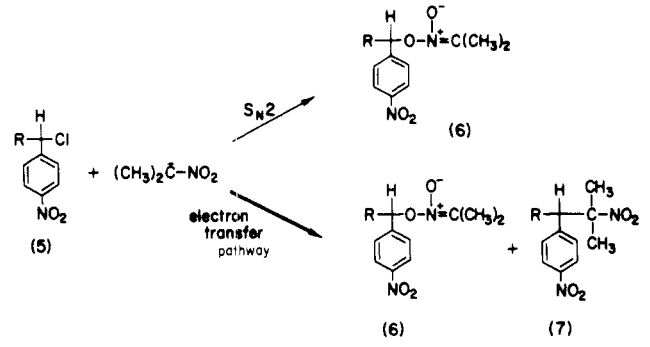
(5) It is of interest that Michael additions of sulfinate salts yield sulfones [L. F. Cason and C. C. Wanser, *J. Am. Chem. Soc.*, **73**, 142 (1951); H. Gilman and L. F. Cason, *ibid.*, **72**, 3469 (1950); R. L. Heath and A. Lambert, *J. Chem. Soc.*, 1477 (1947)] presumably as a consequence of thermodynamic control. However, treatment of alkali metal salts of sulfinic acids with alkyl halides also leads to sulfones. It has been proposed that sulfinate esters are initially produced on alkylating a sulfinate salt with an alkyl halide but that thermodynamic control results in the sulfone [M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **39**, 1296 (1966)]. While there is some evidence that sulfinic ester formation may indeed be the kinetically favored process, this has not really been established.

(6) This is a diagnostic for free radicals.[2]

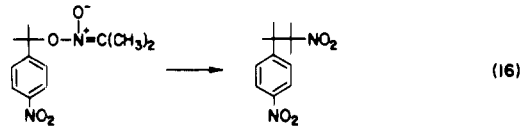
(7) This is a diagnostic for radical anions.[2]

(8) (a) R. K. Norris and D. Randles, *Aust. J. Chem.*, **29**, 2621 (1976); **32**, 1487 (1979). (b) It should be emphasized that Norris and Randles[8a] recognized that the S_N2 process would intrude with the lower homologues of 5.

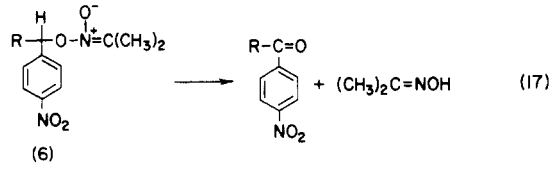
tertiary halides the possibility of the S_N2 mechanism competing with electron-transfer substitution is very real, especially with the lower homologues.[8b] With the salt of 2-nitropropane, for example, this intrusion of the S_N2 process would, as noted earlier, result in oxygen alkylation. On the other hand, as we have just seen, electron-transfer chain substitution will initially produce an indeterminate mixture of the oxygen and carbon alkylates (6 and 7). But



whereas with tertiary halides, such as *p*-nitrocumyl chloride (and its homologues 4), the oxygen alkylate undergoes electron-transfer isomerization to the carbon alkylate (eq 16), the oxygen alkylate (6) derived from secondary halides

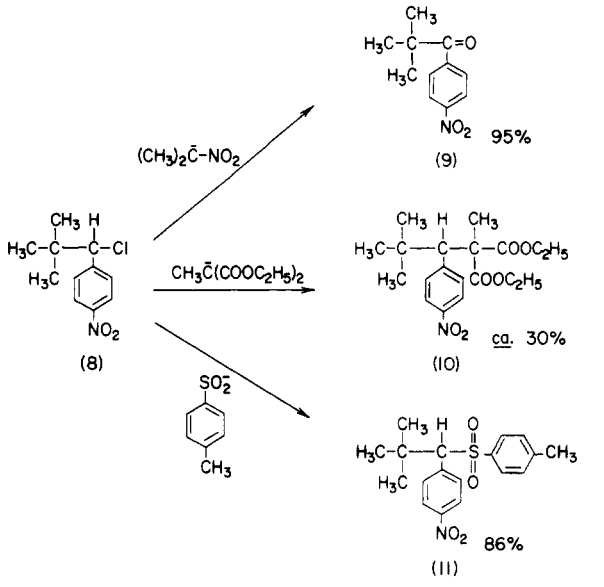


is also able to undergo an alternate reaction—irreversible decomposition to a ketone and acetoxime (eq 17).[2] Since

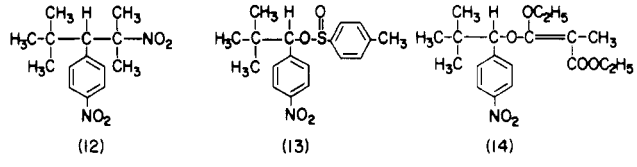


there is no way even to estimate the relative rates of the competing reactions available to 6, it is inappropriate to use the proportions of oxygen and carbon alkylate obtained on treating nitroparaffin salts with 5 as a basis for gauging the importance of steric hindrance in electron-transfer chain reactions.

That this is so is especially clear from the results obtained when 8 is treated with the salts of 2-nitropropane, methyl malonic ester, and *p*-toluenesulfinic acid.[8] (The isolation of the carbon alkylated malonic ester (10) is especially noteworthy when one considers the reaction conditions.[9]) All three compounds, the carbon-alkylated malonic ester (10), the carbon-alkylated 2-nitropropane (12), and the sulfone (11) are very crowded molecules. The failure to isolate any carbon-alkylated 2-nitropropane (12) must mean that the possibility of isomerizing the oxygen



alkylate to the carbon alkylate has vanished thanks to the competitive process of eq 17. With the sulfinate ester (13), and the oxygen alkylated malonic ester (14), competitive



decomposition pathways analogous to that of eq 17 are not available and, in the absence of this complication, they simply isomerize to the sulfone (11) and the carbon alkylated malonic ester (10) via the electron-transfer pathway. It is easy to understand, then, why very hindered molecules can be formed from 8 with the methyl malonic ester anion and the *p*-toluenesulfinate ion but *not* with the 2-nitropropane anion.

Experimental Section

Caution: HMPA should be handled with great care since it has recently been found to cause cancer in laboratory animals.[14]

HMPA (Du Pont) was distilled from calcium hydride under reduced pressure. Sodium benzenesulfinate (Matheson Coleman and Bell) was purified by recrystallization from 95% ethanol; after isolation the crystals were washed with cold 95% ethanol and ethyl ether and, then, dried in a flask on a rotary evaporator at 100–110 °C (0.5 mm) for 4 h. Potentiometric titration with perchloric acid in glacial acetic acid gave a neutralization equivalent of 168 (theoretical 164). Aldrich sodium *p*-toluenesulfinate (~97% pure) similiarly purified gave neutralization equivalent 176 (theoretical 178).

***p*-Nitrocumyl Alcohol.** Into a 2-L flask equipped with 125-mL pressure-equalizing addition funnel, a mechanical stirrer, and a thermometer was placed 480 g (4.0 mol) of cumene (Eastman; 97% cumene by VPC). The cumene was cooled to 0 °C in an ice–salt bath and to it was added, dropwise, a solution of 236 mL of concentrated H_2SO_4 (4.0 mol; Mallinckrodt technical grade, 93%) and 128 mL of concentrated HNO_3 (2.0 mol; Mallinckrodt analytical reagent, 70%) which had previously been cooled to 0 °C. Addition of the acid mixture, which took ca. 2 h, was carried out at such a rate as to maintain the reaction temperature between 0 and +5 °C. When addition was complete the ice–salt bath was removed and the reaction mixture was stirred 1 additional h; at the end of the hour the temperature of the reaction mixture was 41 °C.

The reaction mixture was poured into ca. 1 kg of ice and the organic phase was isolated. The aqueous phase was saturated with sodium chloride and extracted with ethyl ether, and the extracts were combined with the organic phase. The resulting ethyl ether solution was washed with 100 mL of 5% aqueous

(9) After 11 days at 50 °C in Me_2SO the reaction product consists of the starting chloride (15%), *p*-nitropivalophenone (12%), 2,2-dimethyl-1-(*p*-nitrophenyl)propan-1-ol (29%), and the C-alkylated malonic ester (26%). One can only conjecture about the genesis of the ketone and alcohol but based on experience in this laboratory it would not be surprising if under electron-transfer conditions 8 were converted to the O-alkylated Me_2SO; this, by the well-known oxidation–reduction reaction, could well be the source of the *p*-nitropivalophenone. And hydrolysis of the O-alkylated Me_2SO and the O-alkylated malonic ester would explain the formation of the alcohol. In view of the success with which Norris and Randles[8] employed the lithium salt of 2-nitropropane to entrain the sodium *p*-toluenesulfinate and the sodium nitrite reactions with 8, it is regrettable that this was not done for the reaction of 8 with the salt of methyl malonic ester.

sodium hydroxide and, then, twice with 100 mL of water. Finally, it was dried over anhydrous potassium carbonate and the solvent was removed. The resulting orange liquid (538 g) was distilled at 9 mm; this gave 206 g of material boiling in the range of 60 to 100 °C and a second fraction boiling from 101 to 124 °C (311 g). VPC analysis shows that the lower boiling fraction was, essentially, cumene; the higher boiling fraction consisted of 3% cumene and 24, 4, and 69%, respectively, of *o*-, *m*-, and *p*-nitrocumenes. This corresponds to a 65% yield of *p*-nitrocumene. In our earlier studies cumene, and the *o*- and *m*-nitrocumenes, were removed by careful rectification but, eventually, it was recognized that this is unnecessary. Consequently, the above mixture, containing a small amount of cumene and the three nitrocumenes, was employed for the preparation of *p*-nitrocumyl alcohol.

Into a 1-L flask equipped with a thermometer, a gas inlet tube, a 125-mL pressure-equalizing addition funnel, and an efficient mechanical stirrer was placed 60.0 g of the above nitrocumene mixture (0.25 mol of *p*-nitrocumene) and 400 mL of Me_2SO which had been distilled from calcium hydride. Oxygen, carefully dried by passing it through Drierite, was bubbled into the nitrocumene–Me_2SO solution for 15 min with stirring. At this point, 5.61 g (0.05 mol) of alcohol-free potassium *tert*-butoxide (MSA Corp) dissolved in 100 mL of *tert*-butyl alcohol (Baker analyzed reagent) was added, dropwise, with *vigorous stirring* and continued bubbling in of oxygen. Several times during the addition of the *tert*-butoxide solution the temperature of the reaction solution gradually rose to 35 °C whereupon the reaction vessel was *immediately* immersed in an ice bath, cooled to 20 °C, then removed from the ice bath. **Caution**: *Dropwise addition of the tert-butoxide solution, vigorous stirring, and careful temperature control are important. Failure to pay attention to these matters may result in an explosion.* Addition of the *tert*-butoxide solution required about 1 h. Vigorous stirring and the passing in of oxygen were continued for an additional 4 h.

The resulting deep purple solution was poured into 3 kg of ice and then 100 g of sodium chloride was added. The aqueous solution was extracted five times with 200-mL portions of ethyl ether, the combined ether extracts were filtered to remove an insoluble white solid (mp 260–263 °C dec), and then the ether solution was washed four times with 200-mL portions of water and dried over anhydrous potassium carbonate. Removal of the solvent gave 57.9 g of a red-brown liquid which, by VPC, contained a 28:6:2:64 ratio of *o*-nitrocumene–*m*-nitrocumene–unknown–*p*-nitrocumyl alcohol, respectively, and not a trace of *p*-nitrocumene. This red-brown liquid (30 g) was chromatographed on acid-washed alumina (Baker), using a 95% hexane–5% ethyl ether solution. Under these auspices the nitrocumenes and the unknown were eluted. For elution of the *p*-nitrocumyl alcohol, ethyl ether and, finally, a 95:5 mixture of ethyl ethyl–methanol were employed. The *p*-nitrocumyl alcohol thus obtained was short-path distilled. The first 4.67 g of distillate, which boiled in the range 147–150 °C (5 mm) is nearly pure *p*-nitrocumyl alcohol contaminated by very small amounts of *o*- and *m*-nitrocumene and the unknown impurity. Continued distillation at 2-mm pressure gave 15.11 g (66% yield) of VPC-pure *p*-nitrocumyl alcohol: bp 120–121 °C;[10] n^{20}_D 1.5579; NMR ($CDCl_3$) δ 1.62 (s, 6 H), 3.10 (s, 1 H), 7.66 (d, 2 H), 8.13 (d, 2 H).

Anal. Calcd for $C_9H_{11}O_3N$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.86; H, 5.85; N, 7.68.

***p*-Nitrocumyl Chloride.** Into a flask fitted with a stirring bar, a gas dispersion tube, an addition funnel, and a gas outlet tube were placed 20 g of anhydrous zinc chloride (Mallinckrodt analytical reagent; dried at 140 °C and ca. 1 mm for 12 h) and 80 mL of methylene chloride (dried by distillation from P_2O_5). The flask was immersed in an ice bath and, while stirring, a stream of anhydrous hydrogen chloride was passed into the mixture for 20 min. Then 5 g (28 mmol) of *p*-nitrocumyl alcohol dissolved in 25 mL of methylene chloride was added while the temperature of the mixture was maintained at 0 °C. The reaction was allowed to proceed an additional 20 min while the flow of hydrogen chloride was maintained and the mixture was then filtered. Approximately 5 g of silicic acid (Matheson Coleman and Bell) was added to the methylene chloride solution, and the mixture was swirled for a minute or two, filtered, and concentrated under reduced pressure. This gave 4.98 g (89% yield) of pure *p*-nitrocumyl chloride as a very pale yellow liquid: n^{20}_D 1.5560; NMR ($CDCl_3$) δ 2.00 (s, 6 H), 7.94 (AB q, 4 H); IR (neat) 6.51 and 7.38 μm (NO_2).

Anal. Calcd for $C_9H_{10}NO_2Cl$: C, 54.64; H, 5.05; N, 7.02; Cl, 17.76; mol wt 199. Found: C, 54.44; H, 5.06; N, 7.00; Cl, 17.54; mol wt ($CHCl_3$, vapor pressure) 197.

Benzenesulfinyl Chloride. This was prepared according to Douglass and Norton[11] from phenyl disulfide. The yellow liquid had n^{20}_D 1.6054 and an IR spectrum identical with Sadtler spectrum no. 13396 for benzenesulfinyl chloride.

***p*-Nitrocumyl Benzenesulfinate.** A stirred solution of benzenesulfinyl chloride (3.22 g, 20 mmol) in 40 mL of distilled methylene chloride was cooled to −50 °C under dry nitrogen and then ca. 30 mL (ca. 40 mmol) of trimethylamine was allowed to evaporate into the reaction flask. This was followed by the addition of 3.62 g (20 mmol) of *p*-nitrocumyl alcohol in 20 mL of methylene chloride over a 15-min period while the reaction mixture was maintained between −30 and −40 °C. The mixture was stirred for an additional 30 min and then allowed to come to room temperature. It was filtered to remove the white solid and the filtrate was washed with water, ice-cold 10% hydrochloric acid, saturated sodium bicarbonate, and then water. After the solution was dried ($MgSO_4$) and the solvent was removed, a pale yellow viscous oil was obtained which, on treatment with anhydrous methanol at room temperature, gave 2.4 of colorless crystals: mp 92–93 °C; IR ($CHCl_3$) 1125, 1350, 1530 cm^{-1}; NMR ($CDCl_3$) δ 8.20 (m, 2 H), 7.4–7.9 (m, 7 H), 1.97 (s, 3 H), 1.92 (s, 3 H).

Anal. Calcd for $C_{15}H_{15}NSO_4$: C, 59.00; H, 4.95; N, 4.59; S, 10.50. Found: C, 58.98; H, 4.96; N, 4.75; S, 10.56.

***p*-Nitrocumyl *p*-Toluenesulfinate.** At −15 °C a mixture of *p*-tolyl disulfide (1.93 g, 7.8 mmol) and acetic anhydride (1.592 g, 15.6 mmol) was chlorinated as described by Douglass and Norton.[11] After removal of acetyl chloride and excess chlorine 2.695 g of *p*-toluenesulfinyl chloride was obtained. Without further purification this pale yellow oil was dissolved in 30 mL of methylene chloride, cooled to −65 °C, and then 3 mL (34 mmol) of trimethylamine was condensed into the solution. Finally, 2.8 g (15.5 mmol) of *p*-nitrocumyl alcohol in 25 mL of methylene chloride was added in the course of 10 min. The reaction mixture was stirred for an additional 30 min at −65 °C before it was worked up by pouring into ice water and extracting with methylene chloride. The methylene chloride solution was washed with ice-cold 10% hydrochloric acid, aqueous sodium bicarbonate, and water and then dried ($MgSO_4$). Vacuum evaporation of the solvent left a pale yellow viscous liquid to which absolute methanol was added at room temperature. Colorless crystals of the *p*-toluenesulfinate ester resulted (2.97 g, 60% yield): mp 82.5–83 °C; pure by TLC; NMR ($CDCl_3$) δ 8.18 (d, 2 H), 7.59 (d, 2 H), 7.15–7.48 (m, 4 H), 2.41 (s, 3 H), 1.96 (s, 3 H), 1.90 (s, 3 H).

Anal. Calcd for $C_{16}H_{17}NO_4S$: C, 60.17; H, 5.37; N, 4.39; S, 10.04. Found: C, 59.95; H, 5.34; N, 4.10; S, 10.11.

***p*-Nitrocumyl Phenyl Sulfone.** The reaction of *p*-nitrocumyl chloride (1.00 g, 5 mmol) with sodium benzenesulfinate (1.64 g, 10 mmol) in 25 mL of HMPA was conducted for 10 min under an argon atmosphere (freeze–pump–thaw technique),[12] at room temperature, with exposure to two 20-W ordinary fluorescent lights. The product was then poured into water layered with benzene, and the benzene phase was washed repeatedly with water and was then dried ($MgSO_4$); after filtration the solvent was removed under reduced pressure. This gave 1.55 g of a pale yellow solid (mp 128.5–130 °C) which, after one recrystallization from carbon tetrachloride, gave 1.44 g (95% yield) of analytically pure sulfone: white crystals; mp 130–131 °C; IR ($CHCl_3$) 1158, 1302, 1350, 1525 cm^{-1}; NMR ($CDCl_3$) δ 8.12 (d, 2 H), 7.58 (d) plus 7.44 (s) (7 H), 1.82 (s, 6 H).

Anal. Calcd for $C_{15}H_{15}NSO_4$: C, 59.00; H, 4.95; N, 4.59; S, 10.50. Found: C, 59.11; H, 4.93; N, 4.74; S, 10.41.

***p*-Nitrocumyl *p*-Tolyl Sulfone.** This preparation was conducted in the same way as the preparation of *p*-nitrocumyl phenyl

(10) Other preparations had bp 111–112 °C (0.25 mm).

(11) I. B. Douglass and R. V. Norton, *J. Org. Chem.*, **33**, 2104 (1968).

(12) N. Kornblum, S. C. Carlson, J. Widmer, M. J. Fifolt, B. N. Newton, and R. G. Smith, *J. Org. Chem.*, **43**, 1397 (1978).

sulfone except that the reaction time was 45 min; 20 mL of HMPA, 347 mg (1.95 mmol) of sodium *p*-toluenesulfinate, and 243.7 mg (1.22 mmol) of *p*-nitrocumyl chloride were employed. When the product was recrystallized from a chloroform–carbon tetrachloride mixture it yielded 346 mg (89% yield) of white crystals: mp 203–204 °C; NMR ($CDCl_3$) δ 8.15 (d, 2 H), 7.60 (d) plus 7.1–7.5 (m) (6 H), 2.41 (s, 3 H), 1.84 (s, 6 H).

Anal. Calcd for $C_{16}H_{17}NO_4S$: C, 60.17; H, 5.37; N, 4.39; S, 10.04. Found: C, 59.95; H, 5.34; N, 4.10; S, 10.11.

Reactions of Sulfinate Esters. General Procedure. All experiments involving sulfinate esters were conducted with rigorous exclusion of oxygen by the freeze–pump–thaw technique.[12] In all cases the reaction mixture was stirred, the reaction time was 15 min and, except when otherwise specified, the reaction flask was held underneath two 20-W ordinary fluorescent lights at a distance of 10–15 cm.

Unless otherwise specified, workup involved pouring the reaction mixture into ice–water layered with benzene. The benzene phase was then washed five times with water and dried ($MgSO_4$), and then the solvent was removed.

***p*-Nitrocumyl Benzenesulfinate. A. Stability.** A solution of this ester (0.61 g) in 20 mL of HMPA was stirred for 2.5 h under the reaction conditions. Workup yielded 0.58 g (95% recovery) of pure *p*-nitrocumyl benzenesulfinate: mp 92-93 °C; NMR spectrum identical with starting ester.

B. Reaction with Sodium Benzenesulfinate. Treatment of 211.3 mg (0.693 mmol) of *p*-nitrocumyl benzenesulfinate in 15 mL of HMPA with 261.4 mg (1.59 mmol) of sodium benzenesulfinate for 15 min gave, on workup, white crystals, mp 128–130 °C, which by NMR and TLC were *p*-nitrocumyl phenyl sulfone. Recrystallization from carbon tetrachloride gave 202 mg (96% yield) of the pure sulfone, mp and mixture mp 129.5–130.5 °C.

C. Reaction with Sodium *p*-Toluenesulfinate. A solution of the benzenesulfinate ester (215.5 mg, 0.706 mmol) in 15 mL of HMPA was treated with 291.8 mg (1.63 mmol) of sodium *p*-toluenesulfinate. Workup gave 216.3 mg of a crystalline product which melted at 195–197 °C and which by NMR consisted of *p*-nitrocumyl *p*-tolyl sulfone (80%) and *p*-nitrocumyl phenyl sulfone (20%).

In a second experiment 104.8 mg (0.344 mmol) of *p*-nitrocumyl benzenesulfinate was allowed to react with a large excess of sodium *p*-toluenesulfinate (626 mg, 3.52 mmol) in 10 mL of HMPA. The crude crystalline product (118 mg) was found by NMR to be *p*-nitrocumyl *p*-tolyl sulfone of ca. 95% purity. Recrystallization from chloroform–carbon tetrachloride gave 88.9 mg (81% yield) of pure *p*-nitrocumyl *p*-tolyl sulfone, mp and mixture mp 202–203 °C. Evaporation of the mother liquor gave an additional 19.8 g of crystals, mp 192–195 °C. By NMR analysis this is slightly impure *p*-nitrocumyl p-tolyl sulfone.

D. Sulfone Stability. Since *p*-nitrocumyl sulfones are capable of reacting with nucleophiles[2] the unlikely possibility that *p*-nitrocumyl *p*-tolyl sulfone might be produced via *p*-nitrocumyl phenyl sulfone was examined. A solution of *p*-nitrocumyl phenyl sulfone (141.4 mg, 0.464 mmol) in 15 mL of HMPA was allowed to react with 188 mg (1.06 mmol) of sodium *p*-toluenesulfinate under the conditions of experiment C except that now the reaction time was 100 min rather than 15 min. Workup in the usual way gave 152.4 mg of a crystalline product, mp 121–125 °C. By NMR analysis this is a mixture consisting of ca. 13% *p*-nitrocumyl *p*-tolyl sulfone (mp 203–204 °C) and ca. 87% of the starting phenyl sulfone (mp 130–131 °C). Clearly the *p*-tolyl sulfone produced in C does not derived from the phenyl sulfone.[13]

(13) The matter of exchange of sulfone groups will be discussed in a forthcoming paper.

E. Inhibition of the Reaction between Sodium *p*-Toluenesulfinate and *p*-Nitrocumyl Benzenesulfinate by Di-*tert*-Butyl Nitroxide. When 103.4 mg (0.339 mmol) of *p*-nitrocumyl benzenesulfinate (mp 92–93 °C) and 121.3 mg (0.683 mmol) of sodium *p*-toluenesulfinate were allowed to react for 15 min in 10 mL of HMPA which contained 4.7 mg (0.033 mmol) of di-*tert*-butyl nitroxide, the usual workup gave 101 mg (0.332 mmol, 98% recovery) of the starting ester, mp 91–92 °C. This had the NMR spectrum of the starting *p*-nitrocumyl benzenesulfinate and there was no evidence of the characteristic NMR peak of an aromatic methyl group.

***p*-Nitrocumyl *p*-Toluenesulfinate. A. Reaction with Sodium Benzenesulfinate.** A solution of the *p*-toluenesulfinate ester (115.1 mg, 0.36 mmol) in 10 mL of HMPA was treated with sodium benzenesulfinate (114.5 mg; 0.7 mmol) for 15 min. Workup gave 108 mg of crystals which by NMR analysis were ca. 70% *p*-nitrocumyl phenyl sulfone and ca. 30% *p*-nitrocumyl *p*-tolyl sulfone.

In a second experiment 129.4 mg (0.405 mmol) of *p*-nitrocumyl *p*-toluenesulfinate in 10 mL HMPA was allowed to react for 15 min with a large excess of sodium benzenesulfinate (666.9 mg, 4.05 mmol). The crystalline product (123.3 mg) by NMR analysis was found to consist of *p*-nitrocumyl phenyl sulfone (ca. 89%) and *p*-nitrocumyl *p*-tolyl sulfone (ca. 11%). TLC (benzene–ethyl ether, 4:1) failed to detect any additional compounds.

B. Reaction with Sodium Benzenesulfinate in the Dark. Sodium benzenesulfinate (120.5 mg, 0.735 mmol) and *p*-nitrocumyl *p*-toluenesulfinate (106.4 mg, 0.333 mmol) in 10 mL of HMPA were allowed to react for 15 min in total darkness. The usual workup gave a crystalline product which by NMR and TLC consisted only of the starting sulfinate ester. This, when chromatographed on silica gel (benzene–ethyl ether, 4:1), gave 95.2 mg (90% recovery) of pure *p*-nitrocumyl *p*-toluenesulfinate, mp and mixture mp 82–83 °C. Clearly there is a large light effect on the reaction of this sulfinate ester with sodium benzenesulfinate.

C. Inhibition by *m*-Dinitrobenzene. Sodium benzenesulfinate (150.8 mg, 0.92 mmol), the *p*-toluenesulfinate ester 132.8 mg, 0.415 mmol), and *m*-dinitrobenzene (66.1 mg, 0.394 mmol) were allowed to react in 10 mL of HMPA. The crude reaction product was found by NMR analysis to consist of ca. 95% *p*-nitrocumyl *p*-toluenesulfinate and ca. 5% of a mixture of *p*-nitrocumyl phenyl sulfone and *p*-nitrocumyl *p*-tolyl sulfone.

D. Inhibition by Di-*tert*-butyl Nitroxide. Treatment of 100.9 mg (0.316 mmol) of the *p*-toluenesulfinate ester with 122 mg (0.74 mmol) of sodium benzenesulfinate in the presence of 5 μL (0.033 mmol) of di-*tert*-butyl nitroxide in 10 mL of HMPA in the usual way gave a crude product which by NMR analysis contained no sulfones. Recrystallization from methanol gave 76.9 mg (77% recovery) of the pure starting *p*-nitrocumyl *p*-toluenesulfinate, mp and mixture mp 82-83 °C.

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Registry No. 2, 75521-91-4; 3, 75506-56-8; *p*-nitrocumyl alcohol, 22357-57-9; *p*-nitrocumyl chloride, 14500-58-4; *p*-nitrocumyl phenyl sulfone, 70951-74-5; *p*-nitrocumyl *p*-tolyl sulfone, 75506-57-9; cumene, 98-82-8; *p*-nitrocumene, 1817-47-6; benzenesulfinyl chloride, 4972-29-6; sodium benzenesulfinate, 873-55-2; sodium *p*-toluenesulfinate, 824-79-3; *p*-toluenesulfinyl chloride, 10439-23-3; *p*-tolyl disulfide, 103-19-5; *o*-nitrocumene, 6526-72-3; *m*-nitrocumene, 6526-74-5.

(14) *Chem. Eng. News*, 54(39), 17 (1975).