Pathways in the Reactions of Nitronate Ions with Sulphonyl Halides

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Primary and tertiary nitronate ions and sulphonyl bromides and iodides rapidly equilibrate with the nitrohalides and sulphinate ion. Products are determined by solvent and by the occurrence of cross-equilibrium reactions, some of which have single-electron-transfer mechanisms. The reaction of arene-sulphinate and -thiolate ions with 1,2-dibromo-2-nitro-1-phenylethane gave *E*-β-nitrostyrene by *Z*-philic elimination in both cases, but the more basic thiolate ion also gave, by protophilic elimination, 2-bromo-2-nitro-1-phenylethene.

Reactions of nitronate ions with alkyl halides have been widely investigated,[1] as have reactions of halogeno-nitro compounds with nucleophiles,[2] and in many cases single-electron-transfer (SET) pathways have been implicated.[2,†] To date, mechanistic studies have dealt primarily with 2-nitropropane derivatives in aprotic solvents[2–4] and the behaviour of the versatile electrophile, bromonitromethane, with a range of nucleophiles has recently been explored.[5] A particularly striking finding in that work was the susceptibility of the nitrohalide to nucleophilic displacement at bromine with generation of nitronate ion. We now report on the equilibration of nitronate ions and sulphonyl halides with halogeno-nitro compounds and sulphinate ion (Scheme 1) and the subsequent leakage to products from both sides of the equilibrium and across it. Particular attention has been paid to the incidence of SET reactions, the occurrence of *Z*-philic‡ *versus* *C*- and *S*-philic processes, the ambident nucleophilicities of nitronate and sulphinate ions, and the role of the solvent.

Reactions of Nitromethane Derivatives in Methanol.—Addition of sodium toluene-*p*-sulphinate to a solution of bromonitromethane (**3c**) in methanol resulted in a rapid equilibration with the sulphonyl bromide (**1c**) and nitronate ion (**2**) (Scheme 1). This mixture slowly gave rise to the α-nitrosulphone (**8**), a reaction which was inhibited by *p*-dinitrobenzene (*p*-DNB)[3,†] but this inhibition is lifted by u.v. irradiation. Progress of the reaction was conveniently followed by changes in the ^{1}H n.m.r. spectrum using cyclohexane as internal standard. Work-up of the uninhibited reaction mixture afforded the nitrosulphone (**8**) and methyl toluene-*p*-sulphinate (**10**) in a ratio of 63:27 with no methyl tosylate (**7**) observed. When *ca.* 10% *p*-DNB was present, (**8**) and (**10**) were found in a ratio of 48:52, with a small proportion of (**7**). As the formation of the anhydride (**6**) and its subsequent solvolysis to sulphinic ester (**10**) are not affected by the presence of *p*-DNB, the rate of nitrosulphone formation is more than halved by the introduction of the electron acceptor, indicating an electron-transfer chain mechanism.

Yields in these experiments are dependent on concentration and reactant stoicheiometry. A typical pattern of products from a 1:1 (0.2M) mixture of sodium toluene-*p*-sulphinate and (**3c**) is: (**4**) 24%; (**7**) 8%; (**8**) 13%; (**9**) trace; (**10**) 15%; (**12**) 40%. The cross-equilibrium products (**4**) and (**10**) arise from the reaction of sulphinate on sulphonyl halide both as an *S*-nucleophile giving bis-sulphone (**4**) and as an *O*-nucleophile giving the sulphinic sulphonic anhydride (**6**). The evidence for the formation of (**6**) rests on the isolation of the sulphinic ester (**10**) and toluene-*p*-sulphonic acid but *not* sulphone (**11**), which was similarly noted by Grossert *et al.*[7] Methyl toluene-*p*-sulphinate (**10**) and methyl *p*-tolyl sulphone (**11**) are formed in almost equal proportion (54:46), in 83% yield, on alkylation of sodium toluene-*p*-sulphinate with methyl tosylate in methanol.[8]

Table 1. Reaction between $ArSO_2Na$ and $ArSO_2Z$ in methanol[a]

	% Products[b]			
$ArSO_2Z$	(**4**)	(**7**)	(**10**)	(**11**)
(**1a**)[c]			52	12
(**1b**)	6	47	47	
(**1c**)	7	38	56	
(**1d**)	8	23	69	

[a] 0.3M in each reagent with $CaCO_3$ or 2,6-lutidine as H^+ scavenger (3 days) at 20 °C. [b] Based on $ArSO_2Z$. [c] At reflux, recovered (**1a**) (25%).

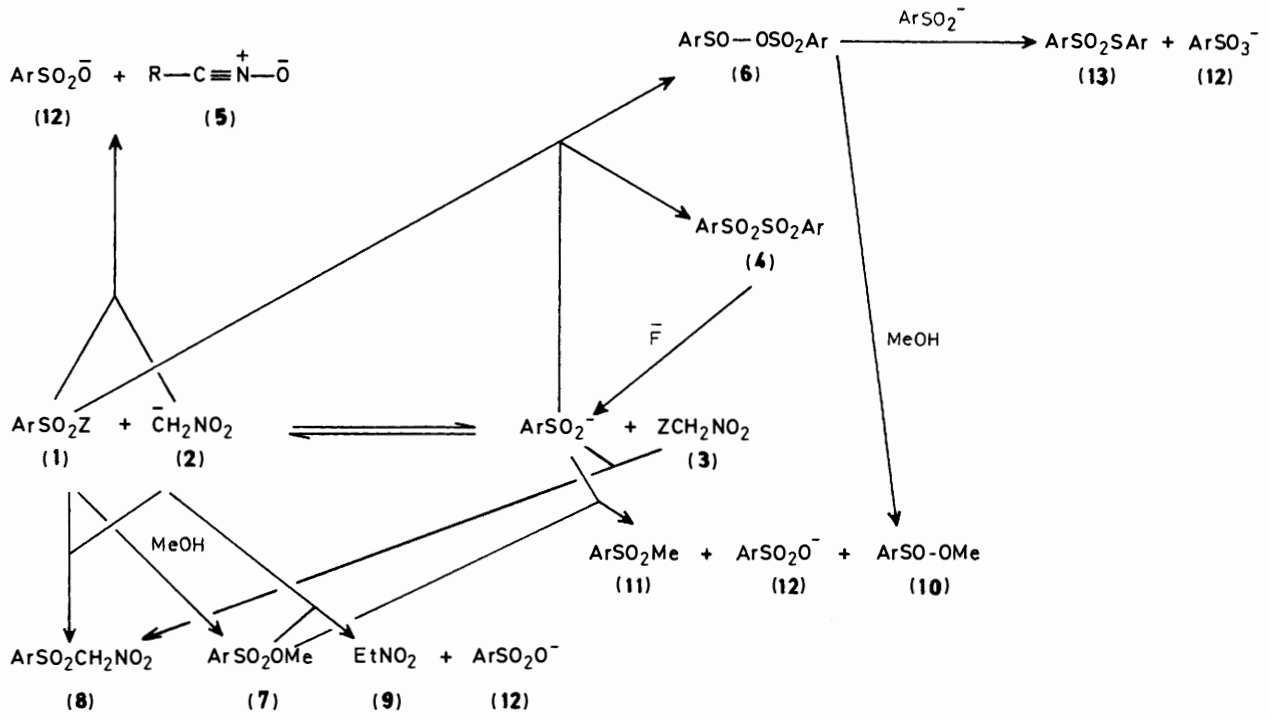
As is evident from Table 1, the sulphinate–sulphonyl chloride or –sulphonyl iodide reactions proceed in the same manner as with the bromide. It is interesting that production of sulphonate ester (**7**) *decreases* along the series Cl, Br, and I. This is concomitant with an increase in the proportion of the sulphinate ester (**10**) formed *via* (**6**) in competition with solvolysis in this series. The sulphonyl fluoride (**1a**) reaction, however, takes a different course and further highlights the array of reaction possibilities open to reaction of these 'simple' compounds. Slow solvolysis, giving (**7**), and *O*- and *S*-nucleophilic substitution by sulphinate, giving (**4**) and (**6**) respectively, allows time for the usually insignificant reaction described above in which sulphinate reacts with methyl sulphonate (**7**) and forms sulphone (**11**). The fact that (**10**) and (**11**) are not formed in equimolar amounts implicates the anhydride (**6**) route to (**10**), which should also produce bis-sulphone (**4**). The absence of (**4**) is probably due to its rapid reaction with fluoride ion,[9] regenerating sulphinate and sulphonyl fluoride (**1a**).

Sulphonyl iodide (**1d**) with nitronate (**2**) undergoes the same set of reactions as the bromide, whereas equilibrium of (**1a** and **b**) with nitronate is not established, and the nitrosulphone (**8**) is not produced, methanolysis to (**7**) being the sole pathway. Reaction of chloronitromethane with sodium toluene-*p*-sulphinate also fails to give halogen exchange and hence none of (**7**) but (**8**) is slowly produced. We do not know if this is an SET process.§

† *p*-Dinitrobenzene has been widely used to detect SET pathways by selective inhibition of the formation of certain reaction products. It acts by acceptance of a single electron to give a stable radical ion and this breaks the SET chain processes in which an intermediate radical anion transfers a single electron to (usually) a starting material.[3]

‡ We prefer this term to X-philic[6] because of the wide use of X as a general substituent.

§ A serious explosion occurred during preparation of (**3b**)[10] and we have discontinued work with this compound.



a; Z = F b; Z = Cl c; Z = Br d; Z = I Ar = *p*-tolyl

Scheme 1.

$Me_2CNO_2^-$ Me_2CZNO_2 $ArSO_2CMe_2NO_2$
(14) (15) (16)

$O_2NCMe_2CMe_2NO_2$
(17)

Reactions of Tertiary Nitro Derivatives in Methanol.—Addition of (**1d**) to a solution of nitronate (**14**) in methanol resulted in immediate disappearance of the nitronate ^1H n.m.r. resonance which was replaced by that of 2-iodo-2-nitropropane (**15d**). As indicated by this result, the equilibrium lies greatly in favour of (**15d**) and sulphinate, and although the rate of reaction (Table 2) is slow, the products of solvolysis make up a very small portion of the product, which contrasts with the observations for (**3c**). After the initial halogen exchange (which is unaffected by *p*-DNB) the reactions involve SET chain processes, as evidenced from the data of Table 2. The pathway leading to the dimer (**17**) is particularly sensitive to inhibition. Halogen exchange is also very fast, and in the same direction for the analogous bromide reaction. Subsequent reactions show similar responses to light and radical inhibitors.

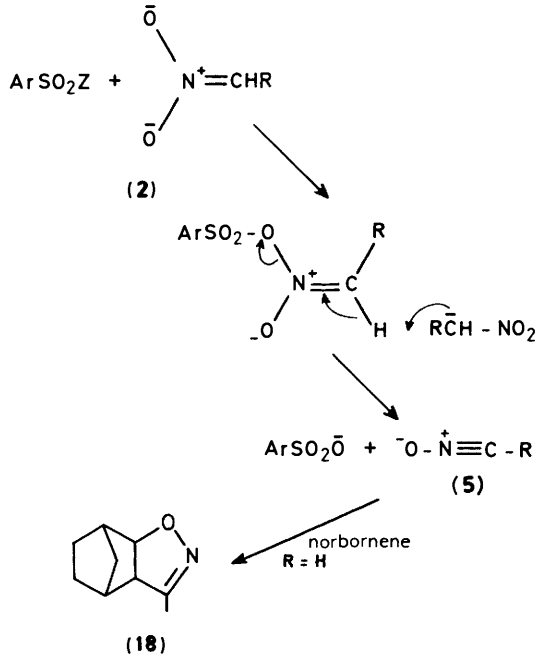
The chloride series represents a significant departure from the type of reaction observed for the bromides and iodides. 2-Chloro-2-nitropropane (**15b**) was inert towards sulphinate in methanol over 4 days at room temperature and several hours of irradiation with u.v. light. The inverse reaction of nitronate (**14**) with (**1b**) led to complete disappearance of the nitronate ^1H n.m.r. signal within the time taken to record the spectrum; none of the new resonances corresponded to (**15b**). The mixture took on a bluish tint almost instantly which then faded slowly. The n.m.r. spectral changes could be essentially duplicated by superposition of those derived from a mixture of methyl tosylate (**7**) and nitronate (**14**) in methanol and the quenching of (**14**) with a slight excess of hydrogen chloride in methanol, which also provided the blue tint. It appears the Nef reaction[1] is important in this case. The reaction of (**1a**) with (**14**) in methanol appears, by ^1H n.m.r., to be consistent with slow quenching of the anion to give 2-nitropropane as (**1a**) solvolyses.

Table 2. Reaction between (**14**) and (**1d**) in methanol[a]

	% Products		
Time (min)	(**15d**)	(**16**)	(**17**)
0[b]	100	0	0
50	80 (97)[c] [<8][d]	11 (3) [71]	5.5 (0) [26]
100	67 (95)	17 (5)	8 (0)
1 000	(73)	(27)	

[a] 0.33M in each reagent reactions at 20 °C. [b] Immediate halogen exchange to (**15d**). [c] Sample contained 20% *p*-DNB. [d] 0.2M in each reagent, sample u.v.-irradiated.

Reaction of Nitromethane Derivatives in DMF.—Change of solvent from methanol to *N*,*N*-dimethylformamide (DMF) prevents solvolysis of sulphonyl halides with its attendant products, and neither of the *C*- or *S*-philic pathways to (**8**) is observed. Instead (**1b**) (1 mol) with nitronate (**2**) (2 mol) gives nitromethane (1 mol), sodium toluene-*p*-sulphonate (**12**) (1 mol), and presumably isocyanic acid (**5**; R = H). Attempts to trap or isolate this acid failed but with the conjugate base of nitroethane in the presence of norbornene, the adduct (**18**) was obtained in 74% yield. Reaction of (**1c** and **d**) proceeded in the same manner as for the chloride, except that for the iodide there is an additional route available [equations (1) and (2)] and *ca.* 5% iodonitromethane was observed, and only a few percent of (**18**) could be isolated. The fluoride (**1a**), although sluggish,



Scheme 2.

reacts in a similar manner to the chloride. A suggested pathway is in Scheme 2, and it is recognised that the nitronate ion may not be reacting directly with sulphonyl halide but with the species, $Me_2{}^+N{=}CHOSO_2Ar$, produced by equilibration of the sulphonyl halide with DMF.[11a,*] Trapping of nitrile oxides formed from nitro compounds is described by Mukaiyama[11b] and reactions of nitronates with acyl chlorides have recently been shown to give nitrile oxides.[12] In these reactions, after the initial *Z*-philic equilibration between sulphinate and (**3c** or **d**), the *O*-nucleophilicity of nitronate and the *S*-electrophilicity of sulphonyl halide are expressed. No inhibition of these reactions by *p*-DNB was observed. In reaction of the sulphinate with (**3b**) there is a significant change in the outcome of the reaction [equation (3)], which again highlights the reluctance for *Z*-philic equilibration when Z = Cl. As the reaction between (**1b**) and (**2**) is fast and leads to sulphonate (**12**), the concentrations of the across-equilibrium species must be low as this reaction does not dominate. That some halogen exchange takes place is evident from the presence of the bis-sulphone (**4**), disulphide (**19**), and thiolsulphonate (**13**). As in methanol, sulphinate acts as both an *O*- and *S*-nucleophile, giving (**4**) and the anhydride (**6**). Under these conditions (**6**) is not solvolysed but reacts further with sulphinate, as described by Lazar and Vinkler[13] [equations (4) and (5)] to produce (**13**) and ultimately (**19**). These products are reproduced in the independent reaction of sulphinate with the sulphonyl halides, and as indicated by the data in Table 3, fluoride (**1a**) once again reacts very slowly in comparison with the others. Iodide (**1d**) gives a yield in excess of 100% based on the stoicheiometry of equations (4) and (5). The reason for this is the intervention of iodide ion as described above [equation (1)].

Reactions of 2-Nitropropane Derivatives in DMF.—A considerable amount of work has been reported on the chemistry of these compounds in polar aprotic solvents. For instance (**15b**) with sulphinate in DMF at 25 °C gave 82% of the nitrosulphone

* In check experiments, toluene-*p*-sulphonyl bromide could be recovered from DMF over the time span of the nitronate ion reactions.

Table 3. Reaction between $ArSO_2Na$ and $ArSO_2Z$ in DMF[a]

	% Products[b]		
$ArSO_2Z$	(**4**)	(**13**)	(**19**)[c]
(**1a**)[d]		7	
(**1b**)	7	76	12
(**1c**)	8	57	5
(**1d**)[e]	7	73	28

[a] 0.3M in each reagent reactions at 20 °C. [b] Yield based on stoicheiometry of equation (4). [c] Yield based on stoicheiometry of equation (5). [d] Recovered (**1a**) (71%) and isolated (**12**) (22%). [e] 0.67M in each reagent. Yield > 100%, see equation (1).

$$ArSO_2I + I^- \rightleftharpoons ArSO_2^- + I_2 \quad (1)$$

$$I_2 + CH_2NO_2^- \longrightarrow ICH_2NO_2 + I^- \quad (2)$$

$$ClCH_2NO_2 + ArSO_2^- \xrightarrow{DMF} (\mathbf{8}) + (ArS)_2 + (\mathbf{13}) + (\mathbf{12}) + (\mathbf{3b}) \quad (3)$$

(recovered)

(**19**)

7% 2% 26% 64% 37%

$$3ArSO_2^- + ArSO_2Z \longrightarrow ArSO_2SAr + 2ArSO_3^- + Z^- \quad (4)$$

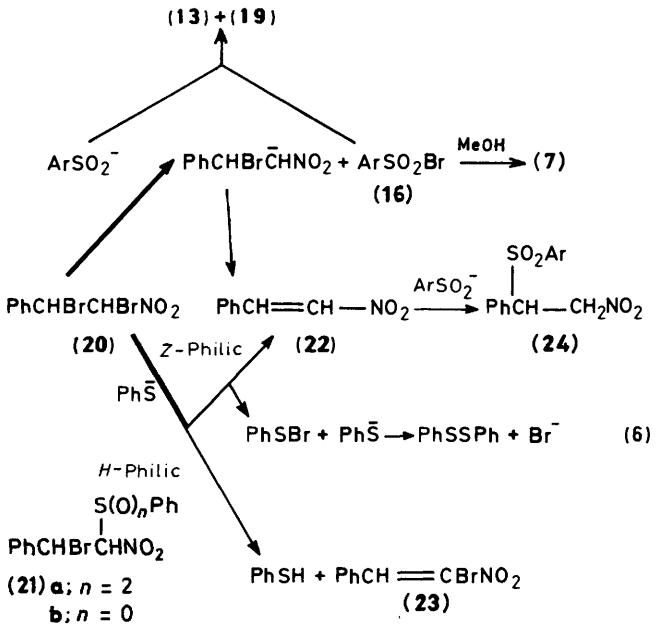
$$5ArSO_2^- + ArSO_2Z \longrightarrow (ArS)_2 + 4ArSO_3^- + Z^- \quad (5)$$

(**19**)

(**16**) after 12 days and 76% after 4 days in DMSO.[2a] The anion of 2-nitropropane with (**1b**) in DMF gave no (**16**), whereas with the sulphonyl bromide, 34% of (**16**) was isolated and with iodide (**1d**) the yield was 81% in a reaction sensitive to radical inhibition.[4] In our hands, repetition of the bromide reaction, which is complete within 5 min, confirmed the formation of (**16**) (31%), but in addition (**12**) (36%), and (**13**) (15%), together with recovered (**15c**) (45%), were obtained. Stoicheiometry of a 1:1 reaction would require *ca.* 40% of sulphonate (**12**) to be produced, leaving *ca.* 50% of bromide (**15c**) unreacted.

Z-Philic Elimination.—With the obvious diversity of mechanism and variation of pathway in these apparently simple systems, we considered the incorporation of further reaction sites to be an intriguing prospect. The substrate chosen was 1,2-dibromo-1-nitro-2-phenylethane (**20**), which presents the possibility of elimination reactions as well as substitution. In preliminary work we have shown that sulphinate reacts rapidly with (**20**) in methanol to give a mixture of *E*-(2-nitroethenyl)-benzene (**22**) and recovered (**20**) in a ratio of 84:16 with (**7**) (*ca.* 60%), the major product derived from sulphinate (Scheme 3). The initial reaction must be *Z*-philic attack followed by elimination which analogously to that of (**8**) is rapid enough to outpace formation of the nitrosulphone (**21a**). The reaction of sulphinate with dibromide (**20**) is faster than formation of anhydride (**6**) as no methyl sulphinate (**10**) was observed.

In DMF, initial addition of sulphinate (1 molar proportion) left (**20**) unreacted (20%) and addition of further sulphinate (*ca.* 0.2 molar proportion) left (**20**) (13%) remaining. Quenching of the mixture with methanol prior to work-up afforded (**7**) (48%) along with (**13**) (18%). These results are in accord with the pathways illustrated in Scheme 3. Anhydride formation



Scheme 3.

competes to a minor extent with *Z*-philic attack, and formation of (7) indicates formation of the sulphonyl bromide (**1b**). The presence of 10—20% *p*-DNB had no effect on these reactions. Alkene (**22**) polymerises under the action of small amounts of sulphinate in DMF or methanol in a reaction easily monitored by disappearance of the alkene resonances in ^{1}H n.m.r. The reaction gives the 1:1 [sulphinate–(**22**)] adduct (**24**) if acetic acid is present as proton donor.[14] No *C*-philic product (**21a**) was observed.

When dibromide (**20**) was treated with sodium benzenethiolate (1 molar proportion) in methanol, reaction was immediate and 55% of the dibromide remained (n.m.r.). Addition of a second molar proportion of thiolate led to complete consumption of (**20**). The products were (**22**) and diphenyl disulphide, isolated essentially quantitatively with a trace of the alkene (**23**) which arises because of the increased basicity of thiolate in comparison with that of sulphinate. Reaction in DMF with portionwise addition of thiolate indicates that the initial reaction is *Z*-philic substitution at bromine to give benzenesulphenyl bromide, which then competes for further thiolate [equation (6), Scheme 3], but not as efficiently as in methanol. Although the products are the same in the two solvents, the amount of (**23**) from protophilic elimination is increased to *ca.* 15% in DMF. In neither case is there any evidence for the substitution product (**21b**).

Conclusions.—Even in such apparently simple systems as these the diversity of mechanisms and variation of pathway are crucially dependent on substrate structure, the nature of the medium, and the presence of inhibitors of SET chain processes. No safe generalisations are yet possible.

Experimental

Light petroleum had b.p. 40—60 °C. Flash chromatography was by Still's[15] procedure on silica. Extracts were dried over $MgSO_4$.

Toluene-*p*-sulphonyl chloride (**1b**) was recrystallised to constant m.p. from dichloromethane–light petroleum. The other sulphonyl halides, (**1c**),[16] (**1d**),[16] and (**1a**),[17] were prepared by literature procedures. Bromonitromethane (**3c**) was prepared as described previously[5] and a similar procedure with 2-nitropropane gave 2-bromo-2-nitropropane (**15c**), $\delta_H(CDCl_3)$ 2.3 (s) [lit.,[2a] δ 2.31 (s)]. 1,2-Dibromo-2-nitro-1-phenylethane (**20**), obtained by addition of bromine to β-nitrostyrene, had m.p. 86 °C (lit.,[18] 86 °C), $\delta_H(CDCl_3)$ 7.35 (s, 5 H), 6.25 (d, 1 H, *J* 10 Hz), and 5.4 (d, 1 H, *J* 10 Hz). 2-Chloro-2-nitropropane (**15b**) was obtained by chlorination of alkaline aqueous solutions of 2-nitropropane,[19] $\delta_H(CDCl_3)$ 2.12 (s) (lit.,[2a] δ 2.14). Sodium toluene-*p*-sulphinate was dried at 120 °C for 16 h before use. Solvents were stored over 4 A molecular sieves.

Chloronitromethane (**3b**).—The above procedure, using a 100% excess of nitromethane, gave a low yield (*ca.* 10%) of (**3b**), $\delta(CDCl_3)$ 5.7 (s), contaminated with nitromethane and a little dichloronitromethane. An attempt to prepare this compound from the sodium nitronate and chlorine at low temperature led to detonation of the mixture.[10]

Sodium Nitronates.—The nitroalkane (0.11 mol) in ethanol (45 ml) was added to a cold (0 °C) ethanolic sodium ethoxide prepared by dissolution of sodium metal (0.1 g atom) in ethanol (30 ml). The solid sodium nitronate was filtered off and washed with ether. Yields were generally >90%. Although the isolation and storage of these salts presented no difficulties it must be remembered that they are potentially dangerous when dry due to the possibility of detonation if heated or struck.

Reactions of Halogenonitromethanes with Sodium Toluene-p-sulphinate.—In methanol. Bromonitromethane (0.7 g, 5 mmol), sodium toluene-*p*-sulphinate (0.89 g, 5 mmol), nitromethane (0.31 g, 5 mmol), and lutidine (0.5 g, 5 mmol) in methanol (25 ml) was stirred at 20 °C. After 48 h, filtration gave bis-sulphone (**4**) (10 mg, 1.5%) and the filtrate was diluted with water and extracted with dichloromethane. The yield of nitrite ion (aqueous portion) was <0.5%.* Evaporation of the organic extracts, and flash chromatography gave methyl toluene-*p*-sulphonate (**7**) (80 mg, 8.5%), methyl toluene-*p*-sulphinate (**10**) (130 mg, 15%), and nitromethyl *p*-tolyl sulphone (**8**) (238 mg, 22%) which were evident by their characteristic singlet resonances at δ 3.7, 3.4, and 5.6, respectively.

In a separate experiment, the total organic residue in ether was extracted with dilute, aqueous sodium hydroxide. The alkaline extract was neutralised with acetic acid and extracted with ether. Evaporation of the ethereal extract and subsequent crystallisation of the residue gave (**8**), m.p. 117—118 °C (from tetrachloromethane) (lit.,[4] 116.1—116.6 °C).

Inhibition Experiments.—Two n.m.r. tubes were charged with (**3c**) (63 mg, 0.45 mmol), methanol (0.5 ml), and cyclohexane (3 mg) (internal standard) then, to one tube, *p*-DNB (8 mg) was added and the mixtures were purged with nitrogen. One equivalent of sodium toluene-*p*-sulphinate in methanol (0.5 ml) was introduced with each tube and the n.m.r. spectrum was taken every few minutes until reaction ceased. This was evident when there were no longer changes in the resonance intensities of (**3c**), (**8**), and sulphinate ion [the methyl resonance of $ArSO_2^-$ is upfield of those for neutral species such as (**7**)] with reference to the internal standard. In the uninhibited sample 33% of (**3c**) remained after 100 min whereas the other sample contained 54%. Work-up of each sample showed the yields of (**8**) to be 20 and 6%, respectively. Repetition of this experiment gave final yields of (**3c**), 37 and 56% and of (**8**), 30 and 18% for the unhibited and *p*-DNB samples respectively.

Reactions in DMF.—A mixture of sodium toluene-*p*-sulphinate (0.45 g, 2.5 mmol), chloronitromethane (**3b**) (0.21 g,

* The concentration of nitrite was determined colorimetrically against standard solutions.[20]

2.25 mmol), and nitromethane (0.15 g, 2.5 mmol) in DMF (7.5 ml) was stirred at room temperature for one day. Dilution with water and extraction with dichloromethane gave recovered (**3b**) (80 mg, 38%). Flash chromatography of the remainder with dichloromethane–light petroleum (1:1) gave disulphide (**19**) (5 mg, 2%) (R_F 0.84), thiolsulphonate (**13**) (90 mg, 26%) (R_F 0.53), m.p. 75—77 °C, and (**8**) (40 mg, 7%) (R_F 0.16). The aqueous portion furnished a solid which was identified as the hydrate of (**12**) (0.34 g, 64%) by comparison of its i.r. spectrum with that of a commercial sample.

Nitronate (**2**) *with Toluene*-p-*sulphonyl Halides.—In methanol.* Toluene-*p*-sulphonyl fluoride (**1a**) (0.87 g, 5 mmol) was added to a solution of (**2**) (5 mmol) in methanol (7.5 ml) at 20 °C. After 20 h, work-up (as described for the halogenonitromethane–sulphinate experiments) gave (**7**) (0.34 g, 37%), with the aqueous solution yielding (**12**) (0.53 g, 54%). Toluene-*p*-sulphonyl chloride (**1b**) gave a 97% yield of (**7**), and toluene-*p*-sulphonyl bromide (**1c**) yielded products as described for the reaction of (**3c**) with sulphinate. Toluene-*p*-sulphonyl iodide (**1d**) reacted as described above except that the organic extracts were washed with aqueous sodium thiosulphate to remove iodine. Products were (**4**) (36%), (**8**) (14%), (**7**) (3%), and (**10**) (4%).

In DMF. Fluoride (**1a**) (0.87 g, 5 mmol) was added to a slurry of (**2**) (0.83 g, 10 mmol) in DMF (7.5 ml) and nitromethane (0.3 g, 5 mmol) at 20 °C. After 24 h, work-up gave (**1a**) (0.21 g, 24%) as the only non-volatile, neutral species recovered.

Stoicheiometry in Reactions of Sulphonyl Chloride (**1b**).—An n.m.r. tube containing a suspension of (**2**) (21 mg, 0.25 mmol) in DMF (0.4 ml), with cyclohexane (2.8 mg) as an internal standard, was charged with small measured increments of (**1b**) and the resultant n.m.r. spectra recorded. From the results below it is clear that one equivalent of (**1b**) consumes 2 equivalents of (**2**) and yields one equivalent of nitromethane.

(**1b**) (mmol)	Yield of $MeNO_2$ (mmol)	$MeNO_2$ % yield w.r.t (**2**)
0	0	0
0.05	0.05	20
0.075	0.08	33
0.10	0.10	42
0.125	0.13	53
0.150	0.13	53

Halides (**1c** and **d**) gave the same results except the latter also gave rise to iodonitromethane (**3d**) (0.01 mmol) together with nitromethane (0.11 mmol).

Trapping of Nitrile Oxide (**5**; R = Me).—Toluene-*p*-sulphonyl chloride (**1b**) (0.95 g, 5 mmol) was added slowly to a slurry of sodium nitroethane (0.97 g, 10 mml) and norbornene (1.88 g, 20 mmol) in DMF (20 ml) at 0 °C over 10 min. The mixture was stirred at 20 °C for 2 h and was then diluted with ether, acidified with acetic acid, and washed sequentially with water, aqueous sodium hydrogen carbonate, and brine. Solvent evaporation gave (**18**) as a yellow oil (0.56 g, 74%), b.p. (Kugelrohr) 120 °C at 10 mmHg, $\nu_{max.}$(neat film) 2 940, 2 860, 1 450, 1 435, 1 382, 1 330, 875, and 864 cm^{-1}, $\delta_H(CDCl_3)$ 4.35 (1 H, d, *J* 8 Hz), 2.95 (1 H, d, *J* 8 Hz), 2.4 (2 H, m), 1.9 (3 H, s), and 1.65—1.0 (6 H, m), $\delta_C(CDCl_3)$ 154.77, 85.64 (d), 42.49 (d), 37.55 (d), 31.58 (t), 26.77 (t), 22.22 (t), and 11.31 (q) p.p.m., *m/z* 152 (*M* + 1), 151 (*M*, 33), 109 (10), 95 (14), 94 (14), 93 (10), 92 (13), 91 (20), 85 (39), 84 (66), 82 (17), 81 (49), 79 (30), 77 (22), 68 (43), and 67 (100) (Found: C, 71.6; H, 8.6; N, 9.3. $C_9H_{13}NO$ requires C, 71.5; H, 8.7; N, 9.3%). The identity of this adduct was also verified by a procedure known to give nitrile oxides.[11] Triethylamine (0.4 g, 4 mmol) in DMF (0.5 ml) was added dropwise by syringe to an ice-cold solution of phenyl isocyanate (0.95 g, 8 mmol), norbornene (0.75 g, 8 mmol), and nitroethane (0.4 g, 4 mmol) in DMF (12 ml). After 2 h the mixture was diluted with ether and washed with water, dilute hydrochloric acid, water, and brine. Diphenylurea (0.62 g, 73%) was filtered off and the filtrate gave adduct (**18**) (0.35 g, 58%) identical with that obtained above.

Reaction of 2-*Bromo*-2-*nitropropane with Sodium Toluene*-p-*sulphinate.—In methanol.* A methanol solution 0.33M in both (**15c**) and sodium toluene-*p*-sulphinate, was stirred at room temperature for 36 h and gave, on evaporation of the solvent and extraction with dichloromethane, a mixture of (**16**) (23%), (**4**) (6%), (**7**) (1%), and (**10**) (2%) together with recovered (**15c**) (57%). Pure (**16**), m.p. 110.5—112 °C (lit.,[4] 110.5—111.7 °C), was obtained by recrystallisation from ethanol.

Effect of U.v. Light and p-*DNB.*—A methanolic solution of (**15c**) and sodium toluene-*p*-sulphinate (each 0.33M) was delivered into three n.m.r. tubes which were then flushed with nitrogen. Light was excluded from one sample, the second was irradiated with u.v. light, and the third sample was treated with 10 mol % *p*-DNB. All samples were kept at 20 °C for 24 h. Comparison of their ^1H n.m.r. spectra indicated that the first sample contained (**16**) (10%) but no (**17**), the irradiated sample contained both (**16**) (13%) and (**17**) (5%), whereas the inhibited (*p*-DNB) sample showed neither of these products. This method does not allow for the determination of (**4**), (**7**), and (**10**) in the product mixture.

In DMF. 2-Bromo-2-nitropropane (**15c**) (0.84 g, 5 mmol) was added to a slurry of sodium toluene-*p*-sulphinate (0.89 g, 5 mmol) in DMF (20 ml) and after 20 min water was added and the mixture extracted with ether. The residue from evaporation of the ether was placed *in vacuo* to remove unreacted (**15c**) (0.21 g, 25%) and was then passed through a short silica column in dichloromethane to give a solid (0.52 g), which on crystallisation from ethanol gave first (**16**) (0.37 g, 31%) and then thiolsulphonate (**13**) (15%). Evaporation of the aqueous extracts and thorough washing of the residue with acetone left (**12**) (sodium salt) (0.35 g, 36%) (i.r. identical with that of an authentic specimen).

Reaction of Sodium 2-*Nitropropane* (**14**) *with Toluene*-p-*sulphonyl Halides.—In methanol.* Toluene-*p*-sulphonyl bromide (**1c**) with (**14**) gave the same products and was worked-up in the way described for the reaction of (**15c**) with sulphinate ion. Similarly, the n.m.r. experiments were duplicated as the initial, fast reaction is halogen exchange to give (**15c**) and sulphinate.

Nitronate (**14**) (0.33 mmol) in methanol (1 ml), with cyclohexane as internal standard, was placed in each of three n.m.r. tubes, one of which contained 20 ml % *p*-DNB. The proton spectra were measured and then (**1d**) (1 equivalent) was introduced and the spectra recorded immediately. The resonance due to (**14**) was replaced by that of (**15d**) in all three samples in the time taken to scan that region (*ca.* 1 min). The sample containing *p*-DNB, and one other, were kept under normal laboratory lighting. The third was irradiated with a u.v. lamp. The product distribution as a function of time is in Table 2.

Reactions in DMF were identical with those above for (**15c**).

Reaction of Toluene-p-*sulphonyl Halides with Sodium Toluene*-p-*sulphinate.—Reactions in Methanol.* Sodium toluene-*p*-sulphinate (0.71 g, 4 mmol), (**1c**) (0.94 g, 4 mmol), and calcium carbonate (0.5 g) in methanol (16 ml) were stirred at 20 °C for 16 h. Solvent was evaporated and the solids were washed thoroughly with dichloromethane. Evaporation of the dichloro-

methane extracts gave an oil and solid (0.72 g). The latter was insoluble in ether and was filtered off to yield (**4**) (90 mg, 7%), m.p. 204 °C. The filtrate contained a mixture of (**7**) (250 mg, 34%) and (**10**) (383 mg, 56%) by ^{1}H n.m.r.

Repetition of the experiment in the presence of *p*-DNB (95 mg, 0.57 mmol) gave essentially the same result: (**4**) (105 mg, 8%), (**7**) (237 mg, 32%), and (**10**) (393 mg, 56%).

Halides (**1b** and **d**) were treated as above and gave the products in Table 1.

Reaction with the fluoride (**1a**) was carried out in refluxing methanol for 3 days. ^{1}H N.m.r. analysis of the crude product showed (**10**) (25%) but no (**7**). The sulphone (**11**) (6%), however, was observed and isolated by recrystallisation from dichloromethane–light petroleum, m.p. and mixed m.p. 86—88 °C (lit.,[21] 88 °C).

In DMF. Sodium toluene-*p*-sulphinate (0.71 g, 4 mmol) and (**1c**) (0.94 g, 4 mmol) in DMF (16 ml) was stirred at 20 °C for 48 h, diluted with water, and extracted with dichloromethane. Evaporation of the extracts followed by addition of a little ether precipitated (**4**) (100 mg, 8%), m.p. 206 °C. The residue from evaporation of the filtrate was flash chromatographed in dichloromethane–light petroleum (1:1) to give (**19**) (20 mg, 2% [8%]), R_F 0.84 , m.p. and mixed m.p. 41—44 °C (lit.,[22] 45.5 °C) and (**13**) (240 mg, 22% [52%]), R_F 0.53, m.p. and mixed m.p. 75—77 °C (lit.,[23] 76—77 °C). The values in square brackets represent yields based on equations (4) and (5).

Halides (**1a,b**, and **d**) were treated in a similar manner and gave the products in Table 3.

Reaction of (1,2-*Dibromo*-2-*nitroethyl*)*benzene with Sodium Toluene*-p-*sulphinate.—In methanol.* Addition of sodium toluene-*p*-sulphinate (63.5 mg, 0.35 mmol) to a solution of (**20**) (110 mg, 0.356 mmol) in methanol (0.5 ml), in an n.m.r. tube at 20 °C with cyclohexane as internal standard, led to rapid consumption (< 1 min) of the dibromide. Evaporation of the solvent and ^{1}H n.m.r. of the $CDCl_3$-soluble residue (108 mg) showed the product distribution to be (**22**) (84%), (**7**) (61%), and unreacted (**20**) (16%).

In DMF. Repetition of the experiment in DMF with 1.2 equivalents of sulphinate resulted in rapid consumption of (**20**). After 20 min, the mixture was diluted with ether and the extracts were washed several times with water. The ethereal solution gave unreacted (**20**) (9%), (**22**) (90%), and (**13**) (18%). When methanol was added to the reaction mixture before working up, (**7**) (62%) was also found in the ethereal extract, as shown by ^{1}H n.m.r.

Reaction of (1,2-*Dibromo*-2-*nitroethyl*)*benzene with Sodium Benzenethiolate.—In methanol.* Sodium benzenethiolate (0.3 mmol) in methanol (0.15 ml) was added to a solution of (**20**) (92.7 mg, 0.3 mmol) in methanol (0.25 ml), in an n.m.r. tube at 20 °C. The ^{1}H n.m.r. spectrum recorded immediately showed that 55% of the dibromide (**20**) remained, by comparison with the internal standard cyclohexane. With the addition of a further equivalent of thiolate, all (**20**) was consumed and a precipitate appeared in the tube. The mixture was diluted with ether and centrifuged. The insoluble solids (65 mg) were water soluble and had no i.r. spectrum (the theoretical amount of sodium bromide is 62 mg). Evaporation of the ethereal extracts gave a residue (109 mg) which by n.m.r. consisted of a mixture of (**22**) and (**19**) in essentially quantitative yield, with a trace of *Z*-(2-bromo-2-nitroethenyl)benzene (**23**) benzylic proton resonance at δ 8.5 (lit.,[24] δ 8.6).

In DMF. Repetition of the above experiment in DMF gave in the ethereal extracts an oil (75 mg) which consisted of β-nitrostyrene (38 mg, 85%), (**23**) (10.3 mg, 15%), and (**19**) (32.7 mg, 100%) by ^{1}H n.m.r. analysis. The mixture was stirred with alkaline aqueous methanol for a few minutes and then extracted with ether to give disulphide (**19**) (29 mg, 89%) identical with an authentic sample.

Reaction of β-*Nitrostyrene* (**22**) *with Sodium Toluene*-p-*sulphinate.*—β-Nitrostyrene (80 mg, 0.537 mmol) in methanol (0.5 ml) was treated with sodium toluene-*p*-sulphinate (7.5 mg, 0.042 mmol) in methanol (0.1 ml) and the disappearance of the alkene resonances was monitored by ^{1}H n.m.r. [time (min), β-nitrosytrene remaining]: 2 (91%), 5 (86%), 10 (72%), 20 (63%), 58 (32%). After a few minutes a solid began to precipitate in the tube and after 3 h the product was filtered off and washed with methanol to leave a solid (54 mg, 68%), m.p. > 300 °C, which was also insoluble in ether, dichloromethane, acetone, dimethyl sulphoxide, or water (Found: C, 64.7; H, 4.85; N, 9.2. Calc. for $C_8H_7NO_2$: C, 64.4; H, 4.7; N, 9.4%). This material is evidently a polymer of that empirical formula and of formula $[CHPhCH(NO_2)]_n$ where *n* is large enough to offset the effect of the head group $CH_6H_4SO_2$ in the C, H, and N determination.

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