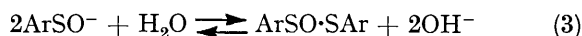


Nucleophilic Substitution at Bivalent Sulphur. Part IV.¹ A Mechanistic Study of the Base-catalysed Hydrolysis of Derivatives of 2-Nitro-4-trifluoromethylbenzenesulphenic Acid using ¹⁹F Nuclear Magnetic Resonance Spectroscopy

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The various intermediates involved in the base-catalysed hydrolysis of bis-2-nitro-4-trifluoromethylphenyl disulphide were detected using the ¹⁹F n.m.r. chemical shift of the singlet from the 4-trifluoromethyl group. The reaction involves an initial nucleophilic substitution at sulphur to give the sulphenate anion and a thiolate ion. A second intermediate, presumably the thioisulphinate, in which the aryl groups have different environments is formed by condensation of the sulphenate anion. The second intermediate gives the corresponding sulphinate and thence sulphonate ions. Surprisingly 2-amino-4-trifluoromethylbenzenesulphonate ion was also detected and isolated. A mechanism for its formation is proposed. The corresponding ethyl arenesulphenate gave similar results but with a higher percentage of the second intermediate. Hydrolysis of the sulphenyl chloride and bromide was much faster at all steps of the reaction and gave disulphide and sulphinate anion as the initial products. The sulphenyl thiocyanate reacted in a similar manner to the sulphenyl halides but gave a substantially higher yield of thiolate ion which is attributed to the simultaneous reaction of hydroxide ion at the thiocyanate sulphur. The aryl thiocyanate did not undergo substitution at sulphur and gave only the thiolate ion.

KINETIC studies on the base-catalysed hydrolysis of ethyl 2-nitro-4-trifluoromethylbenzenesulphenate (I; X = OEt) (Ar = 2-NO₂-4-CF₃C₆H₃ throughout) in 50% v/v aqueous dioxan showed¹ that the reaction leading to the disappearance of the ester was first order in ester and in hydroxide ion, while that leading to the disappearance of the intermediate sulphenate anion was second order in the anion. These results are consistent with the mechanism, equations (1)–(4). The hydrolysis



of bis-2-nitro-4-trifluoromethylphenyl disulphide (I; X = SAr) was considered to follow a similar mechanism with the possible addition of the reversible reaction (5).



The results obtained with 2-nitro-4-trifluoromethylbenzenesulphenyl chloride (I; X = Cl) were best explained by assuming that the disulphide was formed almost instantaneously and that the rate of hydrolysis of this product was then measured.

To obtain further information on the intermediates involved in these hydrolyses, the ¹⁹F n.m.r. spectra of the reaction mixtures were measured. Limited use has been made of the ¹⁹F n.m.r. signals from trifluoromethyl groups attached to aromatic nuclei and to the best of our knowledge they have not been used previously in mechanistic studies. For this purpose they have several useful properties. They occur as singlets like the ¹H n.m.r. signals from tolyl methyl groups but have a much greater

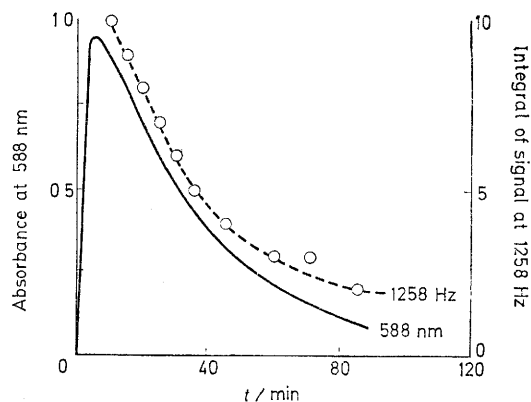
¹ Part III, D. R. Hogg and J. Stewart, *J.C.S. Perkin II*, 1974, 43.

² R. Schiller and R. Otto, *Ber.*, 1876, 9, 1637.

range of chemical shifts. Compounds which do not contain fluorine do not cause complications and deuteriated solvents are not necessary.

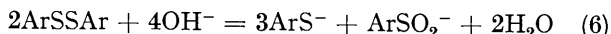
RESULTS AND DISCUSSION

Bis-2-nitro-4-trifluoromethylphenyl Disulphide.—Addition of sodium hydroxide solution to a solution of the disulphide in 30% v/v aqueous dioxan gave a blue solution. The ¹⁹F n.m.r. spectra of this solution originally comprised four signals but further signals appeared as the reaction progressed. Details are in Table 1.



Graph of absorbance at 588 nm and of the integral of the signal at 1258 Hz against time for the base-catalysed hydrolysis of bis-2-nitro-4-trifluoromethylphenyl disulphide in 30% v/v aqueous dioxan

The signal at 1284 Hz, originally 47% of the total signals, was shown by comparison with an authentic specimen to arise from the 2-nitro-4-trifluoromethylbenzenethiolate anion. This signal was expected to increase from an initial value of 50% to a final value of 75% of the total signals according to the stoichiometry expressed by equation (6).² In practice this signal never rose above 50% and finally fell to below 40%.



The signal at 1258 Hz decreased in intensity with time and clearly arose from the other product of the initial reaction. This signal was produced in the base-catalysed hydrolysis of all the other sulphenyl derivatives and is assigned to the 2-nitro-4-trifluoromethylbenzenesulphenate anion. In support of this assignment the decrease in the intensity of this signal with time parallels the decrease with time of the absorption at 588 nm, which was previously^{1,3} attributed to the sulphenate anion. This is shown in the Figure.

The decrease with time in the signal at 1258 Hz during the early part of the reaction is balanced by the increase in the signals at 1184 and 1164 Hz which have the same intensity. These signals must arise either from two

known³ instability of thiolsulphinates containing electron-withdrawing groups.

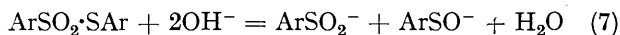
The assignment of these signals to the thiolsulphinate, owing to the instability of the thiolsulphonate in these basic media, is apparently in conflict with the observation that the initial rate of hydrolysis of phenyl benzene-thiolsulphinate⁵ in alkaline solution is several times faster than that of the corresponding thiolsulphonate.⁴ This discrepancy can be resolved if, as has been proposed,¹ the reaction of the thiolsulphinate with hydroxide ion at the sulphenyl sulphur atom is reversible [reaction (3)]. This reaction will then contribute to the measured initial rate of hydrolysis of the thiolsulphinate but not appreciably to the rate of disappearance of this intermediate

TABLE I

¹⁹F N.m.r. signals and their relative intensities from the alkaline hydrolysis of bis-2-nitro-4-trifluoromethylphenyl disulphide in aqueous dioxan

Time (min)	Relative intensity of signal (%)							
	1284 Hz	1258 Hz	1200 Hz	1194 Hz	1184 Hz	1164 Hz	1160 Hz	1152 Hz
10	47	32			10	11		
20	50	28			11	11		
30	50	22			14	14		
35	50	16			13	13		8
45	47	13		7	13	13		7
55	49	12		7	12	15		7
70	50	9	3	6	9	12		9
85	45	9	3	6	12	12	1	12
100	45	6	3	9	9	12	3	12
140	47	4	4	8	8	6	3	20
170	50	5	2	7	7	2	7	20
1080	39		6	4			24	27
Assignment	ArS ⁻	ArSO ⁻		ArSO ₂ ⁻	ArSO ₂ -SAr		ArSO ₃ ⁻	2-NH ₂ ⁻ 4-CF ₃ C ₆ H ₃ SO ₃ ⁻

compounds which are formed and which react at the same rate or, more likely, from two aryl groups in an unsymmetrical molecule. Two possibilities for this molecule are the corresponding thiolsulphinate, ArSO₂-SAr, and the thiolsulphonate, ArSO₂-SAr. An authentic sample of the latter in neutral solution gave two equal singlets at 1130 and 1118 Hz. On addition of sodium hydroxide solution these signals disappeared almost immediately and were replaced by two signals at 1258 and 1194 Hz. From previous studies⁴ on the hydrolysis of thiolsulphonates these signals were assigned to the sulphenate anion and the 2-nitro-4-trifluoromethylbenzenesulphinate ion [equation (7)]. The latter assignment was confirmed by comparison with an authentic specimen. The pair of signals at 1184 and 1164 Hz is



therefore assigned by elimination to 2-nitro-4-trifluoromethylphenyl 2-nitro-4-trifluoromethylbenzenethiolsulphinate. This is in reasonable agreement with the chemical shifts of other compounds in this study but positive evidence could not be obtained owing to the

in the reaction mixture owing to formation of the thiolsulphinate from sulphenate anion in the reverse reaction. It is apparent from Table I that this process does not attain equilibrium under the reaction conditions. For the major proportion of the reaction the concentration of thiolsulphinate does however remain constant to within a few percent, despite considerable reductions in the concentration of sulphenate anion.

The ¹⁹F n.m.r. evidence is completely consistent with the portion of the mechanism proposed for the hydrolysis of diaryl disulphides substituted with electron-withdrawing substituents deduced from kinetic studies.^{1,3} The initial step in the hydrolysis gives a thiolate anion and an intermediate, presumably the sulphenate anion. This reacts reversibly to give a second intermediate in which the two aryl groups have different environments. This latter intermediate, presumably the thiolsulphinate, is formed largely in the absence of an appreciable concentration of disulphide suggesting, in agreement with other studies,^{1,3} that reaction (5) does not represent an important pathway to the second intermediate. On

⁴ S. Oae, R. Nomura, Y. Yoshikawa, and W. Tagaki, *Bull. Chem. Soc. Japan*, 1969, **42**, 2903.

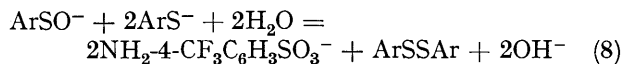
⁵ S. Oae, Y. Yoshikawa, and W. Tagaki, *Bull. Chem. Soc. Japan*, 1969, **42**, 2899.

³ D. R. Hogg and P. W. Vipond, *J. Chem. Soc. (B)*, 1970, 1242.

this evidence however a maximum of 10% of the disulphide could have reacted directly with the sulphenate anion in the initial period of the reaction. The reaction was formerly⁶ thought to continue by disproportionation of the thiolsulphinic acid to give the disulphide and the thiolsulphonate but this possibility can now be eliminated as the rate of disappearance of the second intermediate is much greater than the rate⁷ of disproportionation of thiolsulphinates.

As the reaction progressed, further signals appeared at 1194 Hz, already assigned to the sulphinic acid anion, at 1160 Hz attributed by comparison with an authentic specimen to the 2-nitro-4-trifluoromethylbenzenesulphenate anion, and at 1152 Hz similarly assigned to the 2-amino-4-trifluoromethylbenzenesulphonate anion. The sulphinic acid anion never amounted to more than 10% of the reaction mixture, although from the expected stoichiometry, it should have reached a maximum of 25%. On leaving the reaction overnight the relative concentration of the sulphinic acid anion decreased while that of the corresponding sulphonate increased. The low yield of the sulphinic acid anion is therefore attributed to oxidation giving the sulphonate ion. The combined yield, 28%, of these products was somewhat high suggesting another minor route to these products, or the intermediates leading to them.

According to reaction (4), thiolate ion should be formed simultaneously with sulphinic acid anion but as noted earlier, no increase in the percentage of thiolate ion was observed. This agrees with the low yields of thiol, **34** and 52%, obtained³ in the hydrolysis of ethyl 2-nitrobenzenesulphenate and bis-2-nitrophenyl disulphide. The low yield in the present study would seem to be associated with the unexpected formation and isolation of 2-amino-4-trifluoromethylbenzenesulphonic acid. The presence of an aminosulphonic acid may account for previous³ difficulties in achieving material balances in similar reactions. Although oxygen transfer from the nitro-group to an adjacent sulphur atom is well known⁸ in thermal and in acid-catalysed reactions, to the best of our knowledge it has not previously been observed in the base-catalysed hydrolysis of simple sulphenyl derivatives. The signal for this product appears comparatively early in the reaction and it is suggested that the amino-sulphonate is formed by the rearrangement and reduction of a sulphenate anion [reaction (8)]. The overall effect of this reaction, after

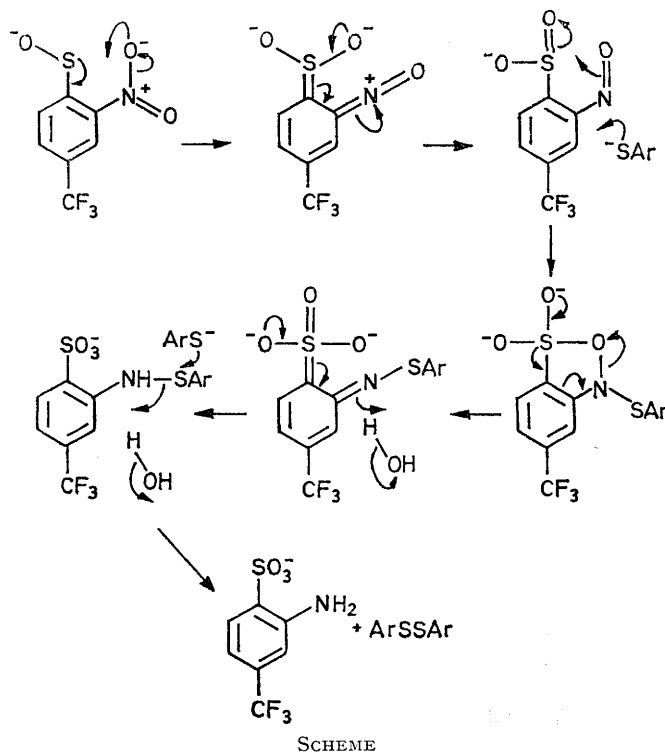


hydrolysis of the resulting disulphide, is the conversion of a thiolate ion into an amino-sulphonate ion. Brown⁹ showed that in the base-catalysed rearrangement of 2-nitrobenzenesulphenanilide to 2-azobenzenesulphonic acid the oxygen atoms were transferred intramolecularly.

⁶ (a) C. Brown and D. R. Hogg, *Chem. Comm.*, 1967, 38; (b) J. P. Danehy, *Internat. J. Sulfur Chem. (B)*, 1971, 6, 103.

⁷ P. Koch, E. Cuiffarin, and A. Fava, *J. Amer. Chem. Soc.*, 1970, 92, 5971.

We propose an analogous intramolecular oxygen transfer coupled with nucleophilic addition of a molecule of thiol to give a sulphenanilide. Removal of 2-nitrobenzenesulphenyl groups from sulphenamides by thiolate ions has been demonstrated¹⁰ in connection with the synthesis of peptides and supports the last step in the



mechanism (Scheme). Further loss of thiolate ion could occur by oxidation to the sulphenate anion by air or peroxides.¹¹ Such oxidation would result in a high combined yield of the nitro-sulphinic acid and -sulphonate as observed.

A small unidentified signal was observed at 1200 Hz. This comprised 6% of the products and was not found in the hydrolysis of any other sulphenyl derivative.

Ethyl 2-Nitro-4-trifluoromethylbenzenesulphenate.—The ¹⁹F n.m.r. spectrum of the blue reaction solution from the hydrolysis of the ethyl sulphenate under similar conditions initially contained only two signals at 1258 and 1207 Hz. Details are in Table 2. The signal at 1207 Hz, which decreased with time, was observed only in this hydrolysis and was assigned to the starting material. This is converted in the initial step of the reaction into the species giving the signal at 1258 Hz, which was previously attributed to the sulphenate anion. These results are consistent with previous observations¹

⁸ J. D. Loudon and G. Tennant, *Quart. Rev.*, 1964, 18, 389; R. S. Gaudie and P. N. Preston, *J. Chem. Soc. (C)*, 1971, 3081; F. A. Davis, R. B. Wetzel, T. J. Devon, and J. F. Stackhouse, *J. Org. Chem.*, 1971, 36, 799.

⁹ C. Brown, *J. Amer. Chem. Soc.*, 1969, 91, 5832.

¹⁰ A. Fontana, F. Marchiori, L. Moroder, and E. Scoffone, *Tetrahedron Letters*, 1966, 2985.

¹¹ D. R. Hogg and J. Stewart, unpublished data.

that the ethyl sulphenate is much less reactive to hydroxide ion than the disulphide.

The signals at 1184 and 1164 Hz, which have the same intensity, appear later in this hydrolysis and arise from the intermediate formed from the sulphenate anion, as before. This intermediate, previously considered to be the thiolsulphinic acid, is not formed significantly faster when the sulphenate anion and the ethyl sulphenate are both present in the reaction mixture in appreciable

thiolate ion was not a final product. It was however replaced with an almost equivalent amount (46%) of 2-amino-4-trifluoromethylbenzenesulphonate ion, thus adding support to the above suggestions on the origin of this compound in these hydrolyses. In contrast to the hydrolysis of the disulphide, the nitro-sulphonic acid was not detected and a high percentage of the nitrosulphinic acid was present at the end of the hydrolysis. The reaction mixture was not however left overnight. An

TABLE 2

¹⁹F N.m.r. signals and their relative intensities from the alkaline hydrolysis of ethyl 2-nitro-4-trifluoromethylbenzenesulphenate in aqueous dioxan

Time (min)	Relative intensity of signal (%)							
	1360 Hz	1284 Hz	1258 Hz	1207 Hz	1194 Hz	1184 Hz	1164 Hz	1152 Hz
5			27	73				
15			46	54				
30			48	21	7	10	14	
38			57	7	7	14	15	
47			40		7	26	27	
60		7	25		12	31	25	
90		6	13		19	31	25	
120		6	6		25	25	25	6
185	5	5			28	17	17	13
210	6	6			29	15	15	28
270	7				31	8	8	29
Assignment		ArS ⁻	ArSO ⁻	ArSOR	ArSO ₂ ⁻	ArSO·SAr		2-NH ₂ -4-CF ₃ C ₆ H ₃ SO ₃ ⁻

amounts, thus supporting previous suggestions^{1,3} that reaction (9) does not represent an important pathway in

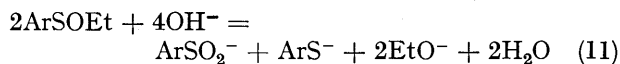


this hydrolysis. Over twice the percentage of thiolsulphinic acid is formed in this reaction as in the hydrolysis of the disulphide, and the sulphenate anion disappears much more rapidly. These effects are attributed to the decreased importance of the reversible reaction (10) in



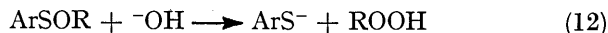
this hydrolysis due to the lower concentration of thiolate ion. In the hydrolysis of the disulphide this reaction tends to recycle the sulphenate anion and reduce the thiolsulphinic acid concentration. The increased rate of conversion of thiolsulphinic acid to product in the hydrolysis of the sulphenate ester is obscured in these data by an approximately two-fold increase in the molar concentration of substrate. A small signal arising from disulphide, formed as above, would be difficult to detect owing to disulphide-thiolate ion exchange broadening.¹¹

The thiolsulphinic acid reacts to give the sulphinate ion as before, and, after some delay, the thiolate ion. The later appearance of this ion may be attributed to the effect of the reversible reaction above, which inhibits the initial build-up of the thiolate ion concentration. The percentage of thiolate ion never approached the 50% predicted from the expected³ stoichiometry (11) and



unidentified signal at 1360 Hz was observed in the final stages of the hydrolysis.

This study confirms the conclusion drawn from kinetic data¹ that the hydrolysis of this sulphenate ester and that of the corresponding disulphide follow basically similar mechanisms. An alternative proposal [reactions (12) and (13)]^{6b} that the initial step in the hydrolysis



of sulphenate esters involves nucleophilic substitution at oxygen liberating a thiolate ion, which is then oxidised, can be eliminated. The thiolate ion formed initially might not be detected if the second step were fast, but the subsequent hydrolysis of the disulphide would form equivalent amounts of sulphenate and thiolate ion which are not found. Furthermore the maximum yield of sulphinate ion predicted by this mechanism is 25%.

2-Nitro-4-trifluoromethylbenzenesulphenyl Chloride and Bromide.—Addition of sodium hydroxide solution to a freshly prepared solution of the sulphenyl halide in 30% aqueous dioxan gave a blue colour which quickly faded. The ¹⁹F n.m.r. spectra from the hydrolysis of the sulphenyl chloride contained only three signals at 1258 (7%, sulphenate anion), 1194 (43%, sulphinate ion), and 1175 Hz (50%, disulphide). In the spectra from the sulphenyl bromide the signal due to the disulphide was replaced by those arising from its immediate hydrolysis products, signals being obtained at 1284 (27%, thiolate

ion), 1258 (22%, sulphenate anion), 1194 (42%, sulphinate ion), and 1162 Hz (9%). The last signal was assigned, by comparison to the nitro-sulphonate anion. Hydrolysis of the sulphenyl chloride to the disulphide and sulphinate anion was complete within 10 min and the bromide hydrolysed at a faster rate.

The results confirm that the hydrolysis of the sulphenyl halides follow a somewhat different reaction path to that of the corresponding sulphenate ester and disulphide. This difference cannot be attributed solely to a more rapid formation of thiolsulphinate by the additional reaction (14)¹² since the thiolsulphinate appears sufficiently stable to persist in the basic medium for several



hours. The hydrolysis is much faster at all stages of the reaction and if the same intermediates are involved their reactivity must be considerably increased by the presence of the sulphenyl halide. An increase in the rate of hydrolysis of the thiolsulphinate due to electrophilic participation by the sulphenyl halide has been proposed,¹ but the reaction is too fast for study by this method. In both cases the yield of sulphinate ion was higher than the 33% predicted by the proposed mechanisms.¹

2-Nitro-4-trifluoromethylbenzenesulphenyl Thiocyanate.—Addition of sodium hydroxide solution to a solution of the thiocyanate gave a similar blue colouration. Although sulphenyl thiocyanates readily add to olefins¹³ and generally resemble sulphenyl halides in their reactions, the ¹⁹F n.m.r. spectra of these solutions differ significantly from those obtained from the sulphenyl halides. Signals were obtained at 1284 (45%, thiolate ion), 1258 (36%, sulphenate anion), and 1194 Hz (19%, sulphinate ion). The high percentage of thiolate ion cannot be explained solely on the basis of the mechanisms discussed for nucleophilic substitution at sulphenyl sulphur and we propose that hydroxide ion can react at both sulphur atoms. Reaction at the sulphenyl sulphur atom gives sulphinate ion and disulphide, or its hydrolysis products, as found for the sulphenyl halides. From the percentage of sulphinate ion formed, *ca.* 50% of the reaction follows this pathway. Reaction at the thiocyanate sulphur is suggested to give initially the thiolate ion which can form the disulphide by reaction with starting material [reactions (15) and (16)]. This reaction may be relatively more important in this series



owing to the high acidity of the thiol and hence the greater reactivity of the thiolate ion as a leaving group. It appears however that the reactivity of the sulphur atoms is not determined entirely by this factor.¹⁴

¹² L. Di Nunno, G. Modena, and G. Scorrano, *Ricerca sci.*, 1966, **36**, 825; J. L. Kice and J. P. Cleveland, *J. Amer. Chem. Soc.*, 1970, **92**, 4757.

¹³ N. Kharasch, H. L. Wehrmeister, and H. Tigerman, *J. Amer. Chem. Soc.*, 1947, **69**, 1612.

2-Nitro-4-trifluoromethylphenyl Thiocyanate.—Addition of sodium hydroxide solution to a solution of the aryl thiocyanate in 30% v/v aqueous dioxan did not give a blue colouration indicating that these compounds should not be regarded as sulphenyl cyanides. The ¹⁹F n.m.r. spectra of the red solution contained only one signal, at 1284 Hz, assigned to the thiolate ion, which is formed¹⁵ by nucleophilic substitution at carbon [reaction (17)]. Oxidation of the thiolate ion by the cyanate ion was not observed.



EXPERIMENTAL

Materials.—2-Nitro-4-trifluoromethylphenyl thiocyanate was prepared by shaking the sulphenyl chloride¹⁶ (2.0 g) in dry benzene (50 ml) with finely divided dry potassium cyanide (10 g) for two days in the dark. The mixture was filtered and the filtrate concentrated to give the thiocyanate (78%), m.p. 77–79° [pale yellow needles from benzene-light petroleum (b.p. 60–80°)], ¹H n.m.r. τ 1.37br (1H) and 1.87 (2H, dd, *J* 9, 1.5 Hz) (Found: C, 39.0; H, 0.9; N, 11.6; S, 13.2. C₈H₃F₃N₂O₂S requires C, 38.7; H, 1.2; N, 11.3; S, 12.9%). 2-Nitro-4-trifluoromethylbenzenesulphenyl thiocyanate was similarly obtained from the sulphenyl chloride and potassium thiocyanate as orange needles (59%), m.p. 64–66° [from benzene-light petroleum (b.p. 60–80°)], ν_{max} 2160, 1515, 1340, 1165, 1145, and 1090 cm⁻¹ (Found: C, 34.6; H, 1.0; N, 9.9; S, 23.2. C₈H₃F₃N₂O₂S requires C, 34.3; H, 1.1; N, 10.0; S, 22.9%). 2-Nitro-4-trifluoromethylbenzenesulphinic acid was prepared by treating the sulphonyl chloride (4.8 g) in benzene (15 ml) with hydrazine hydrate (1.66 g) and heating the resulting precipitate in water (10 ml) to 60°. The sulphinic acid was precipitated with hydrochloric acid, m.p. 104–105°, ν_{max} 1547, 1352, 1323, 1175, 1135, and 1080 cm⁻¹ (Found: N, 5.5; S, 12.6. C₇H₄F₃NO₄S requires N, 5.8; S, 12.6%). 2-Nitro-4-trifluoromethylphenyl 2-nitro-4-trifluoromethylbenzenethiolsulphonate, m.p. 114–115° [pale yellow crystals from benzene-light petroleum (b.p. 60–80°)], was prepared in 60% yield by treating the sulphenyl chloride (2.0 g) in carbon tetrachloride (20 ml) with the thallium(I) salt prepared from the sulphinic acid (2.0 g) (Found: C, 35.5; H, 1.5; N, 6.2; S, 13.4. C₁₄H₆F₆N₂O₆S₂ requires C, 35.3; H, 1.3; N, 5.9; S, 13.5%).

All other materials were as previously¹ described.

¹⁹F N.m.r. Spectra of Reaction Mixtures.—All spectra were obtained at 30° using a Varian A100 n.m.r. spectrometer operating at 94.1 MHz. Signals are expressed in Hz downfield from the internal reference, the trifluoroacetate anion. The solvent was made up from dioxan (70 ml) and an aqueous solution (30 ml) of sodium trifluoroacetate (10 g). The substrate (*ca.* 40 mg) was dissolved in the aqueous dioxan (2 ml), an aliquot portion (0.4 ml) taken, and 5M-sodium hydroxide solution (0.05 ml) added. The spectrum was recorded. No special precautions were taken to remove oxygen. Under these conditions any intermediates present at a concentration of <0.005M could not be detected.

¹⁴ A. J. Parker and N. Kharasch, *Chem. Rev.*, 1959, **59**, 583; *J. Amer. Chem. Soc.*, 1960, **82**, 3071.

¹⁵ E. E. Reid, 'Organic Chemistry of Bivalent Sulfur,' Chemical Publishing Company, New York, 1965, vol. VI, p. 45.

¹⁶ C. Brown and D. R. Hogg, *J. Chem. Soc. (B)*, 1968, 1262.

Product Isolation from the Hydrolysis of Bis-2-nitro-4-trifluoromethylphenyl Disulphide.—5M-Sodium hydroxide (6.25 ml) was added to a solution of the disulphide (1.00 g) in 30% aqueous dioxan (50 ml) and the blue solution set aside for 18 h. The resulting red solution was added to water (50 ml), acidified with 2M-hydrochloric acid (17 ml), and extracted with methylene chloride (2 × 25 ml). The aqueous solution was evaporated to dryness and the residue triturated with a solution of sulphuric acid (1 ml) in water (4 ml). The residue was washed with acetone to give crude 2-amino-4-trifluoromethylbenzenesulphonic acid (0.6 g, 55%). Crystallisation from water gave needles, m.p.

¹⁷ F. C. Novello, S. C. Bell, E. L. A. Abrams, C. Ziegler, and J. M. Sprague, *J. Org. Chem.*, 1960, **25**, 965.

¹⁸ H. L. Yale and F. Sowinski, *J. Org. Chem.*, 1960, **25**, 1824.

335—336° (lit.,¹⁷ 333—334°) identical (i.r., n.m.r.) with an authentic specimen obtained by the reduction of potassium 2-nitro-4-trifluoromethylbenzenesulphonate with iron filings in acetic acid.¹⁸

The solvent was removed from the combined methylene chloride extracts and the residue treated with 1-chloro-2,4-dinitrobenzene and sodium hydroxide in aqueous dioxan to give 2,4-dinitrophenyl 2-nitro-4-trifluoromethylphenyl sulphide (0.45 g, 26%), m.p. 135—137° (Found: C, 39.9; H, 1.5, N, 10.9. $C_{13}H_6F_3N_3O_6S$ requires C, 40.1; H, 1.55; N, 10.8%).

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