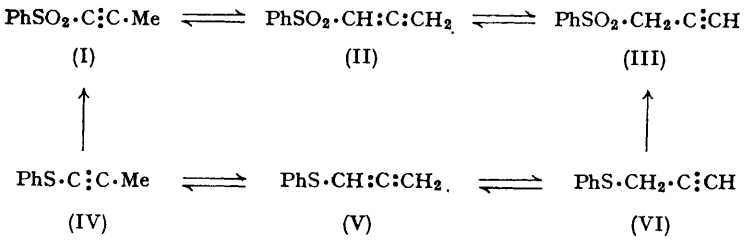
1118. *Elimination–Addition. Part IV.*[1] *Additions of Sulphur Nucleophiles to Allenic and Acetylenic Sulphones.**

By C. J. M. Stirling.

The interconversions of phenylsulphonylpropadiene, 1-phenylsulphonylpropyne, and 3-phenylsulphonylpropyne have been investigated, and the structures of the adducts formed from each by the nucleophilic addition of thiophenol and benzenesulphinic acid have been elucidated. Isomerisation of these adducts has been studied and the mechanisms of the reactions are discussed.

Addition of nucleophiles to βγ- and αβ-unsaturated sulphones has been discussed in Part I.[2] In this and the following Paper, attention is turned to reactions with allenic and acetylenic sulphones. Three sulphones have been studied: phenylsulphonylpropadiene (II), 3-phenylsulphonylpropyne (III), and 1-phenylsulphonylpropyne (I). The three-carbon system was selected because it enabled a comparison of the behaviour of three isomers to be made; choice of the phenyl group was decided upon in order to simplify the proton magnetic resonance spectra used for structural determination of the products of nucleophilic addition.

3-Phenylsulphonylpropyne[3] was available by oxidation of the sulphide[4] (VI) obtained from thiophenol and 3-bromopropyne. 1-phenylsulphonylpropyne has been prepared[5] from the sulphide (IV) produced by methylation of phenylthioacetylene. Recently, however, Pourcelot, Cadiot, and Willemart[3] have reported, without experimental details, the base-catalysed isomerisation of the sulphide (VI) to (IV), *via* the allene (V), and this route was used for the sulphone (I).



Allenic sulphones have not previously been reported; phenylsulphonylpropadiene was obtained by alumina-catalysed isomerisation of the acetylene (III).

In this Paper, the additions of thiophenol and benzenesulphinic acid to each of the three sulphones are reported; reactions with methoxide and amines are discussed in the following Paper.

Experimental

The light petroleum used had b. p. 40—60° and the solvents were anhydrous. Extracts were dried over Na_2SO_4. The alumina was Spence's type H. Unless otherwise stated, oxidation of sulphides to sulphones was effected by keeping the sulphide with aqueous 30% hydrogen peroxide (4 mol.) in twice the volume of acetic acid at 100° for 1 hr. Induction periods in catalytic hydrogenations lasted for up to 24 hr.

* Presented in part at the International Symposium on Organic Reaction Mechanisms, Cork, July, 1964.

1 Part III, A. T. Kader and C. J. M. Stirling, *J.*, 1964, 258.
2 A. T. Kader and C. J. M. Stirling, *J.*, 1962, 3686.
3 G. Pourcelot, P. Cadiot, and A. Willemart, *Compt. rend.*, 1961, **252**, 1630.
4 K. Sato and O. Mujamoto, *J. Chem. Soc. Japan*, 1956, **77**, 1409.
5 W. E. Parham and P. L. Stright, *J. Amer. Chem. Soc.*, 1956, **78**, 4783.

Sodium benzenesulphinate was recrystallised from acetone–water. Triethylamine was treated with benzoyl chloride (10 moles %) before double distillation and storage over sodium.

Dipole moments were measured with a W.T.W. "Dipolmeter" Type DM 01 for determination of dielectric constant, together with a Hilger-Chance refractometer Type M 410. Both determinations were carried out with benzene as solvent at 25°. Values of μ were calculated as outlined by Guggenheim and by Smith.[6]

Proton magnetic resonance spectra were determined for deuterochloroform solutions with tetramethylsilane as internal reference on Varian A-60 and HR-100 spectrometers operating at 60 and 100 Mc./sec., respectively. Results for the adducts obtained from allenic and acetylenic sulphones are collected in the Table.

3-Phenylsulphonylpropyne, m. p. 93° (lit.,[3] 93°) was obtained by oxidation of the sulphide.[4] The infrared spectrum ($CHCl_3$ solution) showed a strong band at 3300 cm.$^{-1}$ (C≡C–H str.), but no band near 2200 cm.$^{-1}$ (C≡C str.). Hydrogenation in ethyl acetate over palladium–charcoal gave phenyl propyl sulphone (86%), m. p. and mixed m. p. 40—41° (lit.,[7] 44°).

Phenylsulphonylpropadiene.—3-Phenylsulphonylpropyne (2 g.) in methylene chloride (20 ml.) was poured on to an alumina column (2 × 20 cm.) and elution with methylene chloride (60 ml.) gave the *allene* (1·76 g.), m. p. 37—40°, raised to 44—45° (from isopropyl ether–light petroleum) (Found: C, 60·2; H, 4·4. $C_9H_8O_2S$ requires C, 60·0; H, 4·5%). The infrared spectrum (KBr) showed no absorption at 3300 or 2200 cm.$^{-1}$ but a strong doublet at 1960 and 1920 cm.$^{-1}$. Hydrogenation as for the isomer above gave phenyl propyl sulphone (87%), m. p. and mixed m. p. 40—41°. The proton magnetic resonance spectrum showed three bands, centred at τ 4·54 (doublet), 3·70 (triplet), and 2·44 (multiplet), respectively, with integrals in the ratio: 2:1:5·3.

1-*Phenylsulphonylpropyne.*—3-Phenylthiopropyne (4 g.) in tetrahydrofuran (40 ml.) was stirred with finely powdered potassium hydroxide (10 g.) at 20°. Progress of the isomerisation was followed by infrared spectroscopy; after 80 min., terminal acetylene had disappeared and after 16 hr., allenic absorption was very weak. The mixture was diluted with water (200 ml.), and extraction with light petroleum gave 1-phenylthiopropyne (3·53 g.), b. p. 116°/16 mm., n_D^{19} 1·5992 (lit.,[5] b. p. 78—81°/0·75 mm., n_D^{25} 1·5953). Oxidation of the sulphide (3·53 g.) gave the sulphone (3·51 g.), m. p. 64—65°, raised to 68—69° (from benzene–light petroleum) (lit.,[3,5] m. p. 69°) (Found: C, 59·9; H, 4·5%).

Isomerisation of 1- *and* 3-*Phenylsulphonylpropynes.*—Each sulphone (250 mg.) in benzene (4·5 ml.) was treated with triethylamine (0·5 ml.). The infrared spectra of the solutions were examined at intervals; in the run with the former sulphone, the concentration of allene reached a maximum after 18 hr., at which time the concentration of the acetylene had fallen to *ca.* 2% of the initial value. With the latter isomer, the allene reached a maximum concentration in less than 12 min., and no acetylene was detectable at this time.

Reactions with Thiophenol.—(*a*) 3-*Phenylsulphonylpropyne.* The sulphone (500 mg.) and thiophenol (0·28 ml., 1 mol.) in methanol (10 ml.) were treated with triethylamine (0·025 ml.). After 105 min. at 20°, evaporation of the solution at 40° gave 3-*phenylsulphonyl*-2-*phenylthiopropene* (VII) (755 mg., 94%), m. p. 59—60° raised to 60—61° (from isopropyl ether) (Found: C, 61·6; H, 4·6. $C_{15}H_{14}O_2S_2$ requires C, 62·1; H, 4·8%). The same yield (m. p. 54—55°) was obtained under the same conditions when benzene was the solvent. Starting material (84%) was recovered when no triethylamine was added.

Oxidation of the adduct (1 g.) gave 2,3-*diphenylsulphonylpropene* (X) (1 g.), m. p. 128—129·5° (from ethanol) (Found: C, 56·1; H, 4·3. $C_{15}H_{14}O_4S_2$ requires C, 55·9; H, 4·4%). The bis-sulphone (500 mg.) was hydrogenated in ethyl acetate over palladium–charcoal, absorption ceasing when 27 ml. (80%) had been absorbed. The product (450 mg.), m. p. 100—102°, still contained unsaturated material, which was removed by treatment with permanganate in acetic acid at 70° for 1 hr. The usual working up gave 1,2-diphenylsulphonylpropane (280 mg., 56%), m. p. and mixed m. p. 113—114° (lit.,[8] 113°).

(*b*) *Phenylsulphonylpropadiene.* The sulphone (1 g.) and thiophenol (0·56 ml.) in benzene (20 ml.) were treated with triethylamine (0·05 ml.) as for the preceding experiment. The same adduct (1·5 g., 93%), m. p. and mixed m. p. 59—61°, was obtained.

(*c*) 1-*Phenylsulphonylpropyne.* The sulphone (500 mg.) and thiophenol (0·28 ml.) in benzene (10 ml.) were treated with triethylamine (0·025 ml.) as in the preceding experiments. The product

[6] E. A. Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 714; J. W. Smith, *ibid.*, 1950, **46**, 394.
[7] R. Otto and W. Otto, *Ber*, 1888, **21**, 992.
[8] R. Otto, *J. prakt. Chem.*, 1895, **51**, 285.

was cis-1-*phenylsulphonyl*-2-*phenylthiopropene* (VIII) (775 mg., 96%), m. p. 97—98° raised to 99—100·5° (from isopropyl ether) (Found: C, 61·8; H, 4·95%). With methanol as solvent, the same adduct was obtained in 95% yield. Oxidation of the adduct (900 mg.) gave cis-1,2-*diphenylsulphonylpropene* (XI) (930 mg.), m. p. 113—114·5° (from ethanol) (Found: C, 55·8; H, 4·2%), $\mu = 4{\cdot}8$D.

Isomerisation of the Adducts.—(*a*) 3-*Phenylsulphonyl*-2-*phenylthiopropene* (VII). The adduct (4 g.) in methanol (20 ml.) was treated with 2N-methanolic sodium methoxide (20 ml.). The mixture was set aside for 10 min., diluted with ether (300 ml.) and washed with water (2 × 200 ml.). The washings were re-extracted with ether and evaporation of the combined ethereal extracts gave a residue (3·79 g.) which, on crystallisation from isopropyl ether, gave trans-1-*phenylsulphonyl*-2-*phenylthiopropene* (IX) (1·30 g.), m. p. 85·5—87° (Found: C, 62·1; H, 4·9%). The mother liquors were evaporated and the residue was chromatographed in benzene on alumina. Elution with benzene first gave further *trans*-isomer (740 mg. total 51%) and then a fraction (370 mg.), m. p. 30—40°, which, on crystallisation from isopropyl ether, gave 3-phenylsulphonyl-2-phenylthiopropene (150 mg.), m. p. and mixed m. p. 60—61°. Subsequent fractions (oils) had infrared spectra closely similar to those of mixtures of the adducts obtained from the acetylenic sulphones on treatment with sodium methoxide (following paper), but no pure compounds were isolated from them.

The adduct was not isomerised by treatment with triethylamine in benzene at 20°.

(*b*) cis-1-*Phenylsulphonyl*-2-*phenylthiopropene*. (i) The adduct (750 mg.) was treated with N-methanolic sodium methoxide as before. The crude product (610 mg.) had m.p. 52—70°; crystallisation from isopropyl ether gave the *trans*-isomer (80 mg.), m. p. and mixed m. p. 85—86°. Chromatography of the mother liquors as before gave further *trans*-isomer (180 mg., total 35%) together with 3-phenylsulphonyl-2-phenylthiopropene (25 mg.), m. p. and mixed m. p. 60—61°. Subsequent fractions again closely resembled methoxy-adducts. No starting material was recovered.

(ii) The adduct (500 mg.) in benzene (10 ml.) was treated with thiophenol (0·352 ml.; 2 mol.) and triethylamine (0·476 ml.; 2 mol.). Removal of volatile material after 16 hr. gave recovered adduct (460 mg.), m. p. and mixed m. p. 87—94°.

(*c*) trans-1-*Phenylsulphonyl*-2-*phenylthiopropene*. Treatment of the sulphone (515 mg.) with methanolic sodium methoxide, as before, gave a crude product (535 mg.). Chromatography gave first, recovered material (200 mg.), m. p. and mixed m. p. 85—86°, and then 3-phenylsulphonyl-2-phenylthiopropene (30 mg.), m. p. and mixed m. p. 60—61°.

trans-1,2-*Diphenylsulphonylpropene* (XII).—Oxidation of the sulphide (IX) (1·3 g.) gave the *bis-sulphone* (1·28 g.), m. p. 144—145° (from ethanol) (Found: C, 56·1; H, 4·45%), $\mu = 4{\cdot}4$D.

Reactions with Sodium Benzenesulphinate.—(*a*) 3-*Phenylsulphonylpropyne*. Sodium benzenesulphinate (1·36 g., 3 mol.) was added to the sulphone (500 mg.) and acetic acid (160 mg.) in methanol (5 ml.). The mixture was warmed until a clear solution was obtained, and set aside at 20° for 19 hr. Water and chloroform were added to the mixture which was filtered. The residue of 1,2,3-triphenylsulphonylpropane (235 mg.) had m. p. 233—238° raised to 242° (from dimethyl sulphoxide–methanol) (Found: C, 54·6; H, 4·5. Calc. for $C_{21}H_{20}O_6S_3$: C, 54·4; H, 4·3%) alone or mixed with an authentic specimen (below) (lit.,[9] m. p. 226°). The organic layer of the filtrate was evaporated and the residue was extracted with boiling benzene. More trisulphone (60 mg., 23% total), m. p. and mixed m. p. 242°, remained. Evaporation of the benzene extracts gave 2,3-diphenylsulphonylpropene (635 mg.; 71%), m. p. and mixed m. p. 126—127°.

(*b*) *Phenylsulphonylpropadiene*. The sulphone (500 mg.) was treated (17 hr. at 20°) with acetic acid (1 mol.) and sodium benzenesulphinate (3 mol.) in methanol as in (*a*). The trisulphone (605 mg.; 47%), m. p. and mixed m. p. 236—240°, and the disulphone (X) (160 mg.; 18%), m. p. and mixed m. p. 126—128° were obtained. Repetition of the experiment with acetic acid (1·5 mol.) and sodium benzenesulphinate (1·5 mol.) gave the trisulphone (26%) and the disulphone (73%).

(*c*) 1-*Phenylsulphonylpropyne*. The reaction was performed as in (*a*) and the mixture was diluted with methanol (10 ml.) and filtered. The residue (20 mg.; 1·5%) was 1,2,3-triphenylsulphonylpropane, m. p. and mixed m. p. 240° (infrared spectra identical). The filtrate was diluted with water and extraction with chloroform gave a crude product (875 mg.; m. p. 100—110°) which, on recrystallisation from methanol, gave *cis*-1,2-diphenylsulphonylpropene (510 mg.,

[9] E. Stuffer, *Ber.*, 1890, **23**, 1408.

57%), m. p. and mixed m. p. 113—114°. Evaporation of the mother liquors gave further material (245 mg., 27%), m. p. and mixed m. p. 108°.

(*d*) 2,3-*Diphenylsulphonylpropene*. The sulphone (300 mg.) in methanol (10 ml.) was treated with acetic acid (160 mg.) and sodium benzenesulphinate (1·36 g.). After 48 hr., dilution with water gave the trisulphone (405 mg., 95%), m. p. and mixed m. p. 239—240°.

(*e*) cis-1,2-*Diphenylsulphonylpropene*. The sulphone (500 mg.) in methanol (5 ml.) was refluxed for 6 hr. with acetic acid (0·1 ml.) and sodium benzenesulphinate (900 mg.). Methanol (10 ml.) was added and filtration gave the trisulphone (75 mg.), m. p. and mixed m. p. 240°. The filtrate was diluted with water and extraction with methylene chloride gave a product (185 mg., m. p. 87—90°), whose infrared spectrum (KBr) was similar to that of the starting material, showing that the *trans*-sulphone (XII) was not the contaminant.

(*f*) trans-1,2-*Diphenylsulphonylpropene*.—The sulphone (340 mg.) was treated with acetic acid and sodium benzenesulphinate as in (*e*). After refluxing for 9 hr., the mixture was filtered and the residue was washed successively with water, methanol, and methylene chloride. It (40 mg.) had m. p. 240°, alone or mixed with the trisulphone. Extraction of the filtrate with methylene chloride gave recovered starting material (305 mg.), m. p. and mixed m. p. 139—141°.

1,2,3-*Triphenylsulphonylpropane*.—The following method was preferred to the literature procedure[9] as it obviates the possibility of isomerisation. 1,2,3-Tribromopropane (7 g., 1·3 mol.) was added to thiophenol (1 mol.) in N-ethanolic sodium ethoxide (1 mol.), and the mixture was refluxed for 2 hr. Dilution with water and extraction with methylene chloride gave 1,2,3-trisphenylthiopropane (3·4 g.), b. p. 226°/0·5 mm., n_D^{17} 1·6565 (Found: C, 68·7; H, 5·4. Calc. for $C_{21}H_{20}S_3$: C, 68·5; H, 5·4%) (lit.,[10] b. p. 210°/0·05 mm., n_D^{20} 1·6490). Oxidation gave the trissulphone, m. p. 240° (from dimethyl sulphoxide–methanol).

Results and Discussion

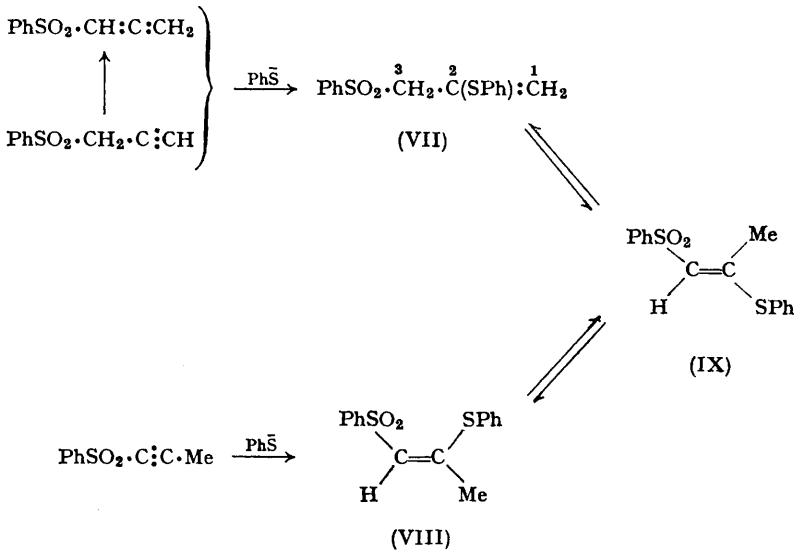
At the outset, it was important to establish the ease of interconversion of the isomers (I), (II), and (III) in view of the possibility of isomerisation before addition. Isomerisation of the sulphides (VI) → (V) → (IV) is in accordance with general experience[11,12] and energy relationships in this type of system have been discussed by Moore and Ward.[13] The ready formation of the allene (II) from the terminal acetylene (III) was, therefore, expected, but conversion of the nonterminal acetylene (I) into allene was not. Allene formation from nonterminal acetylenes has, however, been observed,[14] when a system possessing a greater degree of conjugation is thereby produced. It is noteworthy in this connection that the base-catalysed conversion[15] of buta-2,3-dienoic acid to tetrolic acid has an equilibrium constant of 2·22.

Additions of Thiophenol.—The proton arrangement of the adduct (VII), produced either from the terminal acetylene (III) or from the allene (II) in benzene or methanol, is established by proton magnetic resonance spectra. It is presumed that the terminal acetylene isomerises to the allene before nucleophilic addition occurs. Triple bonds that lack a negative group directly attached to the triple bond are not susceptible to addition under conditions as mild as those employed in this work, and no reaction occurs in the absence of triethylamine. The position of protonation (at C-3) in addition to the allene is in accord with "Ingold's rule"[16] that, in a system of this type, protonation should occur more rapidly to give the isomer of lesser thermodynamic stability. Nucleophilic addition of thiols to an allenic system* does not

* Since this Paper was submitted the Paper by P. Kurtz, H. Gold, and H. Disselnkötter (*Annalen*, 1959, **624**, 1), dealing with additions of sulphur, nitrogen, and oxygen nucleophiles to cyanopropadiene, has come to the author's attention. The products were all of the type $CH_3{\cdot}CX{:}CH{\cdot}CN$, and configurations were not assigned.

[10] R. Kh. Freidlina, A. B. Terent'ev, and R. G. Petrova, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, 1962, 282.
[11] W. J. Gensler and J. Casella, *J. Amer. Chem. Soc.*, 1958, **80**, 1376.
[12] V. A. Engelhardt, *J. Amer. Chem. Soc.*, 1956, **78**, 107.
[13] W. R. Moore and H. R. Ward, *J. Amer. Chem. Soc.*, 1963, **85**, 86.
[14] W. Oroshnik, A. D. Mebane, and G. Karmas, *J. Amer. Chem. Soc.*, 1953, **75**, 1050.
[15] G. Eglinton, E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J.*, 1954, 3197.
[16] C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Bell, London, 1953, p. 565.

appear to have been studied previously, and the present observation is a further supporting example for Ingold's correlation. It is reasonable to assume that protonation will occur at the site of greater electron density in the transition state (or intermediate). The sulphonyl group is a powerful electron acceptor[17] and distorts the electron distribution over carbons 1, 2, and 3, so that electron density is greatest in the vicinity of C-3. A similar situation arising in the isomerisation of allylic sulphoxides has been discussed by O'Connor and Broaddhus.[18]



When sulphone (I) is treated under the same conditions, the product obtained is assigned structure (VIII), in which *trans*-addition to give the *cis*-product has occurred. Many examples of the nucleophilic addition of thiols to acetylenes have been studied,[19] and addition is found to proceed almost invariably in a *trans*-fashion,[20] in spite of variation in thiol and substrate.[21] The steric course is accounted for[20] on the basis of the maximum separation of the entering nucleophile and the electron pair displaced from the triple bond, together with the known configurational stability of vinyl carbanions. Further evidence, based on dipole-moment measurements, that the assignment is correct is mentioned below.

Both adducts are isomerised by N-methanolic sodium methoxide to the *trans*-compound (IX). The arrangement of protons is confirmed by proton magnetic resonance and the τ-value for the protons of the methyl group in (IX) shows that they are considerably more deshielded[22] by the adjacent sulphonyl group than those in (VIII). This isomerisation proceeds in the expected direction; the isomer (IX), with the dipoles of the phenylsulphonyl groups and phenylthio-groups opposed, should have the greatest thermodynamic stability. In this connection, it is interesting that the order of stabilities appears to be (IX) > (VII) > (VIII). Isomers (VII) and (IX) are obtained together when either is treated with sodium methoxide, but no isomer (VIII) was isolated from either (VII) or (IX) under the same conditions.* The

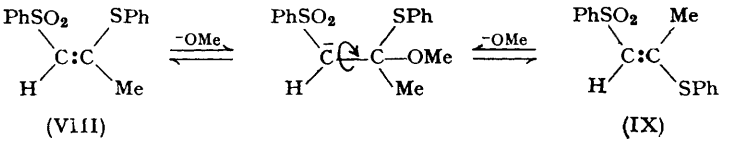
* The failure to isolate isomer (VIII) may be due to side reactions, *e.g.* elimination, but there appears to be no reason why these should occur in (VIII) to a greater extent than in (VII).

[17] J. Strating, "Organic Sulfur Compounds", ed. Kharasch, Pergamon Press, London, 1961, Vol. I, ch. 15.
[18] D. E. O'Connor and C. D. Broaddhus, *J. Amer. Chem. Soc.*, 1964, **86**, 2267.
[19] For references see A. T. Blomquist and J. Wolinsky, *J. Org. Chem.*, 1958, **23**, 551.
[20] W. E. Truce and J. A. Simms, *J. Amer. Chem. Soc.*, 1956, **78**, 2756.
[21] W. E. Truce, W. Bannister, B. Groten, H. Klein, R. Kruse, S. Levy, and E. Roberts, *J. Amer. Chem. Soc.*, 1960, **82**, 3799.
[22] Cf. D. E. Jones, R. O. Morris, G. A. Vernon, and R. F. M. White, *J.*, 1960, 2349.

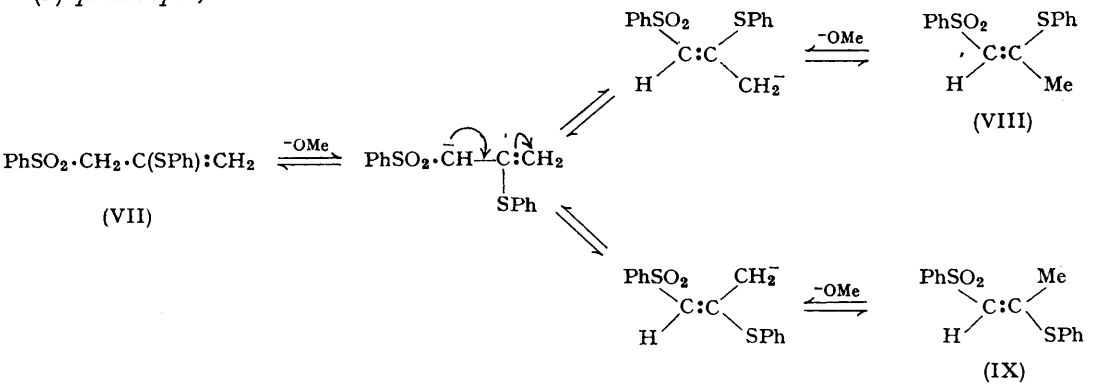
apparently greater stability of the unconjugated isomer (VII) relative to (VIII) is very unusual in this type of compound, but a similar example of a sulphoxide has been noticed recently.[23]

Two mechanisms for isomerisation seem possible:

(i) *addition–elimination*:[24]



(ii) *prototropic*;



The latter is thought to be more important as addition–elimination does not account for the isomerisation of (VII), and elimination of thiophenoxide should occur in preference to that of methoxide. Further, treatment of isomer (VIII) with thiophenol and triethylamine does not cause appreciable isomerisation, in spite of the fact that thiophenoxide is a powerful nucleophile in additions to carbon–carbon double bonds.

Chemical shifts* (p.p.m.) of adducts (d = doublet; q = quartet).

Adduct	$-SO_2\cdot CH:$	$-C:CH_2$	$-SO_2\cdot CH_2-$	$-C\cdot CH_3$
(VII)	—	4·55 4·76 (2·0)	6·05 (2·0)	—
(X)	—	3·25 3·45 (2·0)	5·85 (1·76)	—
(VIII)	3·65q (1·0)	—	—	8·25d (3·01)
(XI)	3·12q (1·0)	—	—	7·90d (3·46)
(IX)	4·22 (1·0)	—	—	7·56 (2·86)
(XII)	2·59 (1·0)	—	—	7·66 (3·10)

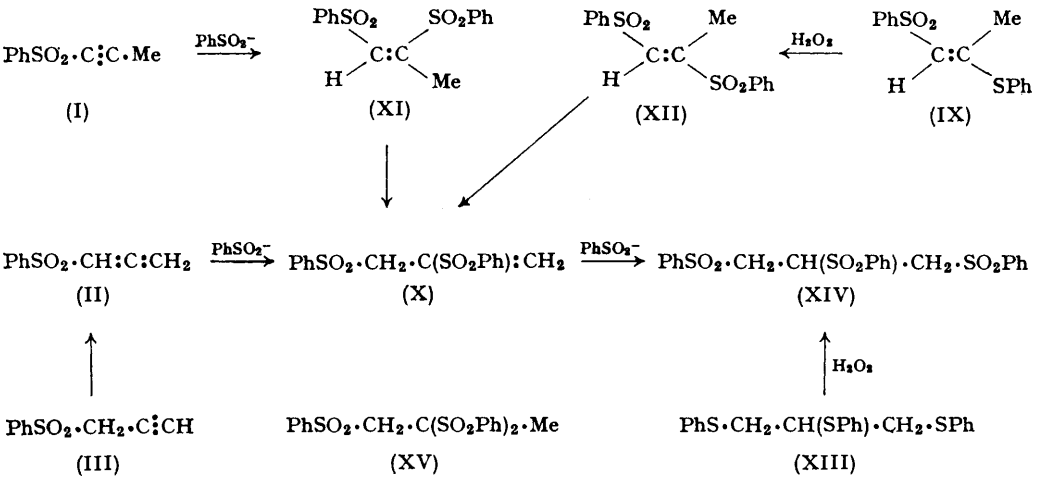
* Integrals (arbitrary units) in parentheses.

Additions of Benzenesulphinate.—Sulphinates have been very much less studied in additions to unsaturated systems. Additions to ethynyl ketones[25,26] have been shown to give mixtures of geometrically isomeric sulphones, which are interconverted by irradiation with ultraviolet light or by acidic or basic catalysts. Assignment of configuration was only tentative.

Reactions of the sulphones (I), (II), and (III) with sodium benzenesulphinate in methanol were buffered with acetic acid to prevent the medium from becoming alkaline.[27] Isomers (II) and (III) gave the adduct (X) whose proton arrangement was checked by proton magnetic resonance spectroscopy; it was identical with the oxidation product of the sulphide (VII).

[23] D. E. O'Connor and W. I. Lyness, *J. Amer. Chem. Soc.*, 1963, **85**, 3045.
[24] Cf. Z. Rappoport, G. Degani, and S. Patai, *J.*, 1963, 4513.
[25] K. Bowden, E. A. Braude, and E. R. H. Jones, *J.*, 1946, 945.
[26] E. P. Kohler and G. R. Barrett, *J. Amer. Chem. Soc.*, 1924, **46**, 747.
[27] Cf. I. Kh. Fel'dman and V. N. Mikhailova, *Zhur. obshchei Khim.*, 1963, **33**, 2111.

Again, isomerisation of the acetylene (III) to the allene (II) must be presumed, and this emphasises not only the lability of the terminal acetylene, but also that the benzenesulphinate ion has a nucleophilic reactivity towards hydrogen greater than would be expected from the dissociation constant of the acid.[2,28] Orientation on addition to the allene is again determined by the tendency for protonation to occur at the site of greater electron density adjacent to the sulphonyl group.



In reactions with sulphone (I), the adduct (XI) is obtained. The *cis*-relation of the phenylsulphonyl groups is assigned by comparison with the oxidation product (XII) of the *trans*-sulphide (IX). The dipole moment of (XI) is 4·8D whilst that of (XII) is 4·4D, and chemical shifts of the methyl protons in each isomer show that those in adduct (XI) are less deshielded than those of (XII). Addition of benzenesulphinate therefore occurs in a specifically *trans*-manner.

In contrast to the reactions with thiols, however, further reaction with the products ensues. Each isomeric bis-sulphone gives the tris-sulphone (XIV), identical with the oxidation product of the tris-sulphide (XIII). Formation of the tris-sulphone from the bis-sulphones (XI) and (XII) is very slow, but is rapid from (X). It appears that the reactions with (XI) and (XII) proceed *via* (X) and that prototropic isomerisation is involved as for the sulphides. Formation of the tris-sulphone (XIV) from the bis-sulphone (X) is easy, because the nucleophile is added at the β-position to a sulphonyl group, whilst formation of the isomeric tris-sulphone (XV) from either (XI) or (XII) would involve addition at the α-position to a suphonyl group.

Mr. W. L. Matier is thanked for assistance with the determination of dipole moments. Proton magnetic resonance spectra in this and the following paper were determined by courtesy of Dr. R. J. Abraham, Dr. R. C. Pink, and Mr. R. J. Spratt. The author is grateful to Dr. R. C. Pink for help in their interpretation.

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