1119. *Elimination–Addition. Part V.*[1] *Reactions of Allenic and Acetylenic Sulphones with Methoxide Ion and with Amino-nucleophiles.**

By C. J. M. Stirling.

Phenylsulphonylpropadiene and 1- and 3-phenylsulphonylpropynes with sodium methoxide in methanol each give, as the kinetic product, 2-methoxy-3-phenylsulphonylpropene. This subsequently isomerises to the thermodynamic product, *trans*-2-methoxy-1-phenylsulphonylpropene.

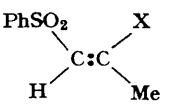
With dibenzylamine, *trans*-2-dibenzylamino-1-phenylsulphonylpropene is the sole product from each sulphone; the course of this reaction has been elucidated by deuterium tracer studies. With benzylamine, a mixture of *cis*- and *trans*-2-benzylamino-1-phenylsulphonylpropenes is formed, and an explanation based on intramolecular hydrogen bonding is advanced for this difference in behaviour. Analogous products are obtained with esters of glycine.

Semicarbazide and phenylhydrazine react with 3-phenylsulphonylpropyne to give the semicarbazone and phenylhydrazone, respectively, of phenylsulphonylacetone.

In Part IV,[1] additions of sulphur nucleophiles to the sulphones (I), (II), and (III) were discussed. Kinetic products were obtained whose formation involved *trans*-addition to sulphone (I) and protonation on carbon adjacent to the sulphonyl group in the allene (II). In this paper, reactions with methoxide and with amino-nucleophiles are reported.

Reactions with Methoxide.—Formation of enol ethers by base-catalysed addition of alcohols to terminal acetylenes is usually considered to involve *trans*-addition.[2] Acetals may be formed by subsequent addition of a further molecule of alcohol.[3] In additions of alkoxides[4] and phenoxides[5] to non-terminal acetylenes bearing an activating group attached directly to the triple bond, the stereochemical assignments have been only tentative, but it has been suggested[5] that initial *trans*-addition may be followed by isomerisation, which results in formation of a *trans*-product.

$PhSO_2 \cdot C{:}C \cdot Me$ (I)



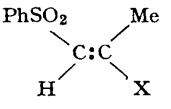
(V)

$PhSO_2 \cdot CH_2 \cdot C(OMe)_2 \cdot CH_3$ (VII)

$PhSO_2 \cdot CH{:}C{:}CH_2$ (II)

$PhSO_2 \cdot CH_2 \cdot CX{:}CH_2$ (IV)

$PhSO_2 \cdot CH_2 \cdot C{:}CH$ (III)



(VI)

$PhSO_2 \cdot CH_2 \cdot C{:}NX(Me)$ (VIII)

In the present work, preliminary experiments involved treatment of each of the sulphones (I), (II), and (III) with N-methanolic sodium methoxide. The same mixture of products, from which the adducts (IV and VI; X = OMe) were separated, were obtained from each isomer. The proton arrangements of these products were confirmed by proton magnetic resonance spectroscopy (Table 1). The chemical shift of the methyl protons of the adduct

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

[1] Part IV, C. J. M. Stirling, preceding Paper.
[2] S. I. Miller, *J. Amer. Chem. Soc.*, 1956, **78**, 6091 and references there cited.
[3] K. Bowden, E. A. Braude, and E. R. H. Jones, *J.*, 1946, 945.
[4] L. N. Owen, *J.*, 1945, 385.
[5] S. Ruhemann and F. Beddow, *J.*, 1900, **77**, 984, 1119, 1179.

TABLE 1.

Proton magnetic resonance spectra of adducts.*
d = doublet.

	-CH=	SO_2 or N}-CH_2-	=CH_2	CMe	-OMe	-NH-
(IV; X = OMe)	—	6·29 (2·0)	5·90 (2·31)	—	6·70 (3·09)	—
(VI; X = OMe)	4·39 (1·0)	—	—	7·77 (3·06)	6·35 (3·06)	—
(VII)	—	6·58	—	8·35	6·95	—
[VI; X = N(CH_2Ph)$_2$]	4·72 (1·0)	5·48 (4·0)	—	7·65 (3·0)	—	—
(V; X = NH·CH_2Ph)	5·34 (0·63)	5·61 (1·33)d	—	8·14 (2·0)	—	2·20
(VI; X = NH·CH_2Ph)	4·92 (0·37)	5·89 (0·67)d	—	7·84 (1·0)	—	5·15
(V; X = NH·CH_2·CO_2Et)	5·28	6·06d	—	8·14 (1·3)	—	2·23
(VI; X = NH·CH_2·CO_2Et)	5·04	6·29d	—	7·80 (1·0)	—	4·95
(V; X = NH·CH_2·CO_2Me)	5·28	6·01d	—	8·12 (1·5)	6·22	not assigned
(VI; X = NH·CH_2·CO_2Me)	5·05	6·27d	—	7·78 (1·0)	6·22	4·93
(VIII; X = NHPh; *syn*-Me)	—	5·93 (1·83)	—	7·93 (2·5)	—	v. broad
(VIII; X = NHPh; *anti*-Me)	—	5·84 (0·42)	—	8·20 (0·5)	—	v. broad

* Integrals (arbitrary units) in parentheses. τ in p.p.m.

(VI; X = OMe) was markedly greater than the shift shown[1] in the adducts (V; X = SPh or SO_2Ph). This suggests that the protons of the methyl group are considerably deshielded by the sulphonyl group, which is, therefore, probably in the *cis*-relation to it. In subsequent experiments, in which 0·01N-methanolic sodium methoxide was used, the adduct (IV) was the sole product from *each* sulphone. In stronger solutions, this product was formed initially, but slowly isomerised to the adduct (VI) which, in hot strong solutions of sodium methoxide, gave the ketal (VII). Isomer (IV) is, therefore, the *kinetic* product, whose formation from the allene results from attachment of the nucleophile at C-2. Subsequent protonation on carbon adjacent to sulphur follows the course discussed previously.[1] Formation of the adduct (IV) from the terminal acetylene (III) involves isomerisation to the more thermodynamically stable allene, which must also be produced from the non-terminal acetylene (I), before addition occurs. These observations indicate that, for methoxide, isomerisation competes very favourably with addition, while for sulphur nucleophiles it does not.[1] Methoxide is, of course, a much stronger base than thiophenoxide but it is usually a weaker nucleophile.[6]

Isomerisation of the adduct (IV) gave no detectable product other than (VI), which is thus the predominant *thermodynamic* product. Its formation from the non-conjugated isomer is expected[1,7] and a *trans*-relation of phenylsulphonyl and methoxyl groups is reasonable for a thermodynamic product, because the dipoles of these groups are opposed in this arrangement. Forcing conditions are required for formation of the ketal (VII); even with N-sodium methoxide at 60°, the product is shown by proton magnetic resonance and infrared spectroscopy to be a mixture of (VI) and (VII), which are probably in equilibrium.

In connection with methoxide addition to acetylenes, Maioli, Modena, and Todesco[8] have suggested that reaction of methoxide with *cis*-2-bromopropenyl *p*-tolyl sulphone (V; X = Br; *p*-Me·C_6H_4 for Ph) involves elimination to give 1-*p*-tolylsulphonylpropyne and subsequent addition of methoxide to give the *cis*-adduct (V; X = OMe; *p*-Me·C_6H_4 for Ph). The tentative assignment of configuration was based on analogy with the additions of thiolates but, in view of the present results, requires confirmation. On the other hand, Jones and Vernon[9] have shown that reactions of the *cis*- and *trans*-β-chlorocrotonates with ethoxide give the *same* product. The higher rate of reaction with the *trans*-isomer suggests that elimination occurs to give ethyl but-1-ynoate; addition of ethoxide follows to give (ultimately) a single isomer. A *trans*-configuration (cf. VI) is assigned to this product in agreement with the conclusions of the present work.

Reactions with Amino-nucleophiles.—Addition of amines to acetylenes bearing activating

[6] J. F. Bunnett, *Ann. Rev. Phys. Chem.*, 1963, **14**, 271.
[7] A. T. Kader and C. J. M. Stirling, *J.*, 1962, 3686.
[8] L. Maioli, G. Modena, and P. E. Todesco, *Boll. sci. Fac. Chim. ind. Bologna*, 1960, **18**, 66.
[9] D. E. Jones and C. A. Vernon, *Nature*, 1955, **176**, 791; D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *J.*, 1960, 2349.

groups directly attached to the triple bond has been much studied.[10] *trans*-Addition is generally favoured[11] but, in certain instances,[12] mixtures of products that were thought to consist of *cis*- and *trans*-isomers in equilibrium have been obtained. *cis*-Addition has, however, been suggested by some workers[13] because of subsequent reactions that required a *cis*-relationship between the two functional groups originally attached to the triple bond. There appears to be no case so far in which a convincing demonstration of product configuration has been reported and, in reactions with primary amines, the question of enamine–imine tautomerism is an added complication. Ethynyl ketones and primary amines, however, give adducts for which imino-structures are ruled out by electronic spectral data.[12]

Reactions of the three isomeric sulphones with dibenzylamine were first investigated. This weakly basic amine ($pK_a = 8{\cdot}43$) was selected in an attempt to simplify the isolation of kinetic products. In the event, all three isomers gave the same product [VI; X = $N(CH_2Ph)_2$]; change of solvent from benzene to methanol caused marked acceleration of the reaction but the products were unaffected. In benzene, the allene reacted at least thirty times as fast as the prop-1-ynyl isomer, in accord with the reactivities found for buta-2,3-dienoic and but-2-ynoic esters in nucleophilic addition.[14]

The proton arrangement of the product was shown by proton magnetic resonance spectroscopy (Table 1) and the large chemical shift of the methyl protons indicated a *cis*-relationship between methyl and phenylsulphonyl groups. In theory, this product could be obtained from the allene by addition at C-2 and protonation at carbon γ to the sulphonyl group, and from isomer (I) by *cis*-addition. Neither alternative seemed likely in view of the results obtained with other nucleophiles, and deuterium labelling was employed to trace the course of isomerisation. The adducts obtained from each isomeric sulphone and *N*-deuterodibenzylamine were analysed by proton magnetic resonance spectroscopy, with the results given in Table 2. They show that the isotope distribution is nearly the same in each adduct

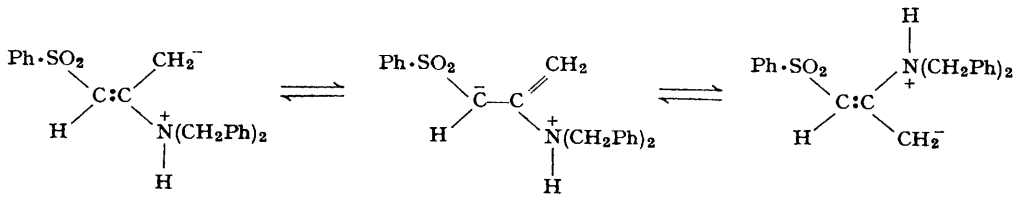
TABLE 2.

Deuterium analysis of dibenzylamine adducts.*

				Corrected % 1 D	
	–CH–	$[CH_2]_2$	$-CH_3$	–CH–	$-CH_3$
(I) + $(PhCH_2)_2ND$	4·67 (1·0)	5·46 (5·3)	7·65 (3·2)	25	75
(II) + $(PhCH_2)_2ND$	4·66 (1·0)	5·48 (5·1)	7·68 (3·0)	27	73
(III) + $(PhCH_2)_2ND$	4·66 (1·0)	5·50 (5·3)	7·65 (3·0)	25	75
[V; X = $N(CH_2Ph)_2$ + $(PhCH_2)_2ND$]	4·64 (1·0)	5·44 (4·1)	7·65 (3·0)	2·5	7

* τ in p.p.m. and integrals (arbitrary units) in parentheses.

and that "scrambling" has occurred. The isotopically normal adduct, however, did not exchange deuterium with *N*-deuterodibenzylamine to an appreciable extent. As "scrambling" in the adducts from sulphones (I) and (III) could be the result of isomerisation *before* addition, the result with the allene is the significant one. Addition of dibenzylamine to the allene is much faster than the isomerisation of (III) to (II), so it is concluded that, with the allene at least, prototropy occurs *after* addition, by internal proton transfer in the adduct:



[10] R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworths, London, 1955.
[11] Y. Iwanami, *J. Chem. Soc. Japan*, 1962, **83**, 600.
[12] E. A. Braude, E. R. H. Jones, and B. C. L. Weedon, *J.*, 1946, 45.
[13] E. R. H. Jones and M. C. Whiting, *J.*, 1949, 1423.
[14] G. Eglinton, E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J.*, 1954, 3197.

This scheme accounts, not only for the statistical distribution of deuterium, but also for the conversion of the various possible kinetic products from each isomer into the single adduct, which, among the three possible alternatives, should have the greatest thermodynamic stability.

In reactions with benzylamine, sulphones (I) and (III) again gave the same product. This product behaved as a single compound, but proton magnetic resonance spectroscopy (Table 1) showed a pair of signals for each of the four types of non-aromatic proton. The integrals and chemical shifts were consistent only with a mixture of the *cis*- and *trans*-adducts (V and VI; X = NH·CH_2Ph). The mixture of adducts appeared to be an equilibrium mixture; attempts to separate the components failed. Further, the same adduct mixture was obtained from benzylamine and phenylsulphonylacetone.

The chemical shifts of the methyl protons allowed the assignment of bands to each isomer. The isomer with $\tau_{(Me)} = 8{\cdot}14$ is assigned the *cis*-structure (V), and it is significant that this is the *predominant* isomer in the mixture. The chemical shift of the amino-proton in this isomer (obtained by spin-decoupling) is very much greater than that in the *trans*-isomer. It is tentatively suggested that this greater shift is caused by hydrogen bonding [15] to an oxygen atom of the sulphonyl group, and that this effect also stabilises the *cis*-isomer relative to the *trans* in this instance. Hydrogen bonding to sulphonyl groups is known to occur [16,17] and in an analogous situation, hydrogen bonding between the amino-proton and the carbonyl group of 2-aminovinyl aryl ketones [18] has been suggested. Preference for the enamine (V) and (VI) rather than imine (VIII) [12,19] structures is doubtless due to the greater stability of the structures in which the double bond is conjugated with the sulphonyl group.

Esters of glycine gave adduct mixtures with the sulphone (III) analogous to those obtained with benzylamine. These reactions were performed to find out whether the polar alkoxycarbonyl group would affect the type of adduct obtained. The results (Table 1) show that the alkoxycarbonyl group has only a slight effect on the composition of the product mixture; the proportions of *cis*- and *trans*-isomers (V and VI; X = NH·CH_2·CO_2R) are approximately 1·3:1 and 1·5:1 for the ethyl and methyl esters, respectively. An interesting feature is found in the proton magnetic resonance spectrum of the ethyl ester adduct. The methyl protons of the ethyl group give a double signal, which is not shown in the spectrum of the methyl ester. This apparent long-range effect of the sulphonyl group will be discussed elsewhere.[20]

Finally, reactions of sulphones (I) and (III) with semicarbazide and phenylhydrazine were investigated. Adducts were readily formed in good yield and were identical with the semicarbazone and phenylhydrazone, respectively, of phenylsulphonylacetone from which they were obtained by conventional means. Kitaev and Troepol'skaya,[21] who have investigated the structures of phenylhydrazones polarographically, conclude that hydrazone, enehydrazine and, in some cases, azoforms may be present in solution. The proton magnetic resonance spectrum (Table 1) of phenylsulphonylacetone phenylhydrazone shows clearly, however, that negligible amounts of tautomers other than hydrazones are present. Both *syn*- and *anti*-methyl isomers of the hydrazone in the approximate ratio of 5:1 were detected. Formation of the hydrazone tautomers in this instance again emphasises the mobility of the protons in the adducts obtained with nitrogen nucleophiles.

Experimental

For general directions see Part IV.[1] Amines were dried over potassium hydroxide and fractionated. Phenylsulphonylacetone [22] had m. p. 56—57°.

[15] C. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman, San Francisco, 1960.
[16] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958.
[17] R. S. Drago, B. Wayland, and R. L. Carlson, *J. Amer. Chem. Soc.*, 1963, **85**, 3125.
[18] V. M. Potapov, F. A. Trofimov, and A. P. Terent'ev, *Zhur. obshchei Khim.*, 1963, **33**, 853.
[19] R. W. Layer, *Chem. Rev.*, 1963, **63**, 489.
[20] R. C. Pink and C. J. M. Stirling, unpublished work.
[21] Yu. P. Kitaev and T. V. Troepol'skaya, *Izvest. Akad. Nauk S.S.S.R., Otdel khim. Nauk*, 1963, 454.
[22] R. Otto and W. Otto, *J. prakt. Chem.*, 1887, **36**, 401.

2-*Methoxy*-3-*phenylsulphonylpropene*.—3-Phenylsulphonylpropyne (1 g.) was kept with 0·01N-methanolic sodium methoxide (20 ml.) for 10 min. Dilution with water and extraction with benzene gave the *enol ether* (1·176 g., 90%), m. p. 60—62°, raised to 65—66° (from isopropyl ether) (Found: C, 56·5; H, 5·6. $C_{10}H_{12}O_3S$ requires C, 56·6; H, 5·7%). On exposure (24 hr.) to moist air, the compound liquefied and later resolidified to give a different compound which was identified as phenylsulphonylacetone, m. p. and mixed m. p. 55—56°.

trans-2-*Methoxy*-1-*phenylsulphonylpropene*.—3-Phenylsulphonylpropyne (2 g.) was kept with 0·25N-methanolic sodium methoxide for 30 min. Dilution with water and extraction with benzene gave the *enol ether* (1·72 g.), m. p. 42—50°, raised to 58·5—59° (from isopropyl ether) (Found: C, 56·6; H, 5·5%). Hydrogenation of the ether (455 mg.) in ethyl acetate over palladium–charcoal gave 2-*methoxypropyl phenyl sulphone* (395 mg.), m. p. 53—54° (from benzene–light petroleum) (Found: C, 55·9; H, 6·45. $C_{10}H_{14}O_3S$ requires C, 56·1; H, 6·55%). The same compound (74%) (m. p. and mixed m. p.) was obtained by treatment of phenyl propenyl sulphone[7] with N-methanolic sodium methoxide.

Dependence of Product Composition on Methoxide Concentration.—Reactions were carried out by mixing solutions of the allenic or acetylenic sulphones in methanol with methanolic sodium methoxide so as to give a 0·1N-solution of the sulphone and a 0·01N-, 0·04N-, or N-solution of sodium methoxide (below). Reactions were followed by the removal of aliquot parts (5 ml.), which were diluted with ether (50 ml.), washed with water (2 × 50 ml.), dried, and evaporated. Infrared spectra of the residues were determined for 7% benzene solutions. The spectrum of *trans*-2-methoxy-1-phenylsulphonylpropene contained bands at 1225 and 915 cm.$^{-1}$, which were absent from that of 2-methoxy-3-phenylsulphonylpropene. The latter showed bands at 850 and 835 cm.$^{-1}$, which were absent from the spectrum of the former isomer. Analysis of mixtures was achieved by mixing appropriate volumes of solutions of the isomers until a match with the spectrum of the product mixture was obtained.

When 0·01N-methanolic sodium methoxide was used, the product, after 10 min. at 20°, from all three isomers, was nearly pure 2-methoxy-3-phenylsulphonylpropene. With phenylsulphonylpropadiene, allene absorption (1960 cm.$^{-1}$) was still present after 30 sec., whilst with 3-phenylsulphonylpropyne, both unchanged material and allene were present after the same period. 1-Phenylsulphonylpropyne, however, reacted more slowly and much was still present after 1 min. Formation of allene from this sulphone was not detected.

When 0·04N-methanolic sodium methoxide was used, the product, after 5 min., from each sulphone was nearly pure 2-methoxy-3-phenylsulphonylpropene. Gradual isomerisation to *trans*-2-methoxy-1-phenylsulphonylpropene was subsequently observed, an approximately 1:1 mixture of the isomers being obtained after 160 min. Conversion was complete in 22 hr.

When N-methanolic sodium methoxide was used, the product, after 20 min., was chiefly the *trans*-isomer, but the infrared spectrum showed absorption at 1050 cm.$^{-1}$, which increased in strength with time. This absorption was due to the slow formation of the ketal (VII). When 3-phenylsulphonylpropyne was refluxed for 1 hr. with N-methanolic sodium methoxide, the product, b. p. 131°/0·2 mm., was shown by proton magnetic resonance spectroscopy to consist of an approximately 7:1 mixture of the ketal (VII) and the *trans*-isomer (VI).

N-*Deuterodibenzylamine*.—Dibenzylamine was shaken for 15 hr. with 99·7% deuterium oxide (12 mol.) and dibenzylamine hydrochloride (0·05 mol.). The organic layer was separated and shaken with more deuterium oxide (12 mol.) together with the dibenzylamine hydrochloride (0·025 mol.) filtered off from the first equilibration. After 17 hr., the organic layer was separated and distilled in apparatus from which deuterium oxide had been distilled immediately previously. The product (b. p. 106°/0·05 mm., n_D^{18} 1·5760) contained at least 98% of $(PhCH_2)_2ND$ as shown by the decrease in the proton magnetic resonance signal at τ 8·81 (neat liquid).

Reactions with Dibenzylamine.—3-Phenylsulphonylpropyne (500 mg.) and dibenzylamine (547 mg.; 1 mol.) in benzene (10 ml.) were kept at 20° for 15 min. Evaporation at 40°/10 mm., gave a residue which, on treatment with light petroleum, gave trans-2-*dibenzylamino*-1-*phenylsulphonylpropene* (995 mg.; 95%), m. p. 100°, raised to 104° (from benzene–light petroleum) (Found: C, 73·0; H, 6·0. $C_{23}H_{23}NO_2S$ requires C, 73·2; H, 6·1%). This product was sometimes obtained in a more stable form of m. p. 110—111°. The same product (95%) was obtained from 1-phenylsulphonylpropyne. With methanol as solvent, a 93% yield of the adduct was obtained from each acetylenic isomer. The adduct was recovered after being kept with dibenzylamine (3 mol.) in benzene at 20° for 30 min.

Hydrolysis of the Dibenzylamine Adduct.—2·5N-Hydrochloric acid (4 ml.) was added to the

adduct (500 mg.) in tetrahydrofuran (10 ml.). After 2 hr., water (50 ml.) was added, and extraction with ether gave phenylsulphonylacetone (235 mg.), m. p. and mixed m. p. 55—56°. The aqueous layer was evaporated down, and addition of acetone to the residue gave dibenzylamine hydrochloride (260 mg.), m. p. and mixed m. p. 275—277°.

Attempted Isomerisation of the Dibenzylamine Adduct.—The adduct (500 mg.) in methanol (20 ml.) was treated with 2N-methanolic sodium methoxide (20 ml.) at 20°. After 1 hr., benzene (150 ml.) was added and the mixture was washed with water and evaporated. The residue (440 mg.), had m. p. 103—104°, alone or mixed with the starting material.

Reactions with N-*Deuterodibenzylamine.*—Each isomeric sulphone (190 mg.) was treated separately with *N*-deuterodibenzylamine (204 mg.) in benzene (4 ml.). Addition of light petroleum (50 ml.) precipitated the adducts in yields of 50% (15 hr.), 88% (30 min.), and 71% (15 hr.) from sulphones (I), (II), and (III), respectively. The product in each case had m. p. 110—111°, unchanged by crystallisation from benzene–light petroleum. The isotopically normal adduct was treated in the same way. The proton magnetic resonance spectrum of each sample was determined and the amounts of deuterium incorporated at C-1 and C-3 were measured by comparison of the integrals for the protons at these positions with that of the methylene protons. Results are given in Table 2.

Reactions with other Amino-nucleophiles.—(a) *Benzylamine.* 3-Phenylsulphonylpropyne (500 mg.) in benzene (10 ml.) was treated with benzylamine (0·31 ml., 1 mol.). After 15 hr., evaporation of the solution and treatment of the residue with light petroleum gave the mixture of *cis*- and *trans*-adducts (Table 1) (770 mg., 96%), m. p. 93—94° (from benzene–light petroleum) (Found: C, 66·9; H, 6·0. Calc. for $C_{16}H_{17}NO_2S$: C, 66·9; H, 5·9%). The same adduct mixture was obtained in 99% yield from 1-phenylsulphonylpropyne. Attempted separation of the adduct mixture by chromatography on alumina caused decomposition with formation of phenylsulphonylacetone.

Phenylsulphonylacetone (450 mg.) was refluxed with benzylamine (1 ml.) and concentrated hydrochloric acid (0·05 ml.) in benzene (15 ml.), the water produced being removed continuously. After 19 hr., the cooled mixture was filtered; evaporation of the filtrate and recrystallisation of the residue from benzene–light petroleum gave the same adduct mixture (480 mg.), m. p. and mixed m. p. 94—95°.

(b) *Glycine methyl ester.* 3-Phenylsulphonylpropyne (500 mg.) and glycine methyl ester hydrochloride[23] (385 mg.) in methanol (10 ml.) were treated with triethylamine (0·43 ml.). The mixture was stirred for 40 min. at 20°; dilution with water and extraction with ether then gave the adduct mixture (Table 1) (380 mg.), m. p. 89—90° (from benzene–light petroleum) (Found: C, 53·4; H, 5·75. Calc. for $C_{12}H_{15}NO_4S$: C, 53·5; H, 5·6%).

(c) *Glycine ethyl ester.* The reaction with 3-phenylsulphonylpropyne was carried out as in (b). The adduct mixture (Table 1) (74%) had m. p. 110—111·5° (from benzene–light petroleum) (Found: C, 55·3; H, 6·1. Calc. for $C_{13}H_{17}NO_4S$: C, 55·1; H, 6·0%).

(d) *Semicarbazide.* 3-Phenylsulphonylpropyne (500 mg.) and semicarbazide hydrochloride (470 mg.; 1·5 mol.), suspended in methanol (10 ml.), were treated with triethylamine (0·58 ml., 1 mol.). A clear solution was quickly obtained and precipitation occurred after 3 hr. After 14 hr., the mixture was evaporated and the residue was extracted successively with boiling benzene and cold water. The residue (580 mg.) of *semicarbazone* had m. p. 177—180° raised to 182—183° (from methanol) (Found: C, 47·3; H, 5·2. $C_{10}H_{13}N_3O_3S$ requires C, 47·1; H, 5·1%). The same product was obtained in the conventional manner from phenylsulphonylacetone. In the absence of semicarbazide hydrochloride, 2-methoxy-3-phenylsulphonylpropene (50%), m. p. and mixed m. p. 65°, was obtained.

(e) *Phenylhydrazine.* 3-Phenylsulphonylpropyne (500 mg.) was kept with phenylhydrazine (0·3 ml., 1·1 mol.) in ethanol (10 ml.) for 3 days. Evaporation of the solution and treatment of the residue with light petroleum gave phenylsulphonylacetone phenylhydrazone (690 mg.), m. p. 131—132° (from ethanol) alone or mixed with a specimen prepared from the ketone in the conventional manner (lit.,[22] 126—127°).

Proton Magnetic Resonance Spectra.—The spectra of adducts in deuterochloroform solution, with tetramethylsilane as internal reference, were recorded on a Varian HR-100 spectrometer operating at 100 Mc./sec. In certain of the adduct mixtures obtained with primary amines, spin-spin decoupling was used to measure the chemical shifts of the amino-protons and to assign these to the appropriate *cis*- or *trans*-isomer. In the adduct mixture (V and VI; X = $NHCH_2Ph$)

[23] T. Curtius and F. Gobel, *J. prakt. Chem.*, 1888, **37**, 150.

obtained with benzylamine, the methylene proton doublet at $\tau = 5{\cdot}61$ was decoupled when an internal modulating frequency of 2028 c./sec. and a decoupling frequency of 1691 c./sec. was used, whilst the doublet at $\tau = 5{\cdot}89$ was decoupled with a decoupling frequency of 1970 c./sec. Similarly, in the adduct mixture obtained with glycine ethyl ester, the methylene doublet at $\tau = 6{\cdot}06$ was decoupled by using the same internal modulating frequency as before and a decoupling frequency of 1648 c./sec., whilst the doublet at $\tau = 6{\cdot}29$ was decoupled by using a frequency of 1894 c./sec.

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