

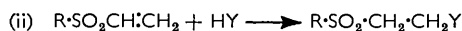
715. Elimination-Addition. Part I.* Displacement of Sulphonyl Groups from Diarylsulphonylalkanes.

By A. T. KADER and C. J. M. STIRLING.

Replacement of sulphonyl groups in disulphones by a variety of reagents has been investigated; reactions with 1,2-diarylsulphonylalkanes are considered to involve initial elimination with formation of $\alpha\beta$ -unsaturated sulphones to which nucleophilic addition rapidly occurs. Related reactions with 1,3-diarylsulphonylpropanes indicate that $\beta\gamma$ -unsaturated sulphones are first formed and subsequently isomerise to the $\alpha\beta$ -unsaturated sulphones. Nucleophilic addition follows. Earlier work which conflicts with these conclusions has been corrected.

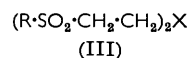
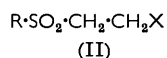
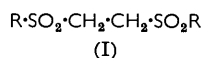
Sulphonyl groups are slowly displaced from 1,1- and 1,4-disulphones by methanolic sodium methoxide, but the mechanisms of these reactions are not clear.

CERTAIN β -substituents in saturated sulphones are readily replaced under basic conditions^{1,2} and, while no detailed examination of the mechanism of these reactions has been made, it has been suggested that they occur¹ by initial elimination, stage (i), with formation of an $\alpha\beta$ -unsaturated sulphone which readily undergoes³ nucleophilic (Michael) addition, stage (ii). Similar suggestions have previously been made⁴ to account for the



easy alkaline hydrolysis of 1,2-disulphones, but no conclusive evidence has been obtained. As part of a general study of the reactivity of sulphones and related compounds, we have investigated reactions of diarylsulphonylalkanes in which one sulphonyl group is displaced, with a view, in particular, to obtain evidence for or against elimination-addition as the mechanism for replacement of β -groups in sulphones.

1,2-Disulphones.—Early studies⁵ of the rapid reactions of 1,2-disulphones (I) with alkali-metal hydroxides to give sulphinic acid ($\text{R}\cdot\text{SO}_2\text{H}$) and β -hydroxy-sulphones (II; $\text{X} = \text{OH}$), sharply differentiated them from other disulphones. Related reactions⁶ with basic nucleophiles such as ethylamine and ethoxide ion gave β -substituted sulphones of



type (II), while ammonia and the HS^- ion gave bis-sulphones of type (III), in each case with loss of one sulphonyl group as sulphinic acid. In view of the weak reactivity of mono-sulphones⁷ it is improbable that these reactions are direct substitutions, but the products are accountable by either substitution or elimination-addition.

We initially investigated the action of a variety of reagents of differing basicity and nucleophilicity on 1,2-di-*p*-tolylsulphonylethane (I; $\text{R} = p\text{-C}_6\text{H}_4\text{Me}$). Treatment of the disulphone with sodium ethoxide in ethanol rapidly gave the ethoxy-sulphone (II; $\text{R} = p\text{-C}_6\text{H}_4\text{Me}$, $\text{X} = \text{OEt}$) and with piperidine slowly gave the piperidino-sulphone (II; $\text{R} = p\text{-C}_6\text{H}_4\text{Me}$, $\text{X} = \text{C}_5\text{H}_{10}\text{N}$). This difference in rate must be due either to the lower

* Part II, *J.*, 1962, 3425.

¹ Stirling, *Chem. and Ind.*, 1960, 933.

² Suter, "Organic Chemistry of Sulfur," Wiley, New York, 1944.

³ Alexander and McCombie, *J.*, 1931, 1913; Truce and Wellisch, *J. Amer. Chem. Soc.*, 1952, **74**, 2881.

⁴ Backer, *Bull. Soc. chim. France*, 1950, 729; Strating, "Organic Sulfur Compounds," ed. Kharasch, Pergamon Press, London, 1961, Vol. I, Chap. 15.

⁵ Stuffer, *Ber.*, 1890, **23**, 1408, 3226.

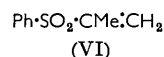
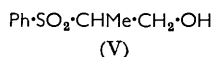
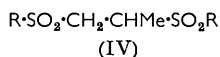
⁶ Otto and Damköhler, *J. prakt. Chem.*, 1884, **30**, 171, 321.

⁷ Cf. *J.*, 1962, 3425, and Fenton and Ingold, *J.*, 1930, 705.

nucleophilicity of piperidine in an S_N2 reaction, or to the weaker reactivity of piperidine in one or both of the stages of elimination-addition. A competitive experiment showed that piperidine added to *p*-tolyl vinyl sulphone, *i.e.*, stage (ii), faster than did ethoxide ion, and that, therefore, if the two-step mechanism operates, the lower reactivity of piperidine is due to its lower capability of promoting elimination. Piperidine, in conjunction with the much stronger base, sodium ethoxide, rapidly reacted with the disulphone to yield the piperidino-sulphone; under the same conditions but in the absence of sodium ethoxide, the disulphone was almost quantitatively recovered. We consider these results to be strong evidence for elimination-addition and the earlier observations^{5,6} are accountable on this basis. A possible alternative explanation of the results is the formation of the highly nucleophilic species⁸ $C_5H_{10}N^-$ from piperidine in the presence of sodium ethoxide; because of the large pK_a difference (at least 9 units⁹) between ethanol and piperidine, it is improbable that an appreciable concentration of this species is formed, and in any event piperidide ion reacts with alkyl aryl sulphones to give alkanesulphinic acids.⁸

As a corollary, any weak base, however nucleophilic, should react slowly, if at all, with the disulphone. We found that sodium iodide, acetate, and benzoate were without action even after long periods of heating. Sodium phenoxide in phenol slowly gave the phenoxy-sulphone (II; $R = p-C_6H_4Me$, $X = OPh$) but in ethanol gave the ethoxy-sulphone, an indication of the very weak nucleophilicity of phenoxide in addition to the vinyl sulphone. Two apparent exceptions were observed: (a) sodium *p*-tolyl sulphide in ethanol reacted more rapidly than sodium phenoxide (although toluene-*p*-thiol is more acidic than phenol), to give the sulphonyl-sulphide (II; $R = p-C_6H_4Me$, $X = p-Me-C_6H_4S$); (b) while sodium benzenesulphinat gave only an inseparable mixture of sulphones, reaction of sodium toluene-*p*-sulphinat with 1,2-diphenylsulphonylthane (I; $R = Ph$) gave the sulphone (I; $R = p-C_6H_4Me$). Replacement of sulphonyl groups in 1,2-disulphones by sulphinate ion has also been observed by Truce and Wellisch¹⁰ and we regard these reactions as a further demonstration by sulphur-containing anions of nucleophilic reactivity towards hydrogen greater than would be expected from their thermodynamic affinity for hydrogen.¹¹ Formation of the sulphonyl-sulphide reflects the high reactivity of toluene-*p*-thiol ion in addition, and, although sodium toluene-*p*-sulphinat and *p*-tolyl vinyl sulphone in ethanol readily afforded the disulphone (I; $R = p-C_6H_4Me$),¹² addition of triethylamine caused formation of the ethoxy-sulphone (II; $R = p-C_6H_4Me$, $X = OEt$).

Otto's claim¹³ that treatment of 1,2-diphenylsulphonylpropane (IV; $R = Ph$) with aqueous sodium hydroxide yielded the hydroxy-sulphone (V) clearly conflicts with the conclusions presented above. If elimination-addition operates, not only should a proton be removed preferentially from the carbon atom which does not bear a methyl group,



giving the olefin (X; $R = Ph$) and thence the isomeric hydroxy-sulphone (XII; $R = Ph$), but non-bonded interactions in the coplanar transition states*¹⁴ for the formation of this olefin (*trans*¹⁵) and the olefin (VI) are greater in the latter. Otto reported m. p. 46° for

* It is assumed that the elimination step is either E_{1cb} or concerted and bimolecular. Kinetic and isotope exchange studies are in progress.

⁸ Bradley, *J.*, 1938, 458.

⁹ McEwen, *J. Amer. Chem. Soc.*, 1936, **58**, 1124.

¹⁰ Truce and Wellisch, *J. Amer. Chem. Soc.*, 1952, **74**, 5177.

¹¹ Bunnett, Hauser, and Nahabedian, *Proc. Chem. Soc.*, 1961, 305; de la Mare and Vernon, *J.*, 1956, 41.

¹² Cf. Ufer, G.P. 663,992.

¹³ Otto, *J. prakt. Chem.*, 1895, **51**, 285.

¹⁴ For references see Battersby and Greenock, *J.*, 1961, 2592.

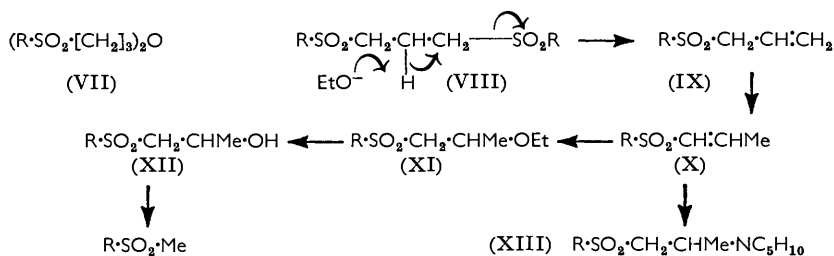
¹⁵ Karaulova, Meilanova, and Gal'pern, *Doklady Akad. Nauk S.S.S.R.*, 1957, **113**, 1280.

the hydroxy-sulphone (V) which has subsequently been obtained as a liquid,¹⁶ while the isomer¹⁶ (XII; R = Ph) has m. p. 46—47°. Stuffer⁵ obtained a liquid product from this reaction and suggested that it was (V), (XII; R = Ph), or a mixture.

We repeated the early work and from the crude product, m. p. 44—46°, isolated phenyl propenyl sulphone (X; R = Ph), m. p. 68—69°. Treatment of the disulphone with hot ethanolic sodium ethoxide gave methyl phenyl sulphone, a product readily derived from a retro-aldol reaction of the hydroxy-sulphone (XII; R = Ph) (see the next section) but not of the isomer (V). Similarly, treatment of the *p*-tolyl analogue (IV; R = *p*-C₆H₄Me) with cold ethanolic sodium ethoxide gave the ethoxy-sulphone (XI; R = *p*-C₆H₄Me) in 86% yield, and, with the hot reagent, methyl *p*-tolyl sulphone. Elimination clearly occurs, therefore, in the expected direction.

1,3-Disulphones.—1,3-Disulphones have been reported⁵ not to react with aqueous alkali, but Otto^{13,17} claimed that the ethers (VII; R = Ph and *p*-C₆H₄Me), m. p. 85° and 79—80°, respectively, were obtained by treatment of the sulphones (VIII; R = Ph and *p*-C₆H₄Me) with ethanolic potassium hydroxide. Our previous conclusions led us to doubt these results and repetition of Otto's experiment with the *p*-tolyl sulphone gave methyl *p*-tolyl sulphone (93%). In partial reactions, only this sulphone and recovered disulphone were obtained, and the use of ethanolic sodium ethoxide gave the same results. The coincidence in melting points between the "ethers" and methyl phenyl (m. p. 87°) and methyl *p*-tolyl (m. p. 85°) sulphone suggested that Otto had obtained the latter compounds. We synthesised the ethers (VII; R = Ph and *p*-C₆H₄Me) by unambiguous routes; they had m. p. 76° and 100—101°, respectively. The *p*-tolyl ether was almost quantitatively recovered from reactions under Otto's conditions and thus, had it been formed, could have been detected.

If the initial stage in reactions with the sulphone (VIII; R = *p*-C₆H₄Me) is slow elimination of toluene-*p*-sulphinic acid to give allyl *p*-tolyl sulphone (IX; R = *p*-C₆H₄Me), the formation of methyl *p*-tolyl sulphone can be explained by the sequence annexed.



Isomerisation of allyl to propenyl sulphones, and the retro-aldol reactions of 2-hydroxypropyl sulphones have been discussed in detail by Rothstein¹⁸ and by Backer and his collaborators.¹⁹ We established that each of the four intermediate sulphones reacted more rapidly than the disulphone, to give methyl *p*-tolyl sulphone in high yields. Isolation of the latter compound from reactions with the ethoxy-sulphone (XI) shows that formation of the hydroxy-sulphone is fairly rapid in spite of the low concentration of water in the ethanol which was used. Formation of the ethoxy-sulphone precedes that of the hydroxy-sulphone in the above sequence; treatment of propenyl *p*-tolyl sulphone with ethanolic potassium hydroxide gives the ethoxy- and not the hydroxy-sulphone. In support of these conclusions, we found that the sequence may be halted at the third stage by the

¹⁶ Fuson and Koehneke, *J. Org. Chem.*, 1949, **14**, 706.

¹⁷ Otto, *Ber.*, 1891, **24**, 1832.

¹⁸ Rothstein, *J.*, 1934, 684.

¹⁹ Backer and De Jong, *Rec. Trav. chim.*, 1948, **67**, 884; Backer, Strating, and Drenth, *ibid.*, 1951, **70**, 365.

addition of piperidine; the piperidino-compound (XIII; R = *p*-C₆H₄Me) formed did not undergo subsequent elimination.

1,1- and 1,4-Disulphones.—Di-*p*-tolylsulphonylmethane did not react with ethanolic sodium ethoxide at 80°, but with sodium methoxide in methanol at 140° slowly gave toluene-*p*-sulphinic acid and methyl *p*-tolyl sulphone in low yield. Hine and Porter²⁰ found that treatment of difluoromethyl phenyl sulphone with sodium methoxide gave difluoromethyl methyl ether, and they suggested that 1,1-elimination occurred with the formation of difluorocarbene and sulphinic acid. The product *p*-C₆H₄Me·SO₂·CH₂·OMe to be expected from an analogous reaction of di-*p*-tolylsulphonylmethane was synthesised but was not recovered from reactions carried out under the same conditions. Bromomethyl sulphones are reduced²¹ by ethoxide ion and, although a similar type of reaction may occur with the disulphonylmethane, this sulphone was unaffected by lithium aluminium hydride.

1,4-Di-*p*-tolylsulphonylbutane did not react with sodium ethoxide at 80°, and with sodium methoxide gave toluene-*p*-sulphinic acid as the only identifiable product.

EXPERIMENTAL

The light petroleum used had b. p. 60–80°, and the ethanol contained 0.34% w/v of water. Extracts were dried over Na₂SO₄. Sulphides were oxidised to sulphones with an excess of 30% hydrogen peroxide in acetic acid at 100°. Infrared spectra of products from displacement reactions were compared in each case with authentic specimens obtained by unambiguous routes.

General Procedure for the Isolation of Products from Displacement Reactions.—Unless otherwise stated, the reaction mixture was added to three volumes of acidified saturated brine and extracted with chloroform. The chloroform extracts were washed with saturated aqueous sodium hydrogen carbonate, dried, and evaporated. The aqueous washings were saturated with sodium chloride, acidified, and extracted with ether. The residue from evaporation of the extracts was refluxed for 4 hr. with an excess of 4-nitrobenzyl bromide and sodium carbonate in aqueous ethanol. Extraction of the mixture with methylene chloride afforded the aryl 4-nitrobenzyl sulphone.

2-Ethoxyethyl *p*-Tolyl Sulphone.—2-Ethoxyethyl bromide²² (7 g.) was refluxed for 30 min. with toluene-*p*-thiol (5 g.) in 5% ethanolic sodium ethoxide (1 mol.). The mixture was poured into water and extraction with chloroform gave the *sulphide* (6.6 g.), b. p. 145°/12 mm., n_D^{22} 1.5340 (Found: C, 67.2; H, 8.4. C₁₁H₁₆OS requires C, 67.4; H, 8.1%). Oxidation gave the *sulphone* (80%), b. p. 135°/0.05 mm., n_D^{20} 1.5218 (Found: C, 58.0; H, 7.3. C₁₁H₁₆O₃S requires C, 57.9; H, 7.0%).

2-Phenoxyethyl *p*-Tolyl Sulphone.—The *sulphide*, prepared from toluene-*p*-thiol and 2-phenoxyethyl bromide,²³ had m. p. 46° (from methanol) (Found: C, 73.8; H, 6.3. C₁₅H₁₆OS requires C, 73.8; H, 6.6%). Oxidation gave the *sulphone* (80%), m. p. 135° (from methanol) (Found: C, 65.4; H, 6.0. C₁₅H₁₆O₃S requires C, 65.2; H, 5.8%).

*Reactions of 1,2-Di-*p*-tolylsulphonylethane.*—(a) *With ethanolic sodium ethoxide.* The sulphone⁶ (3.52 g.), in warm ethanol (75 ml.), was added to 2*N*-ethanolic sodium ethoxide (25 ml.). The mixture was quickly cooled to 20° and after 30 min. was worked up, yielding 4-nitrobenzyl *p*-tolyl sulphone (72%), m. p. and mixed m. p. 184° (lit.,²⁴ m. p. 185°), and 2-ethoxyethyl *p*-tolyl sulphone (98.5%), b. p. 128°/0.01 mm., n_D^{18} 1.5218.

(b) *With sodium *p*-tolyl sulphide.* The sulphone (3 g.) was added to toluene-*p*-thiol (1.65 g.) in ethanolic sodium ethoxide [from ethanol (100 ml.) and sodium (0.3 g.)]. The mixture was refluxed for 2 hr. and the usual working-up gave 4-nitrobenzyl *p*-tolyl sulphone (67.5%) and 2-*p*-tolylthioethyl *p*-tolyl sulphone (1.99 g.) (73%), m. p. and mixed m. p. 82° (from methanol) (lit.,²⁵ m. p. 83–84°). Oxidation gave the disulphone, m. p. and mixed m. p. 200°.

²⁰ Hine and Porter, *J. Amer. Chem. Soc.*, 1960, **82**, 6178.

²¹ Zeigler and Connor, *J. Amer. Chem. Soc.*, 1940, **62**, 2596.

²² *Org. Synth.*, Coll. Vol. III, p. 370.

²³ Bentley, Haworth, and Perkin, *J.*, 1896, **69**, 161.

²⁴ Troger and Nolte, *J. prakt. Chem.*, 1920, **101**, 136.

²⁵ F.P. 45,691.

(c) *With sodium phenoxide in ethanol.* The sulphone (3 g.) was refluxed for 2 hr. with phenol (1.25 g.) in ethanolic sodium ethoxide [from sodium (0.28 g.) and ethanol (100 ml.)]. The usual working-up gave toluene-*p*-sulphinic acid (83%) and 2-ethoxyethyl *p*-tolyl sulphone (1.9 g.) (94%), b. p. 140°/0.01 mm., n_D^{16} 1.5238.

(d) *With sodium phenoxide in phenol.* The sulphone (2 g.) was kept with phenol (50 g.) and sodium phenoxide (1.1 g.) for 2 hr. at 80°. The usual working-up gave recovered disulphone (1.16 g.) (58%), m. p. and mixed m. p. 200—203°, 2-phenoxyethyl *p*-tolyl sulphone (0.50 g.) (31%), m. p. and mixed m. p. 129—131°, and toluene-*p*-sulphinic acid (25%). When the concentration of sodium phenoxide was quadrupled and the period of heating was extended to 24 hr., the yields of phenoxy-sulphone and toluene-*p*-sulphinic acid were 94% and 81%, respectively.

(e) *With sodium benzenesulphinate.* The sulphone (2 g.) in ethanol (150 ml.) was refluxed with sodium benzenesulphinate (5 g., 5 mol.) for 24 hr. The neutral product (1.79 g.) had m. p. 160—164° and was evidently a mixture of sulphones; it could not be purified by recrystallisation. When heating was continued for 5 days, a similar mixture (1.75 g.), m. p. 145—150°, was obtained.

(f) *With piperidine.* (i) The sulphone (2 g.) was refluxed with piperidine (2.5 g.) in ethanol (250 ml.) for 24 hr. Concentrated hydrochloric acid (3.75 ml.) was added and the mixture was evaporated to dryness. The residue was extracted with benzene, and the extracts, on treatment with aqueous sodium hydrogen carbonate, afforded toluene-*p*-sulphinic acid (81% based on sulphone that reacted). Evaporation of the residual benzene solution gave recovered sulphone (0.14 g., 7%), m. p. and mixed m. p. 200—201°. The residue from extraction with benzene was treated with an excess of aqueous sodium carbonate, and the mixture was re-evaporated. Extraction of the dry residue with ethanol and saturation of the extracts with hydrogen chloride gave 2-piperidinoethyl *p*-tolyl sulphone as the hydrochloride (1.32 g.) (80%), m. p. and mixed m. p. 224—226° (lit.,²⁶ m. p. 226°). When the experiment was repeated with a reaction time of 5 min., 93% of the disulphone was recovered.

(ii) The sulphone (2 g.) was refluxed with piperidine (1.15 g., 2.5 mol.) and sodium ethoxide (0.965 g., 2.5 mol.) in ethanol (250 ml.) for 5 min. Treatment of the mixture as in (i) gave 2-piperidinoethyl *p*-tolyl sulphone hydrochloride (1.38 g.) (82%), m. p. and mixed m. p. 224—225°.

2-Ethoxyethyl *p*-tolyl sulphone did not react with piperidine in the absence of sodium ethoxide.

Reactions of p-Tolyl Vinyl Sulphone.—(a) *With sodium ethoxide and piperidine.* The sulphone²⁷ (2 g.), in ethanol (20 ml.), was added to piperidine (2.33 g., 2.5 mol.) and sodium ethoxide (1.77 g., 2.5 mol.) in ethanol (30 ml.). After 10 min., the mixture was saturated with hydrogen chloride. Ether was added until precipitation was complete, and the mixture was filtered. The precipitate, in water, was treated with a slight excess of sodium carbonate and the solution was evaporated to dryness. The residue was extracted with hot ethanol and evaporation of the extracts after saturation with hydrogen chloride gave the hydrochloride of the piperidino-sulphone (2.71 g.) (85%), m. p. and mixed m. p. 221—223°.

(b) *With sodium toluene-*p*-sulphinic acid.* The sulphone (1.82 g.) was refluxed for 1 hr. with sodium toluene-*p*-sulphinic acid (8.9 g.) in ethanol (100 ml.). The usual procedure gave 1,2-di-*p*-tolylsulphonylethane (3.18 g., 94%), m. p. and mixed m. p. 200—201°.

(c) *With sodium toluene-*p*-sulphinic acid and triethylamine.* The sulphone (2 g.), sodium toluene-*p*-sulphinic acid (1.82 g.), and triethylamine (10 ml.), in ethanol (100 ml.), were refluxed together for 24 hr. The usual procedure gave 2-ethoxyethyl *p*-tolyl sulphone (1.98 g.) (80%), b. p. 132—136°/0.05 mm., n_D^{19} 1.5238.

*Reaction of 1,2-Diphenylsulphonylethane with Sodium Toluene-*p*-sulphinic acid.*—The sulphone⁶ (2 g.) was refluxed with sodium toluene-*p*-sulphinic acid (17.25 g.) in ethanol (150 ml.) for 4 days. The neutral product (2.11 g.), m. p. 188—190°, on crystallisation from ethanol afforded 1,2-di-*p*-tolylsulphonylethane, m. p. and mixed m. p. 202—203°.

2-Ethoxypropyl p-Tolyl Sulphone.—Propenyl *p*-tolyl sulphone²⁸ (2 g.) was treated with *n*-ethanolic sodium ethoxide (30 ml.). After 24 hr. at 20° the usual procedure gave the *ethoxy-sulphone* (1.4 g.), m. p. 73—74°, raised to 75° (from benzene-light petroleum) (Found: C, 59.3;

²⁶ Reppe, *Annalen*, 1956, **601**, 111.

²⁷ Smith and Davis, *J. Org. Chem.*, 1950, **15**, 824.

²⁸ Weinstock, Pearson, and Bordwell, *J. Amer. Chem. Soc.*, 1956, **78**, 3468, 3473.

H, 7.2. $C_{15}H_{18}O_3S$ requires C, 59.5; H, 7.5%). Treatment of the sulphone with 55% aqueous hydriodic acid gave 2-hydroxypropyl *p*-tolyl sulphone,²⁹ m. p. and mixed m. p. 77—78°, which was oxidised to *p*-tolylsulphonylacetone,²⁸ m. p. and mixed m. p. 49°.

2-Piperidinopropyl p-Tolyl Sulphone.—Propenyl *p*-tolyl sulphone (0.98 g.) was treated with piperidine (4.25 g.) in ethanol (50 ml.). Removal of the solvent and the excess of piperidine after 10 min. left the sulphone (1.36 g.), m. p. 81—82° (from light petroleum) (Found: C, 63.9; H, 8.3. $C_{15}H_{23}NO_2S$ requires C, 64.1; H, 8.2%).

Reactions of 1,2-Diphenylsulphonylpropane.—(a) *With sodium ethoxide*. The sulphone¹² (3.24 g.) was refluxed with 2*N*-ethanolic sodium ethoxide (100 ml.) for 2 hr. The usual working-up gave methyl phenyl sulphone (1.264 g.) (81%), m. p. 80—81°, raised to 85—86° (from light petroleum) alone or mixed with an authentic specimen (lit.,³⁰ m. p. 88—89°). Benzenesulphonic acid (85%) was characterised as 4-nitrobenzyl phenyl sulphone, m. p. and mixed m. p. 208—209° (lit.,²⁴ m. p. 209°).

(b) *With aqueous sodium hydroxide (Otto's conditions)*. 33% Aqueous sodium hydroxide (5 ml.) was added to a suspension of the sulphone (4 g.), in water (20 ml.). After being kept at 100° for 1 hr., the mixture was cooled, neutralised with hydrochloric acid, and extracted with ether. The extracts were washed with aqueous sodium hydrogen carbonate and evaporated. The residue (2.07 g.) was chromatographed on alumina in chloroform solution, yielding phenyl propenyl sulphone (1.40 g.), m. p. 62—64°, raised to 68—69° (from light petroleum), alone or mixed with an authentic specimen obtained from 2-hydroxypropyl phenyl sulphone¹⁵ by the method used for propenyl *p*-tolyl sulphone²⁸ (lit.,¹⁵ 68.5—69°). Benzenesulphonic acid (88%) was obtained from the aqueous extracts. 2-Hydroxypropyl *p*-tolyl sulphone was unaffected by chromatography on alumina.

Reactions of 1,2-Di-p-tolylsulphonylpropane.—(i) The sulphone³¹ (2 g.) was kept with 0.3*N*-ethanolic sodium ethoxide (100 ml.) at 20° for 30 min. The usual working-up gave 2-ethoxypropyl *p*-tolyl sulphone (1.17 g.) (86%), m. p. and mixed m. p. 73—74°. (ii) The sulphone (1 g.) was refluxed with 2*N*-ethanolic sodium ethoxide (30 ml.) for 2 hr. The product was methyl *p*-tolyl sulphone (0.42 g.), m. p. 76—78°, raised to 84—85° (from light petroleum) alone or mixed with an authentic specimen.

Reactions of 1,3-Di-p-tolylsulphonylpropane.—(a) *With sodium ethoxide*. The sulphone (7.04 g.) was refluxed with 2*N*-ethanolic sodium ethoxide (200 ml.) for 4 days. The usual working-up gave methyl *p*-tolyl sulphone (3.26 g.) (96%), m. p. and mixed m. p. 79—80°, and toluene-*p*-sulphonic acid (77%). When the reflux time was 2 hr., 66% of the starting material was recovered and methyl *p*-tolyl sulphone was obtained in 74% yield based on sulphone that reacted.

(b) *With ethanolic potassium hydroxide (Otto's conditions)*. The sulphone (2 g.), in 10% ethanolic potassium hydroxide (50 ml.), was kept (sealed tube) at 120° for 8 hr. The products were methyl *p*-tolyl sulphone (0.89 g.) (93%), m. p. and mixed m. p. 80—81°, and toluene-*p*-sulphonic acid (88%). After 2 hours' heating, recovered disulphone (41%), m. p. and mixed m. p. 125—126°, and methyl *p*-tolyl sulphone (90% on sulphone that reacted), m. p. and mixed m. p. 83—84°, were obtained.

(c) *With sodium ethoxide and piperidine*. The sulphone (3.52 g.) and piperidine (8.5 g.), in 2*N*-ethanolic sodium ethoxide (100 ml.), were refluxed for 4 hr. Saturation of the mixture with hydrogen chloride and evaporation to dryness gave a residue which was extracted with hot benzene. The extracts were washed with aqueous sodium hydrogen carbonate and evaporated. The residue was recovered sulphone (2.1 g.), m. p. and mixed m. p. 122—124°. The residue of hydrochlorides was treated with aqueous sodium carbonate and evaporated; extraction of the residue with benzene gave 2-piperidinopropyl *p*-tolyl sulphone (0.7 g.), m. p. and mixed m. p. 79—80°.

Tests of Intermediates in the Reaction of 1,3-Di-p-tolylsulphonylpropane with Sodium Ethoxide.—Allyl *p*-tolyl,³¹ propenyl *p*-tolyl,²⁸ 2-ethoxypropyl *p*-tolyl, and 2-hydroxypropyl *p*-tolyl²⁹ sulphone were each refluxed for 2 hr. with a 20-molar excess of 2*N*-ethanolic sodium ethoxide. In each case the product was methyl *p*-tolyl sulphone, isolated in yields of 86, 87, 89, and 89%, respectively.

²⁹ Field and McFarland, *J. Amer. Chem. Soc.*, 1953, **75**, 5582.

³⁰ Otto, *Ber.*, 1885, **18**, 154.

³¹ Otto, *Annalen*, 1894, **283**, 181.

Treatment of propenyl *p*-tolyl sulphone (1 g.) with *n*-ethanolic potassium hydroxide (50 ml.) for 5 min. at 20° gave 2-ethoxypropyl *p*-tolyl sulphone (1.1 g.), m. p. 58—60°, raised to 72—73° (0.92 g., 80%) (from light petroleum) alone or mixed with an authentic specimen.

3,3'-Di-*p*-tolylsulphonyldipropyl Ether.—3,3'-Dichlorodipropyl ether³² (1 g.) was refluxed with toluene-*p*-thiol (1.67 g.) in 0.5*N*-ethanolic sodium ethoxide (1 mol.) for 1 hr. Distillation of the product gave the *bis-sulphide* (1.7 g.), b. p. 180°/0.01 mm., n_D^{20} 1.5804 (Found: C, 69.3; H, 7.9. $C_{20}H_{26}OS_2$ requires C, 69.4; H, 7.5%). Oxidation gave the *sulphone* (95%), m. p. 100—101° (from methanol) (Found: C, 58.7; H, 6.35. $C_{20}H_{26}O_5S_2$ requires C, 58.5; H, 6.3%). The sulphone was recovered (93%) from treatment with potassium hydroxide under Otto's conditions.

3,3'-Diphenylsulphonyldipropyl Ether.—The *sulphone*, obtained in the same way, by using thiophenol, had m. p. 76° (from ethanol) (Found: C, 56.8; H, 5.9. $C_{18}H_{22}O_5S_2$ requires C, 56.55; H, 5.8%).

Reactions with Di-*p*-tolylsulphonylmethane.—(a) The sulphone³³ (3.24 g.) was refluxed in pyridine (25 ml.) and 2*N*-ethanolic sodium ethoxide (125 ml.) for 10 days. The sulphone (3.1 g., 96%), m. p. and mixed m. p. 132—134°, was recovered.

(b) The sulphone (9.72 g.) in 2*N*-methanolic sodium methoxide (300 ml.) was kept at 140° for 10 days. Chromatography of the neutral product (2.62 g.) on alumina in chloroform solution gave methyl *p*-tolyl sulphone (1.34 g.), m. p. and mixed m. p. 78—80°. Toluene-*p*-sulphinic acid in the alkaline extracts was characterised as the 4-nitrobenzyl sulphone (4.56 g.), m. p. and mixed m. p. 189°.

Methoxymethyl *p*-Tolyl Sulphone.—Toluene-*p*-thiol (31 g.) and chloromethyl methyl ether (20 g.) were refluxed with 1.25*N*-ethanolic sodium ethoxide (200 ml.) for 1 hr. Extraction with chloroform and distillation of the extracts gave the *sulphide* (16 g.), b. p. 74°/0.1 mm., n_D^{18} 1.5540 (Found: C, 64.5; H, 6.9. $C_9H_{12}OS$ requires C, 64.3; H, 7.1%). Oxidation gave the *sulphone* (89%), m. p. 72—73°, raised to 74—75° (from ethanol) (Found: C, 54.4; H, 6.3. $C_9H_{12}O_3S$ requires C, 54.0; H, 6.0%).

Treatment of the sulphone with sodium methoxide as for the disulphonylmethane, for 5 days, gave toluene-*p*-sulphinic acid (84%). Toluene-*p*-sulphinic acid under the same conditions (6 days) was recovered in 49% yield.

1,4-Di-*p*-tolylsulphonylbutane.—Toluene-*p*-thiol (52.2 g.) and 1,4-dibromobutane (50 g.) were refluxed in *n*-ethanolic sodium ethoxide (2 mol.) for 1 hr. Extraction with chloroform gave the *sulphide* (58.4 g.), m. p. 65° (from benzene-light petroleum) (Found: C, 71.4; H, 7.2. $C_{18}H_{22}S_2$ requires C, 71.5; H, 7.3%). Oxidation gave the *sulphone* (95%), m. p. 150—151° (from methanol) (Found: C, 58.9; H, 6.1. $C_{18}H_{22}O_4S_2$ requires C, 59.0; H, 6.0%).

The sulphone (3.66 g.), in pyridine (50 ml.) and 2*N*-ethanolic sodium ethoxide (100 ml.), was kept at 80° for 4 days. Recovered sulphone (3.22 g., 91%), m. p. and mixed m. p. 148—151° was obtained. Treatment of the sulphone (3.66 g.) with 2*N*-methanolic sodium methoxide (100 ml.) at 140° (sealed tube) for 10 days gave recovered sulphone (1.86 g.) (51%), m. p. and mixed m. p. 149—150°, together with toluene-*p*-sulphinic acid (81%).

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³² Kamm and Newcomb, *J. Amer. Chem. Soc.*, 1921, **43**, 2228.

³³ Fromm, Forster, and Scherschewitzki, *Annalen*, 1912, **394**, 343.