86. *The Mobility of Groups containing a Sulphur Atom. Part II.*

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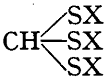
The exchange reaction (I) ⟶ (II; $R' = Ac$) (J., 1932, 1819) has been further explored. With R = Et or *cyclo*hexyl and $R_1 = p$-tolyl, exchange is readily observed, the product being purer than when both R and $R_1 = p$-tolyl, for any unchanged material (I) is an oil

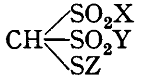
$$\text{(I.)}\quad R{\cdot}SO_2{\cdot}CH_2R' \xrightarrow{R_1{\cdot}SO_2{\cdot}SMe} R_1{\cdot}SO_2{\cdot}CHR'{\cdot}SMe \quad \text{(II.)}$$

in the former case, whereas in the latter case it is a solid, which crystallises with (II). On the other hand, replacement was not observed with $R = p$-tolyl or p-C_6H_4Cl and $R_1 = Et$ or *d*-camphoryl.

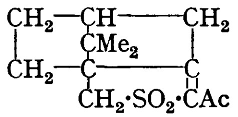
Similar differences in behaviour between alkyl- and aryl-sulphonyl derivatives were found in the work on methionic acid by Schroeter (*Annalen*, 1919, **418**, 167) and by Arndt and Martius (*ibid.*, 1932, **499**, 238) and on chloramine-T by Clutterbuck and Cohen (J., 1922, **121**, 120; 1923, **123**, 2507). Moreover, (III; X = Ph), (IV; X = Y = Z = Et), and (IV; X = Y = Et, Z = Ph) yield the trisulphones (Laves, *Ber.*, 1892, **25**, 348, *vide infra*; Fromm,* *Ann. Chem. Pharm.*, 1889, **253**, 166). On the other hand, (III; X = Et) and (IV; X = Ph, Y = Z = Et) each lose an ethylsulphonyl radical on oxidation (Baumann, *Ber.*, 1886, **19**, 2811; Holmberg, *Ber.*, 1907, **40**, 1742; Tröger and Nolte, *J. pr. Chem.*, 1921, **101**, 136). We found, however, that by oxidising (IV; X = Y = Z = Et) with perhydrol, the trisethylsulphonylmethane can be prepared.



(III.)



(IV.)



(V.)

This one-sided replacement of ethylsulphonyl in (I; R = Et) is in striking contrast to the previous observation that bis-sulphonylmethanes do not undergo exchange at all, and what was then found among the methyl derivatives has now been confirmed for the corresponding ethyl compounds. As, however, there still remained the possibility that some replacement of *p*-tolylsulphonyl by ethylsulphonyl was being overlooked by reason of the product's elusiveness, experiments were tried with *d*-camphorsulphonyl derivatives. *d*-Camphorsulphonylacetone could not be prepared, for it loses water spontaneously,

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* Fromm records it as giving a blue colour with sulphuric acid, which indicates that it was probably contaminated with sulphoxide, but we have obtained a specimen giving no colour.

forming a cyclic *anhydride* (V), which resembles Armstrong and Lowry's camphorsulphonanhydramide (J., 1902, **81**, 1441) in being strongly lævorotatory. On the other hand, Hilditch's methyl *d*-camphorthiolsulphonate (J., 1910, **97**, 1091) converted *p*-tolylsulphonylacetone into *p*-tolylsulphonyl-α-methylthioacetone, and from the fact that the crude material was inactive, it may be inferred that no appreciable exchange of radicals occurred.

Mercaptans readily reduce type II (R′ = Ac or SO_2Et) to unsubstituted sulphonylacetones or sulphonylmethanes, but although the reaction proceeds without alkali (cf. Smiles and Gibson, J., 1924, **125**, 180), a mixture of disulphides, rather than 4-chlorodiphenyl disulphide, was obtained by the action of 4-chlorothiophenol on bisethylsulphonylphenylthiomethane.

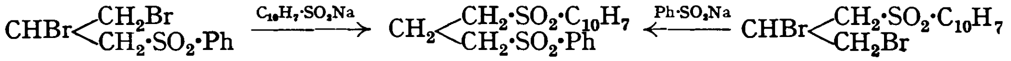
$$\underset{\text{(Type II.)}}{2(C_2H_5{\cdot}SO_2)_2CH{\cdot}SPh} \xrightarrow{2C_6H_4Cl{\cdot}SH} \underset{\text{(Type I.)}}{2(C_2H_5{\cdot}SO_2)_2CH_2} + ({\cdot}SPh)_2 + ({\cdot}S{\cdot}C_6H_4Cl)_2$$

$$\underset{\text{(Type II.)}}{p\text{-}C_6H_4Me{\cdot}SO_2{\cdot}CH(SMe)Ac} \xrightarrow{C_6H_3Cl_2{\cdot}SH} \underset{\text{(Type I.)}}{p\text{-}C_6H_4Me{\cdot}SO_2{\cdot}CH_2Ac} \xrightarrow{C_6H_3Cl_2{\cdot}SO_2{\cdot}S{\cdot}C_6H_3Cl_2} p\text{-}C_6H_4Me{\cdot}SO_2{\cdot}CH(S{\cdot}C_6H_3Cl_2)Ac$$

This reducing action, by mercaptan liberated from thiolsulphonic ester, followed by resubstitution of (I), explains the conversion of *p*-tolylsulphonylmethylthioacetone into *p*-tolylsulphonyl-2 : 5-dichlorophenylthioacetone, recorded previously (Gibson, *loc. cit.*, p. 1822).

These results prompted us to reinvestigate the bisarylsulphonylpropanes. In attempting to prepare αβγ-trisphenylsulphonylpropane, Otto (*Annalen*, 1894, **283**, 183) isolated a substance $C_3H_6(SO_2Ph)_2$, m. p. 101°, which we designate XX′. As it was distinct from the known αβ- and αγ-bisphenylsulphonylpropanes, he tentatively suggested (cf. footnote, *ibid.*, pp. 199, 201) that it might be a stereoisomeric αβ-form. He discovered a corresponding *p*-tolyl derivative also, and Tröger and Artmann (*J. pr. Chem.*, 1896, **53**, 493), who isolated a third " bisnaphthylsulphonylpropane," accepted his explanation. As, however, the mobility of the sulphonyl group introduced a new factor, we re-examined the compounds, and have shown for the three phenyl derivatives that the molecular weights of the relevant compounds are simple and that XX′ cannot be either ββ′-bisphenylsulphonylpropane (Shriner, Struck, and Jorison, *J. Amer. Chem. Soc.*, 1930, **52**, 2060) or αα′-bisphenylsulphonylethane (m. p. 101°, Otto, *J. pr. Chem.*, 1884, **30**, 171) or αα′-bisphenylsulphonylpropane, for these distinctly depress the m. p. of XX′.

Consideration of Stuffer's rule (*Ber.*, 1890, **23**, 1411) suggested that XX′ might be a difficultly separable mixture of αβ-bisphenylsulphonylpropane with one or more other sulphones, but this also must be rejected, for XX′ is distinctly less volatile in a vacuum, and is the only one of all those phenyl derivatives to be oxidised by cold aqueous permanganate. Moreover, an artificial αβ–αγ-mixture was readily separated by crystallisation. Meanwhile the m. p. of a stoppered specimen of XX′ was found to have risen from 101° to 123°, and was then not depressed by admixture with the αγ-disulphone. This observation (incidentally eliminating any possibility of unsaturated or *cyclo*propane sulphones) recalled Kenyon and Phillips's observation (J., 1930, 1677) of the spontaneous change of phenylmethylcarbinyl *p*-toluenesulphinate into the corresponding *p*-tolylsulphone, and supported the idea that Otto's compound is $SO_2Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}SOPh$, which was confirmed by an extension of Tröger's work. By the action of sodium benzenesulphinate on β-naphthylsulphonyl-βγ-dibromopropylsulphone, he obtained what he regarded as α-(β-naphthylsulphonyl)-β-phenylsulphonylpropane, but as we have prepared the same compound from sodium β-naphthylsulphinate and α-phenylsulphonyl-βγ-dibromopropylsulphone, there seems no doubt that the substituents must be in the terminal positions :



$$CHBr{<}\begin{matrix}CH_2Br\\CH_2{\cdot}SO_2{\cdot}Ph\end{matrix} \xrightarrow{C_{10}H_7{\cdot}SO_2Na} CH_2{<}\begin{matrix}CH_2{\cdot}SO_2{\cdot}C_{10}H_7\\CH_2{\cdot}SO_2{\cdot}Ph\end{matrix} \xleftarrow{Ph{\cdot}SO_2Na} CHBr{<}\begin{matrix}CH_2{\cdot}SO_2{\cdot}C_{10}H_7\\CH_2Br\end{matrix}$$

EXPERIMENTAL.

Methane- and ethane-sulphonyl chorides were prepared by shaking Me_2SO_4 and Et_2SO_4 respectively at 75° with Na_2SO_3 aq., evaporating the solution to dryness, refluxing the residue with $POCl_3$, and distilling it in vac. (cf. Dutt, J., 1924, **125**, 1463). The sulphinic acids were obtained by reduction with Zn (*Annalen*, 1890, **259**, 363). Ethylsulphonylacetone (Otto, *Ber.*, 1891, **24**, 868) had b. p. 145°/11 mm. Owing to ease of hydrolysis of the sulphonyl chlorides, a better yield of ethyl ethanethiolsulphonate (b. p. 120°/11 mm.) is obtained by oxidising diethyl disulphide with perhydrol in AcOH at 70° than by Otto's or Fichter and Braun's method (*Ber.*, 1882, **15**, 121; 1914, **47**, 1530).

Ethylsulphonylacetone, ethyl ethanethiolsulphonate, and Na_2CO_3 gave *ethylsulphonylethylthioacetone* (yield 75%), b. p. 102—109°/0·2 mm. (Found: S, 30·2. $C_7H_{14}O_3S_2$ requires S, 30·5%), which on hydrolysis and oxidation gave bisethylsulphonylmethane, m. p. and mixed m. p. 102°, in 60% yield.

Ethylsulphonylacetone, methyl *p*-toluenethiolsulphonate, and Na_2CO_3 (equal mols.) gave a 6% yield of *p*-tolylsulphonyl-α-methylthioacetone, m. p. and mixed m. p. 81°; with 2½ mols. of thiolsulphonate, the yield was 12%. In each case some *p*-tolylsulphonylmethylthiomethane (oxidised, and identified as disulphone) was obtained, but since, in the second expt., 70% of *p*-toluenesulphinic acid was recovered, the max. exchange was less than 30%.

cyclo*Hexylsulphonylacetone* was prepared from Mg or, better, Na, *cyclo*hexylsulphinate, and chloroacetone; the alk.-sol. reaction product solidified on pptn. by H_2SO_4; m. p. 40°, b. p. 135°/0·2 mm. (Found: S, 15·7. $C_9H_{16}O_3S$ requires S, 15·7%). With 2 mols. of methyl *p*-toluenethiolsulphonate (Na_2CO_3) it gave *p*-tolylsulphonyl-α-methylthioacetone, m. p. 82° (identified as above).

p-Tolylsulphonylacetone, Na_2CO_3, and ethyl ethanethiolsulphonate (8 mols.) gave *p*-tolylsulphonyl-α-ethylthioacetone, m. p. and mixed m. p. 96° (60% yield).

p-Tolylsulphonyl-α-methylthioacetone with sodium *cyclo*hexylsulphinate (5 mol.) and Na_2CO_3 gave *p*-tolylsulphonylmethylthiomethane, m. p. and mixed m. p. 81°.

Anhydro-d-*camphorsulphonylacetone*.—Sodium *d*-camphorsulphinate (Hilditch, *loc. cit.*) and chloroacetone gave a *product* largely insol. in alk. (the alk. extract gave the same product on acidification); recryst. from dil. AcOH, it had m. p. 178° (Found: C, 61·0; H, 7·1; S, 12·4, 12·7. $C_{13}H_{18}O_3S$ requires C, 61·3; H, 7·1; S, 12·6%); $[\alpha]^{20°}_{\text{Hg green}}$ −115° (c = 0·5% in EtOH).

p-Tolylsulphonylacetone, Na_2CO_3, and methyl *d*-camphorthiolsulphonate (5 mol.) gave a 70% yield of *p*-tolylsulphonyl-α-methylthioacetone; its solution was inactive. Camphorsulphinic acid (25%) was recovered, but no trace of *p*-toluenesulphinic acid. A parallel expt. with 4-chlorobenzenesulphonylacetone gave 4-chlorobenzenesulphonylmethylthiomethane.

4-Chlorophenylsulphonylacetone, *d*-dicamphoryl disulphoxide, and Na_2CO_3 (equal mols.) gave an alk.-sol. solid which, pptd. by AcOH and recryst., had m. p. 149—150° (Found: C, 55·3; H, 5·7. $C_{19}H_{23}O_4ClS_2$ requires C, 55·0; H, 5·6%).

Trisethylsulphonylmethane.—Bisethylsulphonylmethane, ethyl ethanethiolsulphonate (or ethyl *p*-toluenethiolsulphinate), and Na_2CO_3 gave *bisethylsulphonylethylthiomethane*, m. p. 71° (from H_2O) (Found: S, 37·4. $C_7H_{16}O_4S_3$ requires S, 37·0%). The *trisulphone*, formed by oxidation with H_2O_2, was sol. in hot H_2O and did not separate on cooling till acidified; m. p. 212°, unaffected by sublimation in vac. (Found: C, 28·4; H, 5·5; S, 31·8; equiv., 297. $C_7H_{16}O_6S_3$ requires C, 28·7; H, 5·5; S, 32·9%; equiv., 292).

Attempted Preparation of Phenylsulphonylbisethylsulphonylmethane.—Phenylsulphonylethylsulphonylmethane, ethyl ethanethiolsulphonate (or ethyl *p*-toluenethiolsulphonate) (equal mols. or excess), and Na_2CO_3 gave *phenylsulphonylethylsulphonylethylthiomethane*, m. p. 108° (Found: S, 31·5, 30·9. $C_{11}H_{16}O_4S_3$ requires S, 31·2%). Cold $KMnO_4$ or perhydrol afforded a product, m. p. 135—139°, which gave a blue coloration with anisole in H_2SO_4. The *substance* was destroyed by warm H_2O_2 in AcOH (Found: S, 30·1; equiv., 314. $C_{11}H_{16}O_5S_3$ requires S, 29·6%; equiv., 324).

"*Bisphenylsulphonylpropane*."—The following modification gave a better yield than Otto's method. An alc. sol. of NaOH (1 mol.) and sodium benzenesulphinate (2·2 mol.) was gradually added to a boiling alc. solution of phenyldibromopropylsulphone (1 mol.) during 3 days. The product (yield 35%) had m. p. 101° (Found: *M*, 308. Calc. for $C_{15}H_{16}O_4S_2$: *M*, 324); 12% of trisphenylsulphonylpropane was also formed. The former (XX') was readily hydrolysed by warm alkali and oxidised by cold dil. $KMnO_4$; mixed with αα'-bisphenylsulphonylethane (m. p. 101°) (from CH_3·CHO and Ph·SH, and subsequent oxidation, or by methylation of bisphenylsulphonylmethane), it gave a distinct depression in m. p.

αα′-Bisphenylsulphonylpropane (Found : *M*, 325. $C_{15}H_{16}O_4S_2$ requires *M*, 324) was prepared either by perhydrol oxidation of *αα′-bisphenylthiopropane* (Found : *M*, 247. $C_{15}H_{16}S_2$ requires *M*, 260), from Et·CHO and Ph·SH, or by ethylation of bisphenylsulphonylmethane. Each method gave the same product, m. p. 97—98°, which showed a distinct depression of m. p. with XX′ and differed further in being resistant to hydrolysis and to oxidation. The αβ- and αγ-bis-sulphonylpropanes prepared by Otto's method did not decolorise $KMnO_4$ and showed no evidence of forming a difficultly separable mixture, but the αγ-disulphone underwent practically no depression in m. p. on admixture with XX′. These facts, together with the rise in m. p. on keeping (see p. 307), accord with a sulphinic ester changing to sulphone, and as that spontaneous change with methyl β-naphthylsulphinate is accompanied by the formation of some β-naphthyl β-naphthylthiolsulphonate, we attribute the fact that our XX′ never quite reached the m. p. 128° of our purest specimen of αγ-bisphenylsulphonylpropane to contamination with a little phenyl benzenethiolsulphonate. Several attempts to synthesise the XX′ propane in other ways were unsuccessful. For instance, αγ-dibromopropane gave no reaction with silver benzenesulphinate; the di-iodopropane gave an oil; addition of thiophenol to phenylallylsulphone, followed by oxidation, gave directly αγ-bisphenylsulphonylpropane.

Benzenesulphonyl-β-naphthalenesulphonylpropane.—The reaction of αβ-dibromo-γ-(β-naphthylsulphonyl)propane with sodium benzenesulphinate, carried out as described above for the XX′ propane, gave Tröger and Artmann's compound, m. p. 123°. αβ-Dibromo-γ-phenylsulphonylpropane with sodium β-naphthylsulphinate in the same way gave the same compound. Each specimen was easily hydrolysed and oxidised.

p-*Toluene Derivatives.*—The three compounds (αβ-, αγ-, and XX′-), prepared analogously to the phenyl compounds, melted at 145°, 125—129°, and 154° respectively (Otto gives 145°, 125—129°, and 148°). We found that XX′, but not αβ-, was oxidised by $KMnO_4$, and that a mixture of the two showed a distinct depression in m. p. An attempted prepn. of XX′ by addition of *p*-toluenesulphinic acid to *p*-tolylallylsulphone gave only *p*-tolyl disulphoxide.

β-*Naphthyl Derivatives.*—The three propanes had the m. p.'s given by Tröger and Artmann; only the XX′ isomeride decolorised $KMnO_4$. A mixture of the αγ- and the XX′ compound showed distinct depression of m. p. An attempt to prepare this compound by heating methyl β-naphthalenesulphinate with ethylene glycol gave only β-naphthyl β-naphthylthiolsulphonate.

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