145. *Influence of Poles and Polar Linkings on Tautomerism in the Simple Three-carbon System. Part III. Experiments with Benzyl-Δ^{α}- and -Δ^{β}-propenylsulphones.*

By Eugene Rothstein.

One of the saturated polar groups which might be expected to assist the ionisation of the potentially mobile hydrogen atom in a three-carbon system is SO_2R (Part I; J., 1929, 8). The oxygen atoms of the sulphone group are normally linked to the sulphur atom by semi-polar double bonds, though there is the possibility of the latter becoming non-polar because of the capacity of sulphur to expand its outer shell of electrons to ten.

The substances chosen for a preliminary investigation were an unsubstituted Δ^{β}-propenylsulphone and its Δ^{α}-isomeride,

$$\text{(I.)}\quad R\cdot SO_2\cdot CH_2\cdot CH\colon CH_2 \rightleftharpoons R\cdot SO_2\cdot CH\colon CH\cdot CH_3 \quad \text{(II.)}$$
$$(R = \text{methyl or benzyl})$$

the benzyl compounds being the only ones to be examined in detail.

The structure of *benzyl-Δ^{β}-propenylsulphone* (I) followed from its synthesis from sodium benzylsulphinate and allyl bromide. An attempt to prepare the substance from *benzyl-γ-chloropropylsulphone*, $CH_2Ph\cdot SO_2\cdot CH_2\cdot CH_2\cdot CH_2Cl$ (III), failed owing to the difficulty of eliminating hydrogen chloride by the usual methods.

Benzyl-Δ^{α}-propenylsulphone (II) was prepared from *benzyl-β-chloropropylsulphone*, $CH_2Ph\cdot SO_2\cdot CH_2\cdot CHCl\cdot CH_3$ (IV), the removal of hydrogen chloride being accomplished smoothly with pyridine:

$$\begin{tikzcd} CH_2Ph\cdot SNa + CH_2Cl\cdot CH(OH)\cdot CH_3 \arrow[rrr] & & & CH_2Ph\cdot S\cdot CH_2\cdot CH(OH)\cdot CH_3 \arrow[d] \\ & \text{(II)} & \text{(IV)} \arrow[l] & CH_2Ph\cdot SO_2\cdot CH_2\cdot CH(OH)\cdot CH_3 \ \text{(V.)} \arrow[l] \end{tikzcd}$$

No trace of the Δ^{β}-compound could be detected in it.

Direct interconversion between the two isomerides could not be effected. The substances were unchanged when boiled with water, methyl alcohol, or pyridine. The addition of alkali hydroxide or alkoxide was rapid and led to the formation of β-substituted propylsulphones:

$$\text{(I) or (II)} \xrightarrow{\text{NaOR}} CH_2Ph\cdot SO_2\cdot CH_2\cdot CH(OR)\cdot CH_3 \quad \text{(VI.)}$$
$$(R = \text{H or alkyl})$$

When, by using suitable concentrations of alkali hydroxide or alkoxide, addition was incomplete, no unsaturated sulphone other than the initial compound was found. The formation of a β-substituted addition compound from either of the sulphones did not appear to *follow* an isomeric change, since each of them yielded the same *benzyl-β-iodopropylsulphone* when boiled with concentrated hydriodic acid. Analogous cases of addition are provided by divinylsulphone, which, when treated with sodium hydroxide, yields ββ′-dihydroxydiethylsulphone (Kretov, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1; compare also Cashmore, J., 1923, **123**, 738), and by α- and β-naphthyl-Δ^β-propenylsulphones, which yield the corresponding β-hydroxy-derivatives (Troegar and Artmann, *J. pr. Chem.*, 1896, **53**, 484). On the other hand, phenyl- and *p*-tolyl-Δ^β-propenylsulphones are described by Otto (*Annalen*, 1894, **283**, 181) as being hydrolysed to allyl alcohol and the corresponding sulphinic acids.

The difference in the present case is that, with excess of potassium hydroxide solution, both benzyl-Δ^α- and -Δ^β-propenylsulphones, and also *benzyl-β-hydroxypropylsulphone*, are hydrolysed to benzylmethylsulphone and acetaldehyde. The reaction in the former two cases evidently occurs with the intermediate formation of the latter compound, since it can be isolated from the mixture in cases of incomplete decomposition:

$$\text{(I) or (II)} \xrightarrow{H_2O} CH_2Ph{\cdot}SO_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_3 \xrightarrow{H_2O} CH_2Ph{\cdot}SO_2Me + CH_3{\cdot}CHO$$

This reaction also takes place when the *methoxy*-derivative (VI, R = Me) is boiled with potassium hydroxide (but not when sodium methoxide is used) or when methyl-Δ^β-propenylsulphone is similarly treated. *Benzyl-γ-hydroxypropylsulphone*, however, is stable under these conditions.

The above decomposition does not appear to have been previously observed, though an analogy is presented by the alkaline hydrolysis of β-keto-sulphones (Otto, *J. pr. Chem.*, 1888, **36**, 401):

$$Ph{\cdot}SO_2{\cdot}CH_2{\cdot}COMe \xrightarrow{KOH} Ph{\cdot}SO_2Me + Me{\cdot}CO_2H$$

EXPERIMENTAL.

None of the methods described in Beilstein's "Organische Chemie" was satisfactory for the preparation of benzylsulphinic acid in large quantities. It was prepared in 25% yield by passing dry sulphur dioxide through an ethereal solution of benzylmagnesium chloride. The aqueous layer, after decomposition of the product with water and extraction with ether, was evaporated nearly to dryness in a vacuum, acidified with dilute sulphuric acid, and extracted with ether. This extract yielded the sulphinic acid as a mixture of an oil and a crystalline material which was not further purified, as the sulphone (below) obtained from the mixture was identical with that obtained from the recrystallised sodium salt prepared from the crystals alone.

Benzyl-Δ^β-propenylsulphone (I; R = CH_2Ph) was obtained by boiling a mixture of sodium benzylsulphinate (19 g.), allyl bromide (20 g.), and absolute alcohol (50 c.c.) under reflux for 12 hours. The solution was poured into water, and the sulphone removed; the filtrate yielded a further quantity when extracted with chloroform. The sulphone separated from petrol (b. p. 40—60°), in which it was very sparingly soluble, as colourless plates and from benzene–petrol as prisms, m. p. 64—65°. Yield, 84% (Found: C, 61·4; H, 6·3; S, 16·5. $C_{10}H_{12}O_2S$ requires C, 61·2; H, 6·1; S, 16·3%). It was recovered unchanged after it had been treated with warm concentrated sulphuric acid or boiled with water, methyl alcohol, or dilute sulphuric acid.

αβ-Bisbenzylthiopropane.—In an attempt to prepare benzyl β-bromopropyl sulphide from propylene dibromide, the latter (18 g.) was rapidly added to a cooled solution of sodium benzylthiol (from 10 g. of benzylthiol) in 80% ethyl alcohol (70 c.c.). The product was boiled under reflux for 1 hour, added to water, extracted with ether, and dried. The residue, after removal of the ether, was distilled under reduced pressure and collected at 140—210°/11 mm. Redistilled, b. p. 218—222°/14 mm. Yield, 56%.

αβ-Bisbenzylsulphonylpropane, $CH_2Ph{\cdot}SO_2{\cdot}CH_2{\cdot}CH(SO_2{\cdot}CH_2Ph){\cdot}CH_3$, prepared by oxidation of the above sulphide (6·5 g.) with perhydrol (15 g.) in glacial acetic acid (75 c.c.), crystallised from glacial acetic acid in narrow prisms, m. p. 201° (Found: C, 58·3; H, 5·7; S, 18·5. $C_{17}H_{20}O_4S_2$ requires C, 58·0; H, 5·7; S, 18·2%).

Benzyl β-hydroxypropyl sulphide, prepared in 81% yield from benzylthiol (20 g.), propylene chlorohydrin (14 g.), and alcohol (100 c.c.), had b. p. 55—56°/11 mm.

Benzyl-β-hydroxypropylsulphone (V) was obtained by oxidation of the preceding sulphide (24 g.) with perhydrol (47 g.) in acetic acid solution (100 c.c.). After addition of the product to water, the solid was removed; a further quantity was obtained by extraction of the filtrate with chloroform. The sulphone separated from dry ether or benzene in short colourless prisms,

m. p. 98—99° (Found: C, 56·0; H, 6·2; S, 15·1. $C_{10}H_{14}O_3S$ requires C, 56·1; H, 6·5; S, 15·0%).

Benzyl-β-chloropropylsulphone (IV).—To the hydroxy-sulphone (20 g.) in boiling chloroform (100 c.c.), powdered phosphorus pentachloride (40 g.) was cautiously added, the solution boiled under reflux for ¾ hour, the solvent removed under reduced pressure, and the residue decomposed with ice. The solid obtained crystallised from benzene–petrol (b. p. 40—60°) in prisms, m. p. 88°. Yield, 83% (Found: C, 52·1; H, 5·7. $C_{10}H_{13}O_2ClS$ requires C, 51·6; H, 5·6%).

Benzyl-Δ^{α}-propenylsulphone (II; R = CH_2Ph).—The above chloro-sulphone (10 g.) was boiled under reflux with pyridine (25 c.c.) for 2 hours, the liquid added to a slight excess of dilute hydrochloric acid, and the solution extracted with chloroform. The *sulphone* obtained from the dried extract crystallised from benzene–petrol in short, faintly grey prisms, m. p. 83·6°. Yield, 76% (Found: C, 61·4; H, 6·3; S, 16·6. $C_{10}H_{12}O_2S$ requires C, 61·2; H, 6·1; S, 16·3%). It was soluble in benzene, alcohol, and chloroform, but less so in ether and water. It depressed the m. p. of benzyl-Δ^{β}-propenylsulphone to about 45°. Like its isomeride, the sulphone was unaffected by boiling water, methyl alcohol, or dilute sulphuric acid. A solution in aqueous sodium bicarbonate decolorised cold potassium permanganate.

Benzyl-β-methoxypropylsulphone (VI; R = OMe).—Benzyl-β-chloropropylsulphone (2 g.) was boiled under reflux with a solution of potassium hydroxide (1 g. in methyl alcohol, 10 c.c.) for ½ hour, and the product poured into water. Chloroform extracted a thick oil, b. p. 214°/14 mm., which solidified when cooled but could not be recrystallised (Found: C, 57·5; H, 6·9; OMe, 13·5. $C_{11}H_{16}O_3S$ requires C, 57·9; H, 7·0; OMe, 13·6%). The *sulphone* was converted into the hydroxy-derivative (V) when boiled under reflux for 2 hours with a solution of hydrogen iodide in glacial acetic acid. 3*N*-Potassium hydroxide hydrolysed the sulphone to benzylmethylsulphone.

Benzyl γ-hydroxypropyl sulphide, prepared in 88% yield from benzylthiol (20 g.), trimethylene chlorohydrin (14 g.), and alcohol (120 c.c.), had b. p. 185°/19 mm.

Benzyl-γ-hydroxypropylsulphone, prepared by the oxidation of the above sulphide (38·7 g.) with perhydrol (72 g.) in glacial acetic acid solution (150 c.c.), crystallised from benzene in needles, m. p. 127°. Yield, 77·6% (Found: C, 56·0; H, 6·3; S, 15·2. $C_{10}H_{14}O_3S$ requires C, 56·1; H, 6·5; S, 15·0%). The sulphone was stable to 3*N*-potassium hydroxide. When the substance (1 g.) was heated with potassium hydrogen sulphate (3 g.) to 220°, a dark-coloured product was obtained, which was boiled in alcoholic solution with norit and crystallised from benzene–petrol (b. p. 40—60°); it then had m. p. 111—112° and was evidently *di-(γ-benzylsulphonylpropyl) ether*, $(CH_2Ph\cdot SO_2\cdot CH_2\cdot CH_2\cdot CH_2)_2O$ (Found: C, 58·7; H, 6·5; S, 16·2; *M*, 371, 385. $C_{20}H_{26}O_5S_2$ requires C, 58·5; H, 6·6; S, 15·6%; *M*, 410).

Benzyl-γ-chloropropylsulphone (III), prepared by addition of phosphorus pentachloride (22 g.) to the hydroxy-sulphone (11 g.) dissolved in hot chloroform (40 c.c.), crystallised from dilute acetic acid in short prisms, m. p. 96°. Yield, 71% (Found: C, 52·4; H, 5·6; S, 13·7. $C_{10}H_{13}O_2ClS$ requires C, 51·6; H, 5·6; S, 13·8%). When boiled with pyridine or alcoholic potash under reflux, it was converted into the corresponding hydroxy-sulphone.

Methyl-Δ^{β}-propenylsulphone (I; R = Me) was prepared by boiling under reflux a mixture of allyl bromide and magnesium methanesulphinate (obtained by passing dry sulphur dioxide through an ethereal solution of methylmagnesium bromide). It was a colourless liquid, b. p. 130°/15 mm. (Found: C, 39·9; H, 6·7. $C_4H_8O_2S$ requires C, 40·0; H, 6·7%), which yielded acetaldehyde when boiled with 3*N*-potassium hydroxide.

Addition of Methyl Alcohol to Benzyl-Δ^{α}- and -Δ^{β}-propenylsulphones.—Either sulphone (1·5 g.) was dissolved in *N*-sodium methoxide (22 c.c.) and kept, or boiled under reflux, for 20 hours, the same product being obtained in both cases and also when a solution of the sulphone in *N*/10-sodium methoxide was kept for 30 minutes. Benzyl-β-hydroxypropylsulphone was obtained when the product was boiled with hydriodic acid.

Action of Potassium Hydroxide Solution.—(i) Benzyl-Δ^{β}-propenylsulphone (2 g.) was boiled under reflux with 3*N*-potassium hydroxide (50 c.c.) for 1½ hours. The product crystallised from benzene in slightly discoloured needles of benzylmethylsulphone, m. p. and mixed m. p. 125° (Found: C, 56·5; H, 6·0; S, 18·7. Calc.: C, 56·5; H, 6·0; S, 18·8%).

(ii) Benzyl-Δ^{β}-propenylsulphone (1 g.), when boiled under reflux with 0·1*N*-potassium hydroxide (10 c.c.) for 2 hours, yielded a mixture of benzyl-β-hydroxypropylsulphone and benzylmethylsulphone.

(iii) When a mixture of the Δ^{α}- or the Δ^{β}-sulphone with 3*N*-potassium hydroxide was distilled for 20 minutes, acetaldehyde was produced (*p*-nitrophenylhydrazone, m. p. 128°. Found:

C, 53·8; H, 4·9. Calc.: C, 53·6; H, 5·0%). The aqueous residue contained the hydroxy-sulphone and benzylmethylsulphone. The same three substances were obtained when benzyl-β-hydroxypropylsulphone was similarly treated with 3*N*-potassium hydroxide.

Action of Sodium Carbonate Solution.—(i) When either of the unsaturated sulphones was boiled under reflux with *N*-sodium carbonate for 2 hours, a mixture of hydroxy- and unchanged sulphone was obtained. Neither the other isomeride nor benzylmethylsulphone could be detected.

(ii) In order to discover whether there was any difference in the rates of conversion of the unsaturated sulphones into the hydroxy-sulphone, each of the former (0·5 g.) was boiled under reflux with 0·1*N*-sodium carbonate (25 c.c.) for 40 minutes. The product, extracted and dried (calcium chloride) in chloroform and recovered, had m. p. 84·0° (from the Δ^{β}-sulphone), corresponding to a 76% conversion, and 86·5° (from the Δ^{α}-sulphone), corresponding to 81% conversion. The melting-point curves for the three substances are:

Mixtures of the Δ^{β}-sulphone with the β-hydroxy-sulphone.

Hydroxy-sulphone, %	0·0	18·0	29·2	42·9	53·2	64·7	86·7	100·0
M. p.	64·5°	54·0°	51·9°	66·6°	72·7°	78·8°	88·2°	98·0°

Mixtures of the Δ^{α}-sulphone with the β-hydroxy-sulphone.

Hydroxy-sulphone, %	0·0	11·2	25·0	35·1	50·0	70·2	86·3	100·0
M. p.	83·6°	78·6°	71·5°	67·0°	69·8°	81·2°	89·2°	98·0°

Addition of Hydrogen Iodide.—The Δ^{α}-sulphone (1 g.) was boiled under reflux for 1 hour with 5 c.c. of hydriodic acid (*d* 1·9), and the mixture poured into water. The product, isolated in chloroform and crystallised twice from benzene–petrol (b. p. 40—60°), formed needles, m. p. 105—107° of *benzyl-β-iodopropylsulphone* (Found: C, 37·2; H, 4·0; S, 10·1. $C_{10}H_{13}O_2IS$ requires C, 37·0; H, 4·0; I, 39·2; S, 9·9%), hydrolysis of which with 1% sodium hydroxide in 50% ethyl alcohol yielded the β-hydroxy-sulphone.

The iodo-sulphone similarly obtained from the Δ^{β}-sulphone was contaminated with iodine-free products and after three crystallisations had m. p. 99° (Found: C, 37·5; H, 4·0; I, 39·0%). It did not depress the m. p. of the preceding iodo-sulphone, and hydrolysis converted it into the β-hydroxy-sulphone.

Fission of Benzyl-Δ^{α}-propenylsulphone by Ozone.—The sulphone was ozonised in chloroform for 48 hours. No aldehyde was produced when the residue after evaporation of the chloroform was boiled with water. The only product obtained from the residual liquid was benzoic acid.

Fission of Benzyl-Δ^{β}-propenylsulphone by Ozone.—The sulphone was ozonised in chloroform for 1 hour. After distillation of the chloroform, the residue was boiled with water and the vapours were passed into an acetic acid solution of *p*-nitrophenylhydrazine; the hydrazone obtained could not be purified owing to the presence of sulphone which had distilled with the steam. The residual sulphone in the flask was isolated and warmed with *p*-nitrophenylhydrazine solution, yielding *benzylsulphonylacetaldehyde*-p-*nitrophenylhydrazone*,

$$CH_2Ph\cdot SO_2\cdot CH_2\cdot CH{:}N\cdot NH\cdot C_6H_4\cdot NO_2,$$

which separated from dilute alcohol in orange crystals, m. p. 195—196° (Found: C, 53·5; H, 4·4. $C_{15}H_{15}O_4N_3S$ requires C, 54·1; H, 4·5%).

When treatment with ozone was prolonged to 48 hours, further fission took place and the product finally isolated appeared to be *benzylsulphonylformaldehyde*-p-*nitrophenylhydrazone*, $CH_2Ph\cdot SO_2\cdot CH{:}N\cdot NH\cdot C_6H_4\cdot NO_2$, m. p. 178—180° after crystallisation from dilute alcohol (Found: C, 52·5; H, 4·3. $C_{14}H_{13}O_4N_3S$ requires C, 52·7; H, 4·1%).

All the analyses were carried out by Dr. A. Schoeller of Berlin.

The author thanks the Chemical Society for a grant.

THE UNIVERSITY, LEEDS. [*Received, February 8th*, 1934.]