65. *Influence of Poles and Polar Linkings on Tautomerism in the Simple Three-carbon System. Part V. The Course of Prototropic Change in the Bissulphonylpropenes.*

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IN the preceding paper (Part IV), it is shown that α-benzylsulphonyl-γ-ethylsulphonyl-Δ^{α}- and -Δ^{β}-propene (I and II) are tautomeric either when boiled with a solvent or on melting.

When these compounds are treated with alkali alkoxide, stable alkali metal derivatives are formed having the composition $C_{24}H_{31}O_8S_4X$ or $C_{36}H_{46}O_{12}S_6X_2$ according to the solvent used (X = K or Na). The sulphones obtained therefrom after acidification were not crystalline; the amorphous solids which were formed when the syrups were rubbed with ether were hygroscopic and became syrupy again when treated with a solvent. Analysis of the crude substances was necessarily only approximate, but it indicated that the metal had been replaced by water leading to the formula $C_{24}H_{32}O_9S_4$. Treatment of the metal derivatives with methyl iodide yielded similar substances with higher carbon and hydrogen contents. The substances did not contain alkoxyl, nor did they form derivatives characteristic of a hydroxyl group, and they remained unchanged when boiled with concentrated hydriodic acid. When they were heated to 100°, some decomposition took place and thereafter the sulphones no longer solidified. Since the metallic derivatives contained no extra oxygen, it follows that they were true substitution products and not addition compounds, *i.e.*, self-addition was consequent on their formation. It was subsequently confirmed that hydrogen was evolved when the bis-sulphones were shaken with " molecular " potassium in xylene.

It was evident that by reducing the large number of possible isomerides having the dimeric composition, a crystalline material might be isolated from the mixture, and this was realised when *αγ-bis(ethylsulphonyl)propene*, $Et{\cdot}SO_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}SO_2Et$, was dissolved in alkali alkoxide, and the metallic derivative isolated and decomposed by acid. In these circumstances, the syrupy mixture afforded a good yield of a crystalline sulphone, m. p. 94—98°, which had the composition of the bis-sulphone but with a molecular weight double that required for the monomeric substance. The rather low and indefinite melting point was probably due to the presence of more than one isomeride, as was suggested by the appearance of the crystals, but separation was not achieved. The remaining syrup was not identified. The metal derivative furnished a *dimethylated dimeride*, $C_{16}H_{32}O_8S_4$, m. p. 160—161°, when boiled with methyl iodide.

β-Hydroxy-αγ-bis(ethylsulphonyl)propane also gave the dimeric sulphone after prolonged boiling with alkali alkoxide. It is concluded, however, that dehydration preceded the formation of the metal derivative and dimerisation, because the saturated bis-sulphones did not appear to contain a reactive methylene group. Neither the bis-sulphonyl-β-hydroxypropanes, $R{\cdot}SO_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}SO_2R'$, nor α-benzylsulphonyl-γ-ethylsulphonylpropane, $CH_2Ph{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2Et$, condensed with benzaldehyde, nor did the latter form a potassio-derivative. Moreover, whilst the bis-sulphonylpropenes formed the polymerised product in the presence of dilute potassium methoxide solution containing less than 3% of the potassium necessary to react with the sulphone present, the hydroxy-bis-sulphonylpropanes were completely unchanged by this treatment, even after prolonged boiling. Finally polymerisation occurred in the absence of water, when, for instance, a benzene solution of the bis-sulphone was warmed with " molecular " potassium, or when it reacted with diazomethane in ether–chloroform solution.

Since the removal of the proton by alkoxide must produce the kinetically free anions,

$$\mathrm{R{\cdot}SO_2{\cdot}CH{:}CH{\cdot}\overset{-}{C}H{\cdot}SO_2R'} \text{ and } \mathrm{R{\cdot}SO_2{\cdot}\overset{-}{C}H{\cdot}CH{:}CH{\cdot}SO_2R'}$$

resonance between which leads to the formation of the mesomeric ion and thence to self-addition, it is clear that interchange between (I) and (II) cannot take place with these ions as intermediates. The bis-sulphonylpropenes must therefore be classed with systems where the tautomeric change operates according to Lowry's termolecular mechanism (J., **1927**, 2554; cf. Ingold, Salas, and Wilson, J., **1936**, 1328). This is analogous to the preservation of asymmetry of an optically active methylazomethine during its interconversion to the racemic form of its isomeride, an observation which was advanced by Hsü, Ingold, and Wilson as the first unambiguous case of such a mechanism (J., **1935**, 1779).

Consequently, though the canonical structure $\mathrm{R{\cdot}SO_2{\cdot}\overset{H^+}{CH}{:}CH{\cdot}\overset{-}{C}H{\cdot}SO_2R'}$ postulated in Part IV can be regarded as playing only a small part in the resonance of the molecule, it enables the completed change to take place with the removal of the proton from one carbon atom and the simultaneous recombination at another part of the system, a second molecule furnishing the rôle of both base and acid respectively.

It appeared that the formation of a methylated monomeric derivative could only be expected to take place in the presence of a kation which could combine with the anion formed by the action of the alkoxide, before mesomerisation occurred. This was realised when 0·1*N*-potassium methoxide was slowly added to a cold mixture of the sulphonylpropene with methyl iodide. Under these conditions *αγ-benzylsulphonylethylsulphonyldimethylpropene* was isolated in about 30% yield, the remaining product being the polymerised sulphone.

EXPERIMENTAL.

(A) *αγ-Bis(ethylsulphonyl)propene.*—Oxidation of β-hydroxy-αγ-bis(ethylthio)propane (Tschugajev, and Kobljansky, *Z. anorg. Chem.*, 1913, **83**, 18) with perhydrol furnished *β-hydroxy-αγ-bis(ethylsulphonyl)propane* in 89% yield. It was isolated from the water–acetic acid solution by evaporation to dryness on the steam-bath and crystallised from benzene or ethyl alcohol in needles, m. p. 113—114° (Found: C, 34·5; H, 6·6; S, 26·4. $C_7H_{16}O_5S_2$ requires C, 34·4; H, 6·6; S, 26·2%).

β-Chloro-αγ-bis(ethylsulphonyl)propane, obtained in 71% yield when the above sulphone (30 g.) was treated with phosphorus pentachloride (28 g.) in chloroform solution (200 c.c.), separated from benzene in fine needles, m. p. 81° (Found: C, 32·4; H, 5·8; Cl, 12·7; S, 24·7. $C_7H_{15}O_4ClS_2$ requires C, 32·0; H, 5·7; Cl, 13·5; S, 24·4%).

αγ-Bis(ethylsulphonyl)propene resulted when the chloro-compound (23 g.) was boiled under reflux with pyridine (25 c.c.) for 3 hours. It crystallised from benzene, in which it was not very soluble, in needles, m. p. 117—118° (Found: C, 37·1; H, 6·2; S, 28·2; *M*, 229. $C_7H_{14}O_4S_2$ requires C, 37·2; H, 6·2; S, 28·3%; *M*, 226). The bis-sulphone condensed with benzaldehyde in the presence of piperidine, yielding *βδ-bis(ethylsulphonyl)-α-phenylbutadiene*,

$$\mathrm{Et{\cdot}SO_2{\cdot}CH{:}CH{\cdot}C(SO_2Et){:}CHPh},$$

which crystallised in feathery needles, m. p. 137—139°, from ethyl acetate (Found: C, 52·9; H, 5·8; S, 20·5. $C_{14}H_{18}O_4S_2$ requires C, 53·5; H, 5·7; S, 20·4%).

(B) *Sodio- and Potassio-derivatives of αγ-Benzylsulphonylethylsulphonylpropene.*—(i) The bis-sulphone (3 g.) was mixed with 0·05*N*-sodium ethoxide (25 c.c.). The orange solution quickly deposited the *sodio*-derivative as a buff precipitate, which changed to red when exposed to air (Found: C, 47·7; H, 5·0; S, 21·1; Na, 3·4. $C_{24}H_{31}O_8S_4Na$ requires C, 48·2; H, 5·2; S, 21·4; Na, 3·8%). Repetition of the experiment with excess of *N*-sodium ethoxide yielded a *compound* containing 4·9% of sodium ($C_{36}H_{46}O_{12}S_6Na_2$ requires Na, 5·1%). The sodio-derivatives were partly hydrolysed by cold water, giving alkaline solutions.

(ii) The bis-sulphone (1·75 g.) was boiled under reflux with *N*-potassium *iso*propoxide (7 c.c.) for 1½ hours, and the precipitate collected and washed with *iso*propyl alcohol (Found : C, 45·9; H, 5·4; S, 20·4; K, 8·4. $C_{36}H_{46}O_{12}S_6K_2$ requires C, 46·0; H, 4·9; S, 20·4; K, 8·3%). When ethyl alcohol was used as the solvent, a *potassium* derivative of the dimeric sulphone resulted (Found: C, 46·8; H, 5·2; S, 20·8; K, 6·4. $C_{24}H_{31}O_8S_4K$ requires C, 46·9; H, 5·0; S, 20·8; K, 6·4%)

(iii) In order to confirm the reality of the two series of metallic derivatives, parallel experiments with *N*-solutions of the alkoxides were carried out; in each case the sulphone (0·3 g.) was boiled under reflux for 7 hours with *N*-alkoxide solution (5 c.c.), and the resulting derivative washed with the appropriate alcohol and analysed :

			Calc. for	
Alkoxide.	Colour of derivative.	Metal, %.	$C_{24}H_{31}O_8S_4X$.	$C_{36}H_{46}O_{12}S_6X_2$.
KOPr	Buff	7·5	K = 6·4%	K = 8·3%
KOMe	White	6·4		
NaOPr	Buff	4·9	Na = 5·1%	Na = 3·9%
NaOMe	White	4·2		

(C) *Sulphones from Metallic Derivatives.*—(i) The dimeric sodio-derivative was decomposed by carbon dioxide in alcohol–chloroform suspension. No acid was formed, but when excess of petrol was added to the filtered solution a *dimeric sulphone* was obtained, which separated from benzene–petrol (b. p. 40—60°) as an amorphous solid, m. p. *ca.* 83° (decomp.) (Found : C, 48·7; H, 5·8; S, 21·0; *M**, 643. $C_{24}H_{32}O_9S_4$ requires C, 48·6; H, 5·7; S, 21·6%; *M*, 592).

(ii) The sodio-derivative was boiled under reflux with methyl iodide in ethyl alcohol until solution was complete. The usual amorphous solid was obtained when the sulphone was mixed with ether. As with all these polymeric sulphones, the addition of most solvents caused the substance to become syrupy; an exception was *iso*propyl alcohol, but even in this case it separated from its solution in this solvent as an oil which solidified on scratching. Analysis showed that the sulphone was probably a *tetramethylated dimeride* (Found : C, 53·1; H, 6·1; S, 19·9; OEt, 0. $C_{28}H_{40}O_8S_4$ requires C, 53·2; H, 6·3; S, 20·3%).

(iii) The bis-sulphone (2 g.) was boiled under reflux with *N*-lithium ethoxide (7 c.c.). A red solution was formed, but only a slight precipitate. Excess of methyl iodide was added, and the heating continued for a further 1½ hours. The product appeared to be a *trimethylated trimeric sulphone*; it separated from *iso*propyl alcohol as an amorphous solid, indef. m. p. 65° and decomposing at 100°. Analysis indicated the presence of an extra molecule of water (Found : C, 50·8; H, 6·2; S, 20·1; *M*, 859. $C_{39}H_{56}O_{13}S_6$ requires C, 50·8; H, 6·1; S, 20·8; *M*, 924).

(iv) The sulphones obtained from the potassio-derivatives were similar to those described above. They all had indefinite m. p.'s and lost solvent at about 85°. Similar analysis figures were obtained whether the sulphone was heated above its m. p. in a vacuum until decomposition was complete (Found : C, 48·7; H, 5·7; S, 21·6%; *M*, 517), or allowed to separate from its solution in a large quantity of ether (Found : C, 48·9; H, 5·7; S, 21·9%; *M*, 532).

(v) Potassium (0·1 g.) was " molecularised " under benzene (5 c.c.), and the bis-sulphone (0·5 g.), dissolved in hot benzene (5 c.c.), added; hydrogen was evolved. The liquid, after boiling for 1 hour under reflux, was acidified by the gradual addition of glacial acetic acid (0·5 c.c.). The resulting sulphone was exactly similar to those described above (Found : *M*, 587).

(D) *Action of Alkoxides on αγ-Bis(ethylsulphonyl)propene.*—(i) The *sodio-* and *potassio-*derivatives were prepared as before (Found : C, 35·9; H, 5·7; S, 26·2; Na, 5·2. $C_{14}H_{27}O_8S_4Na$ requires C, 35·5; H, 5·7; S, 27·0; Na, 4·9%. Found: C, 34·6; H, 5·5; S, 26·1; K, 7·5. $C_{14}H_{27}O_8S_4K$ requires C, 34·3; H, 5·5; S, 26·1; K, 7·9%).

(ii) The sodio-derivative was decomposed by formic acid, and the sulphone rubbed with ether–ethyl acetate, yielding the *dimeride* of αγ-bis(ethylsulphonyl)propene, which after crystallisation from benzene separated from ethyl acetate–petrol (b. p. 60—80°) in mixed prisms, m. p. 94—95°; yield, *ca.* 55% (Found : C, 37·4; H, 6·3; S, 28·2; *M*, 435, 445. $C_{14}H_{28}O_8S_4$ requires C, 37·2; H, 6·2; S, 28·3%; *M*, 452).

(iii) The *dimeride* of *αγ-bis(ethylsulphonyl)-α(?)-methylpropene* was formed when *N*-sodium ethoxide (7 c.c.) was gradually added to a boiling solution of the bis(ethylsulphonyl)propene (0·5 g.) in methyl iodide. The resulting syrupy *sulphone*, when treated with methyl alcohol–ether, afforded a small quantity of crystalline material, which separated from ethyl acetate in

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* The molecular weights, determined by Rast's method, are of necessity minimum figures for these substances owing to the difficulty of purification. There is therefore the probability that some of them are mixtures of dimeric and trimeric sulphones.

prisms, m. p. 160—161° (Found: C, 39·9; H, 6·6; S, 27·0; *M*, 511. $C_{16}H_{32}O_8S_4$ requires C, 40·0; H, 6·7; S, 26·7%; *M*, 480).

(E) *Action of Alkoxide on the Hydroxy-bis-sulphonylpropanes.*—(i) β-Hydroxy-α-benzylsulphonyl-γ-ethylsulphonylpropane (2 g.) was boiled under reflux with *N*-potassium ethoxide (12 c.c.), the yellow solution gradually depositing the potassio-derivative (Found: C, 46·3; H, 5·4; S, 21·8; K, 6·3%). It was not produced when small concentrations of alkoxide were used, the original sulphone being recovered unchanged. The corresponding propene, on the other hand, gave the polymerised sulphone when boiled with 0·1*N*-sodium methoxide for 30 minutes (Found: *M*, 532. See section C, iv).

(ii) β-Hydroxy-αγ-bis(ethylsulphonyl)propane (0·7 g.) gave a dark brown solution when boiled with *N*-potassium methoxide (5 c.c.), no solid being precipitated. The semi-solid, dark brown product obtained from the solution was purified by boiling with norit in ethyl acetate and isolated in 50% yield by careful precipitation with ether. Two recrystallisations from ethyl acetate–petrol afforded mixed prisms, m. p. 95—98°. It was not identical with the dimeride previously obtained (section D, ii), since the m. p. was lowered to 90° when the two were mixed (Found: C, 37·1; H, 6·3; S, 28·3%; *M*, 490).

(F) *Methylation of Benzylsulphonylethylsulphonylpropene.*—(i) 0·1*N*-Sodium methoxide (40 c.c.) was slowly added to a cold stirred suspension of the bis-sulphone (2·0 g.) and methyl iodide (20 c.c.) in methyl alcohol (20 c.c.), the sulphone gradually dissolving. The mixture was boiled under reflux for 5 minutes, diluted with water, and extracted with chloroform. Removal of the solvent yielded a semi-solid which, after washing with methyl alcohol, afforded *α-benzylsulphonyl-γ-ethylsulphonyldimethylpropene* in about 50% yield; this crystallised from ethyl acetate–petrol (b. p. 60—80°) in needles, m. p. 135—136° (Found: C, 53·2; H, 6·4; S, 20·2; *M*, 292, 267, 338. $C_{14}H_{20}O_4S_2$ requires C, 53·2; H, 6·3; S, 20·3%; *M*, 316).

The corresponding hydroxybis-sulphonylpropane was unchanged by this treatment.

(ii) The bis-sulphone (1 g.) was dissolved in chloroform, and ethereal diazomethane (from 2 c.c. of nitrosomethylurethane) added. Nitrogen was evolved and the mixture grew warm. The residue left when the solvent was distilled contained nitrogen, and had all the properties of the polymerised sulphones. The bis-sulphone had undoubtedly been methylated, since the analysis figures for the substance after it had been heated in a vacuum showed that the carbon content was much greater than would be required for the simple addition of diazomethane to give the pyrazolone derivative (Found: C, 52·3; H, 5·3; S, 16·9; N, 8·2%).

The analyses in this and the preceding paper were carried out by Dr. Ing. A. Schoeller of Berlin or Dr. G. Weiler of Oxford.

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[*Received, December 8th,* 1936.]