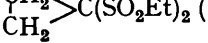
294. *Influence of Poles and Polar Linkings on Tautomerism in the Simple Three-carbon System. Part VI. Unbalanced Systems.*

By Eugene Rothstein.

Most of the three-carbon systems hitherto investigated in this series fall into two classes, those with a polar group at each end of the carbon chain and those with only one such group, and of these only the former are mobile. It appears that only those systems are mobile (*i.e.*, in the cases where there is no permanent seat for the anionic charge formed by the separation of a proton as is present in unsaturated acids, etc.) where the two isomerides have a very similar constitution. There was, however, the possibility that with only one pole present the ionisation of the hydrogen atom was too difficult. For this reason *αα-bis(ethylsulphonyl)-Δ^{α}-propene* has been prepared and it is found that, unlike the cases of the αγ-bis(alkylsulphonyl)propenes, there is no movement of the double bond when the substance is distilled. This may be due to the equilibrium position leading to 100% of the Δ^{α}-compound. It was unfortunately not possible to test this by the synthesis of the Δ^{β}-isomeride because all the methods tried led either to the production of 1 : 1-*bis(ethylsulphonyl)*cyclo*propane* or to αγ-bis(ethylsulphonyl)propene.

The investigations described in this series of papers have shown that the more mobile systems are those which are activated by two polar groups, examples being αγ-bis-quaternary ammonium salts and αγ-bis-sulphones, $R\cdot CH_2\cdot CH{:}CHR$ ($R = NR_3X$, Part II, J., 1931, 1666; and $R = SO_2Et$, Part IV, J., 1937, 309). On the other hand, no tautomerism was observed in benzylpropenylsulphones where only one such activating group was present (Part III, J., 1934, 684). The trialkyl-γ-chloropropenylammonium salts reported in Part I (J., 1929, 8) may be classed with the first two systems and it can be concluded from the experiments described in this paper that the halogen atom itself functions as a pole, forming a balanced system and facilitating the separation of a proton from the α-carbon atom. It is known that trimethylallylammonium salts, $CH_2\!:\!CH\cdot CH_2\cdot NMe_3X$ (I), show no tendency to pass into the Δ^{α}-isomeride, $CH_3\cdot CH\!:\!CH\cdot NMe_3X$ (II), and it has now been found that the latter, which has been synthesised, is likewise stable and that neither of these two substances is interconverted in alkoxide solution.

In all these classes of compounds there is no permanent seat for the anionic charge as is formally the case with unsaturated esters, ketones, etc., and for tautomerism to occur it may be necessary for the two isomerides to have approximately equal energies. It was in order to throw some light on this point that the synthesis of αα-bis(ethylsulphonyl) derivatives, $CH_2\!:\!CH\cdot CH(SO_2Et)_2$ (III) and $CH_3\cdot CH\!:\!C(SO_2Et)_2$ (IV), was undertaken, since in these compounds there can be no doubt about the ease of separation of the hydrogen atom and therefore of the potential mobility of the system (cf. Part IV, *loc. cit.*). However, although the preparation of (IV) was possible, that of the Δ^{β}-sulphone (III) could not be accomplished. The oxidation of the corresponding thioacetal, $CH_2\!:\!CH\cdot CH(SEt)_2$ (this vol., p. 1551), is accompanied by the migration of the ethylthio-group and the only product was αγ-bis(ethylsulphonyl)propane. This anionotropic change is being investigated. The elimination of hydrogen chloride from *γ-chloro-αα-bis(ethylsulphonyl)-propane*, $CH_2Cl\cdot CH_2\cdot CH(SO_2Et)_2$ (V), gave a substance which was not unsaturated, was very stable to oxidising agents, and with hydriodic acid furnished the γ-iodo-compound, $CH_2I\cdot CH_2\cdot CH(SO_2Et)_2$. It was probably 1 : 1-*bis(ethylsulphonyl)*cyclo*propane*,



$\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!\!>\!C(SO_2Et)_2$ (VI).

The sulphone (IV) is stable to heat and can be distilled without change. This is in marked contrast to the αγ-bis(ethylsulphonyl)propenes, $R\cdot SO_2\cdot CH_2\cdot CH\!:\!CH\cdot SO_2R'$, which form equilibrium mixtures under these conditions. The main reaction of (IV) is that of addition, which in aqueous neutral or alkaline solution is accompanied by fission :

$$CH_3\cdot CH\!:\!C(SO_2Et)_2 + HX \longrightarrow CH_3\cdot CHX\cdot CH(SO_2Et)_2 \xrightarrow{X\,=\,OH} CH_3\cdot CHO + CH_2(SO_2Et)_2.$$

The chief product of alkylation was a methylated dimeric *sulphone*, $C_{15}H_{30}O_8S_4$, which when oxidised with ozone afforded a small amount of a *bis(ethylsulphonyl)propionic acid*. It is difficult to envisage the formation of a substituted propionic acid except from the product of an αβ–βγ change during some stage of the alkylation, but this was the only evidence obtained that such a change might have occurred with this substance.

EXPERIMENTAL.

Section I. Experiments with Trialkylpropenylammonium Compounds.—(i) Trimethylallylammonium chloride was obtained by condensing allyl chloride with alcoholic trimethylamine at room temperature and completing the reaction on the steam-bath.

Fission by ozone. This was best carried out with the hydroxide, which was dissolved in glacial acetic acid and treated with ozonised oxygen for 36 hours. The ozonide was boiled with water and evaporated to dryness; the residue yielded betaine picrate, m. p. 180° (Found : 38·0; H, 4·1. Calc. : C, 38·2; H, 4·0%).

Action of alkoxide. Sodium methoxide in boiling solution had no action on the chloride, which was also recovered unchanged when warmed at 45° for 12 hours with 0·5N-sodium *iso*propoxide. Prolonged action of this reagent at this temperature or higher temperatures led to the formation of dimethylamine, the picrate of which was identified by comparison (m. p. and mixed m. p.) with a synthetic specimen (Found: C, 35·3; H, 3·9. Calc. : C, 35·0; H, 3·6%).

(ii) *Preparation and properties of trimethyl-Δ^{α}-propenylammonium salts* (II). *Trimethyl-β-hydroxypropylammonium salts.* The confusion that has arisen in the literature (cf. Beilstein, "Organische Chemie," Supplement, **4**, 433, 437) regarding the structure and identities of the hydroxypropylammonium salts prepared by different methods has been satisfactorily clarified by Major and Cline (*J. Amer. Chem. Soc.*, 1932, **54**, 242), who found that the substances obtained by the condensation of propylene chlorohydrin and trimethylene chlorohydrin with trimethylamine are those to be expected and that no isomerisation takes place. The β-hydroxy-compound prepared in this way yielded a picrate which after several recrystallisations from alcohol had

m. p. 157—159°. Major and Cline found 163° (Found : C, 41·8; H, 5·4. Calc. : C, 41·6; H, 5·2%).

Trimethyl-β-chloropropylammonium salts. These salts were probably first prepared by Partheil (*Annalen*, 1892, **268**, 170) by the addition of hydrogen chloride to trimethylallylammonium chloride; he considered them, however, to be the γ-chloro-derivatives.

Trimethyl-β-hydroxypropylammonium chloride (43 g.), suspended in chloroform (250 c.c.), was treated with phosphorus pentachloride (90 g.) and refluxed for 20 minutes. After cooling, the solution was mixed with dry ether, the ethereal layer decanted, and the residue dissolved in alcohol, reprecipitated with ether, and left over sulphuric acid. The yield of trimethyl-β-chloropropylammonium chloride was 80%. The *picrate* separated from absolute alcohol or water in needles, m. p. 161—162° (Found : C, 39·9; H, 4·7; Cl, 8·8. $C_6H_{14}NCl,C_6H_3O_7N_3$ requires C, 39·5; H, 4·7; Cl, 9·6%).

Trimethylpropenylammonium salts (II). Partheil (*loc. cit.*) isolated trimethylallylammonium salts only, when he treated his " trimethyl-γ-iodopropylammonium iodide " with alcoholic potash. Trimethyl-β-chloropropylammonium chloride (26·5 g.) was mixed with a solution of potassium hydroxide (8·5 g.) in ethyl alcohol (200 c.c.) and kept overnight.* The liquid was filtered, neutralised (to congo) with hydrochloric acid, and evaporated to dryness, and a slight excess of aqueous sodium picrate added. Fractional crystallisation from ethyl alcohol yielded *trimethyl-Δ^{α}-propenylammonium picrate* (II, X = picrate), separating from this solvent in thick needles, m. p. 170—172°. Yield, 30% (Found : C, 43·7; H, 5·0; N, 17·2. $C_6H_{13}N,C_6H_3O_7N_3$ requires C, 43·9; H, 4·9; N, 17·1%). Evaporation of the filtrate yielded a small quantity, varying in amount, of trimethylallylammonium picrate. The Δ^{α}-isomeride showed no tendency to be converted into the allyl compound, and the chloride was recovered unchanged after standing for 12 hours at 30° in admixture with 0·1N-sodium *iso*propoxide; higher temperatures and more concentrated solutions caused decomposition.

Fission of trimethyl-Δ^{α}-propenylammonium chloride with ozone. The pure picrate was converted into the chloride, which was dissolved in glacial acetic acid and treated with ozonised oxygen. The product was refluxed with twice its volume of water, and the vapours passed into a hydrochloric acid solution of 2 : 4-dinitrophenylhydrazine; the hydrazone of acetaldehyde thus obtained was identified in the usual way (Found : C, 43·0; H, 3·8. Calc. : C, 42·9; H, 3·6%). The aqueous filtrate on evaporation and treatment with sodium picrate afforded a very small quantity of a *picrate* crystallising from ethyl alcohol in needles, m. p. 189° (Found : C, 35·7; H, 4·1%).

Section II. Attempted Preparation of αα-Bis(ethylsulphonyl)-Δ^{β}-propene (III).—(i) *From acraldehyde.* Powdered zinc chloride (55 g.) was slowly added to a stirred and cooled mixture of ethylthiol (25 g.), acraldehyde (22 g.), and carbon tetrachloride (200 c.c.). When the vigorous reaction had subsided, a further portion of ethylthiol (25 g.) was added, and the liquid kept overnight; it was then washed with water and dried with fused calcium chloride. Distillation yielded three fractions : (a) β-*Ethylthiopropaldehyde* (3·5 g.), b. p. 60°/10 mm. (Found : C, 51·3; H, 8·4. $C_5H_{10}OS$ requires C, 50·8; H, 8·5%). Oxidation with perhydrol in acetic acid furnished β-ethylsulphonylpropionic acid, m. p. 115—118° after crystallisation from ethyl acetate (Found : C, 36·6; H, 5·9; S, 19·3. Calc. : C, 36·1; H, 6·0; S, 19·3%). (b) Impure ααγ-Tris(ethylthio)propane (14·5 g.), b. p. 100°/0·3 mm. (cf. this vol., p. 1557) (Found : C, 49·0; H, 8·8; S, 36·7. Calc. : C, 48·2; H, 8·9; S, 42·9%). It was obtained in a purer form by the use of glacial acetic acid as a solvent for the reaction instead of carbon tetrachloride (Found : C, 49·0; H, 9·3; S, 42·3%). In both cases ααγ-tris(ethylsulphonyl)propane was obtained on oxidation (Found : C, 33·8; H, 5·9; S, 30·4. Calc. : C, 33·8; H, 6·3; S, 30·0%). (c) An unidentified fraction (9·5 g.), b. p. 160—170° (decomp.)/0·5 mm.

(ii) *From γ-chloro-αα-bis(ethylthio)propane.* The sulphide was oxidised with perhydrol, affording an 88% yield of *γ-chloro-αα-bis(ethylsulphonyl)propane* (V), crystallising from ethyl acetate in prisms, m. p. 96—97° (Found : C, 32·2; H, 5·4; Cl, 13·5. $C_7H_{15}O_4ClS_2$ requires C, 32·0; H, 5·7; Cl, 13·5%).

γ-Ethoxy-αα-bis(ethylsulphonyl)propane, similarly obtained from the corresponding sulphide, separated from ether in needles, m. p. 35—37° (Found : C, 39·6; H, 7·2; OEt, 16·0. $C_9H_{20}O_5S_2$ requires C, 39·7; H, 7·4; OEt, 16·5%). Treatment with hydriodic acid (*d* 1·7) resulted in

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* Boiling the solution for 20 minutes resulted in the formation of what appeared to be a *NNNN'N'N'*-hexamethylpropylenediammonium salt, affording a *picrate* which crystallised from methyl alcohol in long needles, m. p. 315—316° (Found : C, 40·5; H, 4·5; N, 18·1. $C_9H_{22}N_2,2C_6H_3O_7N_3$ requires C, 40·9; H, 4·5; N, 18·2%). It was much less soluble in alcohol than the propenylammonium picrates.

the formation of *γ-iodo-αα-bis(ethylsulphonyl)propane*, crystallising from ethyl acetate in yellowish needles, m. p. 95° (Found : C, 23·9; H, 4·3; I, 34·8. $C_7H_{15}O_4IS_2$ requires C, 23·7; H, 4·2; I, 35·9%). All the samples of this substance had a low halogen content.

Action of alkali on γ-chloro- or γ-iodo-αα-bis(ethylsulphonyl)propane. When the halogen compounds were boiled with pyridine, aqueous sodium carbonate or acetate, the sole product was 1 : 1-*bis(ethylsulphonyl)*cyclo*propane* (VII), which crystallised from ether, alcohol or ethyl acetate in fine needles, m. p. 131—132° (Found : C, 37·3; H, 6·5; S, 28·3; *M*, 228. $C_7H_{14}O_4S_2$ requires C, 37·2; H, 6·2; S, 28·3%; *M*, 226). The sulphone did not decolourise dilute permanganate solution, was unaffected by ozone, and yielded no condensation products with aldehydes. It could not be alkylated by any of the usual methods; in fact this substance was formed by the action of methyl iodide and sodium methoxide on the chloro-bis(ethylsulphonyl)propane. Therefore no α-hydrogen atom was present. Boiling hydriodic acid converted it into the γ-iodo-derivative.

(iii) *From βγ-dibromo-αα-bis(ethylthio)propane.* Freshly distilled dibromopropaldehyde (70 g.) was mixed with ethylthiol (52 c.c.) in carbon tetrachloride (50 c.c.) and cooled in ice. Anhydrous zinc chloride (55 g.) was slowly added to the stirred solution and when the reaction was complete, water was added, and the separated carbon tetrachloride solution dried, dissolved in acetic acid (600 c.c.), and warmed with perhydrol (130 c.c.). Only a small quantity of crystalline solid resulted, which was probably *γ-bromo-αα-bis(ethylsulphonyl)-Δ^{β}-propene*, although it contained a deficiency of bromine. It separated from ethyl acetate and petrol (b. p. 60—80°) in needles, m. p. 102° (Found : C, 26·9; H, 4·3; Br, 24·8; S, 20·4. $C_7H_{13}O_4BrS_2$ requires C, 27·5; H, 4·3; Br, 26·2; S, 21·0%). The halogen atom is very unreactive, indicating its proximity to the double bond, and this with the known lability of halogen in the β-position to the bis-ethylthio-groups suggests the above structure.

(iv) *From αα-bis(ethylthio)-Δ^{β}-propene.* Oxidation of the sulphide with perhydrol yielded αγ-bis(ethylsulphonyl)propene in 72% yield (Found : C, 37·4; H, 5·9. Calc. : C, 37·2; H, 6·2%). Its structure was determined by comparison with the specimen previously prepared (J., 1937, 318) and by fission with ozone, which led to the formation of methylethylsulphone by methods described in Part IV (*loc. cit.*). Condensation with benzaldehyde resulted in βδ-bis(ethylsulphonyl)-α-phenylbutadiene (Found : C, 53·6; H, 5·9. Calc. : C, 53·5; H, 5·7%).

(v) *From glyceraldehyde diethylacetal.* In this and the next experiments it was hoped to prepare βγ-disubstituted αα-bis(ethylsulphonyl)propane which could be converted into the βγ-dibromide and thence by the action of zinc dust into the required unsaturated sulphone. The intermediate compounds, however, were unstable.

βγ-Dihydroxy-αα-bis(ethylthio)propane was prepared in 51% yield from glyceraldehyde acetal (20 g.) dissolved in water (40 c.c.), ethylthiol (20 c.c.), and concentrated hydrochloric acid. After 3 hours' stirring, excess of potassium carbonate was added, and the sulphide extracted with ether. B. p. 106°/0·1 mm. (Found : C, 42·9; H, 8·6; S, 32·6. Calc. : C, 42·9; H, 8·2; S, 32·6%) (Arnold and Evans, *J. Amer. Chem. Soc.*, 1936, **58**, 1950, give b. p. 156—158°/3 mm.). Oxidation led to fission with the production of bis(ethylsulphonyl)methane in 48% yield :

$$CH_2(OH)\cdot CH(OH)\cdot CH(SO_2Et)_2 \longrightarrow CH_2(OH)\cdot CHO + CH_2(SO_2Et)_2$$

(vi) *From αβ-dimethoxypropaldehyde diethylacetal.* This *acetal* was obtained impure from glyceraldehyde diethylacetal (1 mol.), methyl iodide (4 mols.), and dry silver oxide (4 mols.). B. p. 83—85°/10 mm. Yield, 44% (Found : C, 54·9; H, 10·4. $C_9H_{20}O_4$ requires C, 56·2; H, 10·4%). Treatment of a mixture of the acetal (13 g.) and ethylthiol (10 c.c.) in 90% acetic acid (20 c.c.) with hydrochloric acid (30 c.c.) furnished *βγ-dimethoxy-αα-bis(ethylthio)propane*, b. p. 129—130°/8 mm., in 66% yield (Found : C, 48·1; H, 9·1. $C_9H_{20}O_2S_2$ requires C, 48·2; H, 9·0%). Oxidation resulted in the formation of *γ-hydroxy-β-methoxy-αα-bis(ethylsulphonyl)-propane*, separating from ether in needles, m. p. 108° (Found : C, 35·2; H, 6·6. $C_8H_{20}O_6S_2$ requires C, 35·9; H, 6·6%). Since the substance does not dissociate, it follows that the hydroxyl group cannot be in the β-position. About 3·3 g. of the sulphone were obtained from 10 g. of the sulphide, and of this two-thirds was obtained as a crystalline solid. Treatment of the sulphone (liquid or solid portion) with hydriodic acid afforded αα-bis(ethylsulphonyl)-Δ^{α}-propene as the sole product :

$$CH_2(OH)\cdot CH(OMe)\cdot CH(SO_2Et)_2 \longrightarrow CH_3\cdot CHI\cdot CH(SO_2Et)_2 \longrightarrow CH_3\cdot CH{:}C(SO_2Et)_2.$$

(vii) *By distillation of trimethyl-γγ-bis(ethylsulphonyl)propylammonium hydroxide.* β-Chloropropaldehyde acetal was heated overnight at 100° in a sealed tube with 33% alcoholic trimethylamine (72 c.c.). Approximately 25 g. of ammonium salt were obtained, and 20 g. of the acetal recovered. The ammonium salt was mixed with an equal weight of water and ethylthiol and stirred overnight after addition of concentrated hydrochloric acid (30 c.c.); excess of silver oxide was then added, and the filtered solution evaporated to dryness. The residue furnished a somewhat impure specimen of *trimethyl-γγ-bis(ethylthio)propylammonium picrate*, crystallising from water in needles, m. p. 94° (Found: C, 43·7; H, 6·0; S, 14·1. $C_{10}H_{23}NS_2,C_6H_3O_7N_3$ requires C, 42·7; H, 5·8; S, 14·2%). Oxidation of the ammonium hydroxide was accomplished in the usual way, and the solvent distilled under reduced pressure, leaving a residue containing some free sulphuric acid. The latter was removed by neutralisation with barium carbonate, followed by filtration, acidification with hydrochloric acid, and evaporation to dryness. The residue was mixed with moist silver oxide, and the ammonium hydroxide so obtained heated to 170°, decomposition taking place. The product was 1 : 1-bis(ethylsulphonyl)*cyclo*propane.

Section III. Experiments with αα-Bis(ethylsulphonyl)-Δ$^{\alpha}$-propene (IV).—(i) *Action of acids and alkalis.* Dilute mineral acids, concentrated sulphuric acid, and glacial acetic acid had no action on the bis-sulphone. Prolonged shaking of the substance with cold water or sodium acetate, boiling water, sodium carbonate or pyridine decomposed it with formation of bis(ethylsulphonyl)methane:

$$CH_3\cdot CH{:}C(SO_2Et)_2 \longrightarrow CH_3\cdot CH(OH)\cdot CH(SO_2Et)_2 \longrightarrow CH_3\cdot CHO + CH_2(SO_2Et)_2.$$

The acetaldehyde was identified in the usual way.

(ii) *Fission by ozone.* As acetaldehyde was one of the expected products, "AnalaR" chloroform was washed free from alcohol with water, dried with calcium chloride, and distilled. A blank ozonolysis with this did not yield any acetaldehyde. Also duplicate experiments with those described below showed that there was no unchanged bis-sulphone under the conditions used.

(*a*) The sulphone in chloroform solution was treated with ozonised oxygen for 12 hours, and the solvent removed in a vacuum at room temperature. The residue was boiled with water, but no aldehyde was obtained, the solution containing some free sulphuric acid, which was removed by use of barium carbonate. Evaporation of the filtered solution left a barium salt, which was refluxed for 20 hours with a slight excess of *p*-nitrobenzyl chloride in 95% alcohol, thus affording ethyl-*p*-nitrobenzylsulphone, crystallising in needles, m. p. 139—140° (Found: C, 47·4; H, 5·0; S, 14·1. Calc.: C, 47·2; H, 4·8; S, 14·0%). Zahn and Koch (*Chem. Zentr.*, 1936, **1**, 3023) record m. p. 133—134°.

(*b*) Fission with ozone was carried out as before but for a shorter time, and after distillation of the chloroform the residue was boiled with dilute sulphuric acid. Acetaldehyde was obtained. Even if unchanged sulphone were present, it would not afford acetaldehyde in sulphuric acid solution (experiment i above).

(iii) *Reduction.* The bis-sulphone (0·3 g.) was dissolved in glacial acetic acid (20 c.c.) and shaken with Adams's catalyst in an atmosphere of hydrogen until no further absorption took place (2½ days). The resulting αα-bis(ethylsulphonyl)propane was identified by comparison (m. p. and mixed m. p.) with a specimen synthesised from propaldehyde and ethylthiol, and by analysis (Found: C, 37·0; H, 7·0; S, 28·1. Calc.: C, 36·8; H, 7·0; S, 28·1%).

(iv) *Addition of bromine.* The bis-sulphone was heated in a sealed tube at 100° for 2 hours with an excess of bromine, the latter being removed by evaporation at room temperature. A *dibromide* was obtained (Found: Br, 41·4. $C_7H_{14}O_4Br_2S_2$ requires Br, 44·3%), but recrystallisation caused loss of bromine with the eventual production of the starting material; this was also the result of boiling the bromide with sodium acetate in glacial acetic acid.

(v) *Action of alkoxides.* (a) The bis-sulphone (1 g.) was refluxed for 2 hours with N-sodium methoxide (14 c.c.). Apart from some non-crystalline material, a small quantity of a *sulphone*, which was crystallised from ethyl acetate (Found: C, 42·7; H, 6·2; S, 25·7. $C_9H_{18}O_4S_2$ requires C, 42·9; H, 6·3; S, 25·4%), was obtained. Some bis(ethylsulphonyl)methane was also isolated from the syrupy material. A crystalline sulphone could not be obtained when sodium *iso*propoxide was used; potassium *tert.*-butoxide afforded bis(ethylsulphonyl)methane only.

(b) The sulphone was treated with sodium methoxide as before, but excess of methyl iodide was also added. The product was a mixture containing some bis(ethylsulphonyl)methane and a dimeric methylated *sulphone*, which crystallised from ethyl acetate in prisms, m. p. 162°. Yield, approx. 30% (Found: C, 38·7; H, 6·4; S, 27·5; *M*, 380. $C_{16}H_{30}O_8S_4$ requires C, 38·6; H, 6·4; S, 27·4%; *M*, 466).

Fission with ozone. The sulphone, m. p. 162°, was treated with ozonised oxygen in chloroform solution, and the solvent removed at room temperature in a vacuum. No aldehyde was evolved when the residue was boiled with water, and evaporation of the aqueous solution furnished a *bis(ethylsulphonyl)propionic acid,* $CH_3 \cdot C(SO_2Et)_2 \cdot CO_2H$ or $CH(SO_2Et)_2 \cdot CH_2 \cdot CO_2H$, m. p. 131° (Found : C, 32·8; H, 6·0; S, 24·3. $C_7H_{14}O_6S_2$ requires C, 32·6; H, 5·4; S, 24·8%).

(vi) *Addition of methylmagnesium iodide.* The sulphone (5 g.) in ethereal suspension was mixed with a cold solution of methylmagnesium iodide (from 1 g. of magnesium) in ether. Reaction took place and a gas appeared to be evolved. Acidification yielded a sulphone, which separated from ethyl acetate and petrol (b. p. 40—60°) in needles, m. p. 97—98° (Found : C, 39·5; H, 7·2; S, 27·1. Calc. for $C_8H_{18}O_4S_2$: C, 39·7; H, 7·4; S, 26·4%). The sulphone was probably bis(ethylsulphonyl)*iso*propylmethane, $CH(CH_3)_2 \cdot CH(SO_2Et)_2$, described by Fromm (*Annalen*, 1889, **253**, 152) as having m. p. 94°.

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