291. *Experiments with Thioacetals and Related Substances. Part I. The Polar Effect of Sulphur in Thioacetals.*

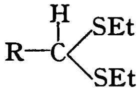
By Eugene Rothstein.

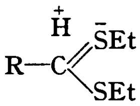
It was suggested (J., 1937, 309) that part of the polar character of sulphones is due to the expansion of the valency shell of the sulphur atom. In seeking further experimental evidence of this the examination of certain thioacetals was undertaken, since in these substances, unlike sulphonyl derivatives, there are no dipoles which can mask any effects due to this expansion. It is found that when *γ-chloro-αα-bis(ethylthio)propane* is treated with potassium *tert.*-butoxide, *αα-bis(ethylthio)-Δ^{α}-propene* is formed by a pinacolic electron displacement mechanism. This reaction is enabled to proceed because of the resonance contribution to the transition state of valency structures which can be set up only if the above expansion of the sulphur octet is taken into consideration.

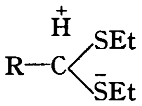
It was postulated in a previous communication (J., 1937, 309) that the relatively great mobility of αγ-bis(ethylsulphonyl)propenes as compared to the corresponding αγ-bis-quaternary ammonium salts was largely due to resonance between the various canonical structures obtained by expansion of the sulphur octet. The probability of such an expansion had previously been recognised and the interatomic distances in the sulphate ion also support this view (cf. Pauling, "Nature of the Chemical Bond," pp. 222 *et seq.*). Furthermore it was noticed that α-benzylsulphonyl-γ-ethylthio-Δ^{α}-propene,

$CH_2Ph{\cdot}SO_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}SEt$,

appeared to be tautomeric with its Δ^{β}-isomeride. Although the evidence as regards this instance was not conclusive, it encouraged the supposition that in favourable cases it might be possible to detect a polar effect in sulphides and in these examples it would not be complicated by the masking effect of the dipoles between the oxygen and the sulphur atoms. A suitable class of substance appeared to be the thioacetals, where there was the possibility of resonance between the following structures :



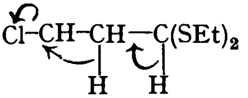


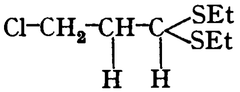


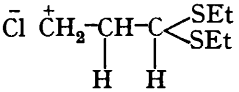
and where therefore reactions depending on the consequent potential ionisation of the hydrogen atom might be observed.

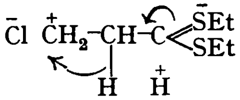
The substances chosen for investigation were the αα-bis(ethylthio)propenes and it was in the course of their preparation that evidence illustrating the foregoing hypothesis was obtained. When *γ-chloro-αα-bis(ethylthio)propane*, $CH_2Cl{\cdot}CH_2{\cdot}CH(SEt)_2$ (I), was boiled with alcoholic potash, a mixture of *γ-ethoxy-αα-bis(ethylthio)propane*, $CH_2(OEt){\cdot}CH_2{\cdot}CH(SEt)_2$, and *αα-bis(ethylthio)-Δ^{α}-propene*, $CH_3{\cdot}CH{:}C(SEt)_2$ (II), was obtained. In order to avoid the formation of large quantities of ethoxy-derivatives, potassium *tert.*-butoxide was used in subsequent experiments (cf. Beyerstadt and McElvain, *J. Amer. Chem. Soc.*, 1936, 58, 5301), whereby the unsaturated thioacetal (II) was formed in 77% yield with little or no substitution product.

For reasons discussed later in this paper it is evident that the process by which the Δ^{α}-propene is formed is that termed by Ingold and Shoppee (J., 1928, 361) "pinacolic electron displacement" and symbolised by (*A*) in the present instance. The possible valency structures taking part in the normal state of the molecule of the chloro-acetal


(*A*)


(i.)


(ii.)


(iii.)

(I) are (i), (ii), and (iii), but in the absence of reagents, the contributions of (ii) and (iii) must be considered small, since the substance shows no tendency to lose hydrogen chloride. This, however, is not the case in the transition complex formed when alkoxide ions are present, and the reaction proceeds to completion with formation of the Δ^{α}-compound. The formation of this isomeride is dependent on the possibility of setting up the valency structure (iii); in its absence (*e.g.*, when the sulphur atom is replaced by oxygen) only the Δ^{β}-isomeride should be formed (cf. Part III; this vol., p. 1558).

The possible alternative mechanism for the formation of the Δ^{α}-thioacetal, namely, that the removal of the hydrogen chloride from the γ-chloro-compound first yielded the Δ^{β}-isomeride, from which the former was obtained by a prototropic change, is shown to be untenable because both these substances are stable in boiling potassium *tert.*-butoxide and no interconversion takes place.

The synthesis of *αα-bis(ethylthio)-Δ^{β}-propene*, $CH_2{:}CH{\cdot}CH(SEt)_2$ (III), was accomplished by the treatment of *βγ-dibromo-αα-bis(ethylthio)propane*, $CH_2Br{\cdot}CHBr{\cdot}CH(SEt)_2$, with zinc dust. A second method was to condense αα-dichloro-Δ^{β}-propene, $CH_2{:}CH{\cdot}CHCl_2$, with sodium ethylthiol; accompanying the required product was a large proportion of *γ-chloro-α-ethylthio-Δ^{β}-propene*, $CHCl{:}CH{\cdot}CH_2{\cdot}SEt$. This substance, the formation of which is paralleled by the condensations of the dichloropropene with sodium ethoxide, sodium acetate or diethylamine (Kirrman, Pacaud, and Dosque, *Bull. Soc. chim.*, **1934**, **1**, 860), does not undergo further reaction with sodium ethylthiol.

The structure of (III) was determined by boiling with aqueous mercuric chloride, which converted it into acraldehyde, and by fission with ozone, yielding glyoxal:

$$CH_2{:}CH{\cdot}CH(SEt)_2 \longrightarrow CHO{\cdot}CH(SEt)_2 \xrightarrow{O} CHO{\cdot}CHO + Et_2S_2$$

Similarly aqueous mercuric chloride decomposed the Δ^{α}-isomeride (II) with the production of propionic acid:

$$CH_3{\cdot}CH{:}C(SEt)_2 \longrightarrow CH_3{\cdot}CH{:}CO \xrightarrow{H_2O} CH_3{\cdot}CH_2{\cdot}CO_2H$$

EXPERIMENTAL.

Impure *γ-chloro-αα-bis(ethylthio)propane* (I) was obtained in nearly theoretical yield when γ-chloropropaldehyde diethylacetal (60 g.) (*Organic Syntheses*, XI, 26), ethylthiol (59 c.c.), and 66% acetic acid (150 c.c.) were treated with concentrated hydrochloric acid (150 c.c.). The bis-sulphide, b. p. 115—117°/11 mm., was probably contaminated with some γ-ethoxy-compound, which has nearly the same b. p. (below), arising from γ-ethoxypropaldehyde acetal in the starting material (Found: C, 43·4; H, 7·6; Cl, 15·0. $C_7H_{15}ClS_2$ requires C, 42·3; H 7·6; Cl, 17·9%).

Reaction with alcoholic potash. The chloro-sulphide (26·6 g.) was refluxed for 20 hours with a solution of potassium hydroxide (30 g.) in 90% alcohol (80 c.c.), diluted with water, and extracted with ether. Distillation of the residue remaining after removal of the solvent led to two main fractions: (a) *αα-Bis(ethylthio)-Δ^{α}-propene* (II), b. p. 83°/9 mm.; yield, 24% (Found: C, 52·0; H, 9·1. $C_7H_{14}S_2$ requires C, 51·9; H, 8·7%). Oxidation of the sulphide with perhydrol in glacial acetic acid furnished *αα-bis(ethylsulphonyl)-Δ^{α}-propene* (cf. Part II) (Found: C, 37·4; H, 6·2. $C_7H_{14}O_4S_2$ requires C, 37·2; H, 6·2%). (b) *γ-Ethoxy-αα-bis(ethylthio)propane*, b. p. 115°/9 mm., 65—67°/0·2 mm.; yield, 52% (Found: C, 52·3; H, 9·6; S, 30·8. $C\ H_{20}OS_2$ requires C, 51·9; H, 9·6; S, 30·8%). When this was oxidised with perhydrol, *γ-ethoxy-αα-bis(ethylsulphonyl)propane*, $CH_2(OEt){\cdot}CH_2{\cdot}CH(SO_2Et)_2$, was obtained; it 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, 39·6; H, 7·4; OEt, 16·5%).

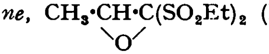
Reaction with potassium tert.*-butoxide.* γ-Chloro-αα-bis(ethylthio)propane (40 g.) was refluxed for 16 hours with a solution of potassium (20 g.) in *tert.*-butyl alcohol (300 c.c.). The main product (77% yield) was αα-bis(ethylthio)-Δ^{α}-propane. The remainder was unchanged chloro-sulphide with a small amount of *γ-hydroxy-αα-bis(ethylthio)propane*, which on oxidation yielded the corresponding *γ-hydroxy-αα-bis(ethylsulphonyl)propane*, $HO\cdot CH_2\cdot CH_2\cdot CH(SO_2Et)_2$, separating from ethyl acetate in needles, m. p. 105—107° (Found: C, 34·1; H, 6·6. $C_7H_{16}O_5S_2$ requires C, 34·4; H, 6·6%). The hydroxy-sulphide was also obtained (yield, 68%) in an impure form from γ-hydroxypropaldehyde diethylacetal (8 g.), ethylthiol (12 g.), 90% acetic acid (20 c.c.), and hydrochloric acid (20 c.c.) (Found: C, 48·7; H, 8·7. $C_7H_{16}OS_2$ requires C, 46·7; H, 8·9%). The product (b. p. 143—145°/10 mm.) on oxidation furnished the pure hydroxy-sulphone.

Formation of Propionic Acid from αα-Bis(ethylthio)-Δ^{α}-propene.—The bis-sulphide (3·5 g.) was refluxed with mercuric chloride (22 g.) and water (100 c.c.) for 1 hour. The precipitated ethylthiomercuric chloride (yield, theoretical) was filtered off, the excess of mercuric chloride destroyed with hydrogen sulphide, the filtered liquid continuously extracted with ether for several days, the ethereal layer dried with anhydrous sodium sulphate, and the ether removed. The acid residue was found by titration to correspond to a 53% yield of propionic acid, identified as its *p*-bromophenacyl ester (Found: C, 48·7; H, 4·0; Br, 29·2. Calc.: C, 48·7; H, 4·1; Br, 29·5%), the yield of which was approximately quantitative.

There were also small quantities of unidentified aldehydes present in the mother-liquor after removal of the excess of mercuric chloride. Also, if methyl alcohol were used instead of water as a solvent, an aldehyde yielding a 2 : 4-*dinitrophenylhydrazone* crystallising from petrol (b. p. 80—100°) in needles, m. p. 149° (Found: C, 47·1; H, 4·7; N, 22·4. $C_{10}H_{12}O_4N_4$ requires C, 47·6; H, 4·8; N, 22·2%), was obtained. Its nature was not determined.

Other Reactions of αα-Bis(ethylthio)-Δ^{α}-propene.—(i) Bromine gave a tarry material with evolution of hydrogen bromide. Substitution next to a double bond probably takes place, since the halogen could not be removed by refluxing in xylene solution with anhydrous potassium carbonate (cf. Part II, following paper).

(ii) *Ethylthiol.* A benzene solution of the sulphide (3 g. in 2 c.c.) was mixed with ethylthiol (2 c.c.), kept for several days, warmed on the steam-bath, and fractionated. About 80% of unchanged bis-sulphide was recovered; the remainder, b. p. 130—135°/9 mm., was probably ααβ-tris(ethylthio)propane (Found: C, 48·6; H, 8·9; S, 42·9. Calc.: C, 48·2; H, 8·9; S, 42·9%), which on oxidation yielded a sulphone, m. p. 114° after crystallisation from ethyl acetate. A fuller description of these substance is given in Part II.

(iii) *Perbenzoic acid.* The sulphide (4·5 g.) was added to perbenzoic acid (22 g.) in chloroform (280 c.c.) solution. Heat was evolved and the liquid boiled. After 15 hours it was shaken with sodium bicarbonate solution and dried with fused calcium chloride. The yellow solid obtained when the solvent was distilled was boiled in ethyl acetate with norit and recrystallised twice from the same solvent. The substance, m. p. 75—77°, appeared to be *αβ-epoxy-αα-bis(ethylsulphonyl)propane*,  $CH_3\cdot\underset{\diagdown O \diagup}{CH\cdot C}(SO_2Et)_2$ (Found: C, 35·3; H, 6·0; S, 27·0; *M*, in benzene, 254, 231. $C_7H_{14}O_6S_2$ requires C, 34·7; H, 5·8; S, 26·4%; *M*, 242). Treatment with boiling hydrochloric acid afforded a *sulphone* crystallising from ethyl acetate in needles, m. p. 109—110° (Found: C, 34·0; H, 6·4; S, 29·7. $C_6H_{14}O_4S_2$ requires C, 33·5; H, 6·4; S, 29·4%). There was insufficient for a molecular weight determination.

(iv) *Methyl alcohol and sodium methoxide.* Neither of these reagents affected the bis-sulphide either in the cold or in boiling solution.

Preparation of αα-Bis(ethylthio)-Δ^{β}-propene (III).—(i) *From αβ-dibromopropaldehyde.* Freshly distilled dibromopropaldehyde (40 g.), dissolved in benzene (50 c.c.), was mixed with ethylthiol (30 g.) and cooled in ice. Dry hydrogen chloride was passed for 1 hour through the stirred solution, which was then washed with water and dried with fused calcium chloride. The solution when first prepared was colourless, but hydrogen bromide was slowly evolved and after 12 hours' standing the colour had changed to dark brown and no recognisable product could then be isolated. Subsequent treatment was therefore carried out without delay. The liquid was diluted with methyl alcohol (200 c.c.), and pure zinc dust (50 g.) slowly added with stirring. Solution was rapid at first with some evolution of heat; the slow reaction that followed was completed by boiling the mixture under reflux for 2 hours. The filtered liquid was freed from methyl alcohol by distillation, and the residue dissolved in ether, washed with dilute acid and water, and dried. Fractionation of the residue after distillation of the ether afforded a 65% yield of *αα-bis(ethylthio)-Δ^{β}-propene*, b. p. 73°/0·5 mm. (Found: C, 52·4; H, 8·9; S, 39·0. $C_7H_{14}S_2$ requires C, 51·9; H, 8·6; S, 39·5%).

(ii) *From αα-dichloro-Δ^{β}-propene.* The dichloropropene (54 g.) was added with stirring to a solution of sodium ethylthiol (from 62 g. of ethylthiol and 23 g. of sodium) in 90% alcohol (300 c.c.) cooled in ice. After 12 hours water was added, and the sulphide isolated in the usual way. Distillation furnished two main fractions. The first (yield, 28 g.) was *γ-chloro-α-ethylthio-Δ^{β}-propene,* b. p. 60—61°/12 mm. (Found: C, 43·7; H, 6·5; Cl, 25·7. C_5H_9ClS requires C, 43·9; H, 6·6; Cl, 26·0%). This substance is stable to alkalis and in particular did not react when boiled with a further molecule of sodium ethylthiol. The second fraction was the Δ^{β}-propene described above.

Reactions. All these were carried out in duplicate, a sample prepared by each method being used.

(i) *Fission by ozone.* The bis-sulphide, dissolved in dry chloroform, was treated for 12 hours with ozonised oxygen; after removal of the solvent in a vacuum, the residue was boiled with water to which a little zinc dust had been added. No formaldehyde could be detected, but the aqueous solution yielded glyoxal 2 : 4-dinitrophenylosazone, which separated from anisole as a powder, m. p. 293° (decomp.) (Found: C, 40·9; H, 2·7. Calc.: C, 40·2; H, 2·4%). The decomposition point of the osazone appears to vary with the solvent used for recrystallisation, since this was 275° when the latter was glacial acetic acid (Found: C, 40·2; H, 2·8%), whereas Glasstone and Hickling (J., 1936, 820), using nitrobenzene, found it to be 330°.

(ii) *Mercuric chloride.* A boiling solution of mercuric chloride (17 g.) in water (35 c.c.), gradually treated with the bis-sulphide, gave a large amount of acraldehyde, identified as its 2 : 4-dinitrophenylhydrazone (Found: C, 46·0; H, 3·5; N, 24·1. Calc.: C, 45·7; H, 3·4; N, 23·7%).

(iii) *Potassium* tert.*-butoxide.* The sulphide (2·6 g.) was mixed with a solution of potassium (3 g.) in boiling *tert.*-butyl alcohol (50 g.) and refluxed for 6 hours. Most of the material was recovered unchanged, though there was also a small amount of high-boiling fraction which was not identified. The amount of the latter substance varied in different experiments, but in no case was any of the Δ^{α}-isomeride isolated.

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THE UNIVERSITY, LEEDS.

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