293. *Experiments with Thioacetals and Related Substances. Part III. Comparison of the Polar Effect of Sulphur with that of Oxygen and Nitrogen.*

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The reactions of the thioacetals noticed in Parts I and II (preceding papers) are dependent on the possibility of the setting up of valency structures which are consequent on the expansion of the valency shell of the sulphur atom. Since this is not possible in the cases of nitrogen and oxygen, neither the formation of a Δ^{α}-unsaturated compound from a γ-chloro-derivative, nor the easy elimination of the β-halogen atom, should be observed in cases analogous to the thioacetals. The recorded experiment (Lucius, *Arch. Pharm.*, 1907, **245**, 249) that trimethyl-γ-chloropropylammonium chloride affords trimethylallylammonium salts is confirmed, and it has also been found that β-chloropropaldehyde diethylacetal yields acraldehyde acetal and not methylketen acetal, $CH{\cdot}Me{:}C(OEt)_2$, when boiled with potassium *tert.*-butoxide. Methylketen acetal is found to be stable to this reagent and is therefore not an intermediate in the formation of acraldehyde acetal.

THE mechanism suggested in Part I for the formation of a Δ^{α}-unsaturated thioacetal from the γ-chloropropaldehyde derivative is dependent on the possibility of setting up the valency structure $\overset{-}{Cl}\ \overset{+}{CH_2}—\underset{\underset{H}{|}}{CH}—C\overset{\overset{-}{SEt}}{<_{\underset{+}{H}}^{SEt}}$ and such structures are not possible with acetals owing to the small tendency of oxygen to expand its outer electron shell. Furthermore, the extremely facile release of the halogen atom from β-bromothioacetals was likewise considered to arise from resonance between similar canonical structures (Part II), and the difference between these sulphur and the corresponding oxygen compounds is very apparent when the instability of the β-halogen atom in the former is contrasted with its relative inertness in the latter substances. It has already been shown (Part II) that

this cannot be due to a $+M$ effect, but two other points remain. The first, that this mesomeric effect may in some way be responsible for the formation of αα-bis(ethylthio)-Δ^{α}-propene from γ-chloro-αα-bis(ethylthio)propane, is negatived by the observation of Knorr and Roth (*Ber.*, 1906, **39**, 1424) that dimethyl-γ-chloropropylamine furnishes the γ-ethoxy-derivative when heated with sodium ethoxide at 150° and it might have been expected that the influence of the lone electrons on the sulphur atom would be exerted by the corresponding electrons on the tertiary nitrogen also. The other possibility is that any group with a $-I$ effect might enable this reaction to take place owing to the potential loosening of the α-hydrogen atom. Such a group is present in quaternary ammonium salts, but it has already been noticed by Lucius (*Arch. Pharm.*, 1907, **245**, 249) that trimethylallylammonium salts are formed by the action of alkali alkoxide on trimethyl-γ-chloropropylammonium chloride. His experiments were not, however, conclusive because the allylammonium compound was identified solely by its platinichloride and it was not, therefore, impossible that trimethyl-Δ^{α}-propenylammonium salts, $CH_3{\cdot}CH{:}CH{\cdot}NMe_3X$, were present in the products. For this reason the γ-chloro-compound has been prepared by an unambiguous method, namely, from the γ-hydroxy-derivative, and treated with alcoholic potash. The product was converted into the picrate, m. p. 214—216°, which was therefore trimethylallylammonium picrate. Had any of the Δ^{α}-picrate * been present, it would have been identified easily, since it has m. p. 171—172° and there is no difficulty in separating the two.

A direct comparison between the effects of the oxygen and the sulphur atom was made by boiling γ-chloropropaldehyde diethylacetal with potassium *tert.*-butoxide. The chief product was acraldehyde diethylacetal, $CH_2{:}CH{\cdot}CH(OEt)_2$, and no methylketen diethylacetal, $CH_3{\cdot}CH{:}C(OEt)_2$, could be detected. The possibility that the methylketen acetal might have been destroyed in the course of the reaction, or that it might have been converted into acraldehyde diethylacetal by a prototropic change is not tenable. Methylketen diethylacetal has been prepared by Walter and McElvain (*J. Amer. Chem. Soc.*, 1940, **62**, 1482) by the action of metallic sodium on ethyl α-bromo-orthopropionate and they reported that there appeared to be no tendency for it to change into the isomeric allyl derivative. This has been confirmed by boiling methylketen diethylacetal with potassium *tert.*-butoxide, at least 60% of the substance being recovered unchanged. This is a conservative estimate, since repeated fractionation of the product would be necessary to ensure that none of the acetal was present in the butyl alcohol fraction. This experiment also demonstrates that there would have been no difficulty in detecting any methylketen acetal, had it been formed from the γ-chloropropaldehyde acetal.

Experimental.

Trimethyl-γ-hydroxypropylammonium chloride was prepared in 90% yield by heating trimethylene chlorohydrin (20 g.) with 37% alcoholic trimethylamine (45 c.c.) in a sealed tube for 2 hours at 100° and precipitating it with dry ether. The *picrate*, obtained by adding a deficiency of sodium picrate to an aqueous solution of the salt and partially evaporating the solution, separated from ethyl alcohol in needles, m. p. 158—159° (Found: C, 42·3; H, 5·4. $C_6H_{15}ON,C_6H_3O_7N_3$ requires C, 41·6; H, 5·2%).

The corresponding chloro-derivative resulted when the hydroxy-compound (15 g.) was refluxed for ½ hour with thionyl chloride (20 c.c.), and the excess of the latter removed in a vacuum. The compound was boiled in alcoholic solution with norit and reprecipitated with dry ether. Yield, 17 g. The *picrate* crystallised from water in needles, m. p. 132—134° (Found: C, 39·6; H, 5·0. $C_6H_{14}NCl,C_6H_3O_7N_3$ requires C, 39·5; H, 4·7%).

Action of sodium ethoxide. The chloro-ammonium salt (3 g.) was kept overnight in admixture with 2N-sodium ethoxide (35 c.c.). After filtration, acidification with hydrochloric acid, and evaporation to dryness the trimethylallylammonium chloride was extracted from the residue with absolute alcohol and identified by conversion into the *picrate*, which crystallised from water in needles, m. p. 214—215° (Found: C, 44·4; H, 5·0. $C_6H_{13}N_7,C_6H_3O_7N_3$ requires C, 43·9; H, 4·9%).

Action of Potassium tert.*-Butoxide on γ-Chloropropaldehyde Diethylacetal.*—(i) The chloroacetal (55 g.) was slowly added to a solution of potassium (25 g.) in boiling *tert.*-butyl alcohol

* The synthesis of this substance is described in another communication.

(420 g.), and the heating continued for a further 8 hours. After cooling, the solution was saturated with dry carbon dioxide, the precipitated potassium carbonate removed in the centrifuge and washed with ether, and the washings added to the main bulk of liquid, which was then fractionally distilled at 200 mm. through a Dufton column 70 cm. long. Complete separation of the *tert.*-butyl alcohol (b. p. 51°/200 mm.) and acraldehyde diethylacetal (b. p. 85°/200 mm.) was not achieved even after three fractionations; various intermediate fractions were obtained all of which yielded precipitates of acraldehyde-2 : 4-dinitrophenylhydrazone when treated with the appropriate reagent. The total yield of acraldehyde diethylacetal was 21·9 g. (excluding that still contained in the butyl alcohol), which represents more than 50% of that theoretically obtainable. No methylketen diethylacetal was detected, but there was a higher-boiling substance (5·5 g.) which is described in more detail later.

(ii) The chloro-acetal (61 g.) was refluxed for 16 hours with the butoxide (2 mols.), and the product washed with water, dried with potassium carbonate, and distilled at 200 mm. through a 40 cm. Widmer column. There was a large amount of acraldehyde, most of which distilled with the alcohol, together with a residue, b. p. 120—190°/200 mm., of which 84% consisted of acraldehyde acetal and the remainder of two acetals which could not be identified. The first, b. p. 52°/9 mm. (Found: C, 65·5; H, 11·1%), furnished acraldehyde-2 : 4-dinitrophenylhydrazone, and the second, b. p. 69—71°/9 mm. (Found: C, 63·7; H, 11·6; OEt, 20·9%), a 2 : 4-*dinitrophenylhydrazone* which after three crystallisations from alcohol had m. p. 78—79° (Found: C, 45·9; H, 4·6; N, 20·7%).

Action of Potassium tert.-*Butoxide on Methylketen Diethylacetal.*—The acetal (10 g.) was refluxed for 6 hours with 6% potassium *tert.*-butoxide solution (50 g.). Excess of carbon dioxide precipitated the potassium as the carbonate, which was separated from the solution in the centrifuge as in the case of the acraldehyde acetal. Fractionation of the product afforded unchanged methylketen acetal in 60% yield, together with an unidentified higher-boiling fraction (6%). Neither this nor the recovered *tert.*-butyl alcohol yielded a precipitate when treated with a hydrochloric acid solution of 2 : 4-dinitrophenylhydrazine, showing the absence of acraldehyde and its acetal.

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