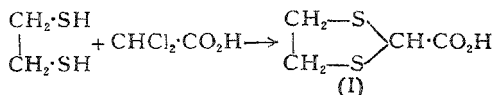


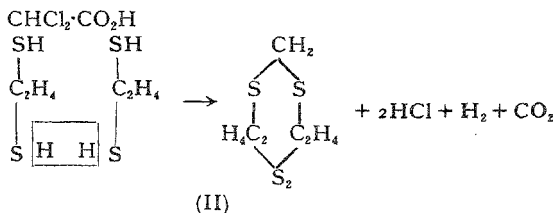
II.—ORGANIC CYCLIC POLYSULPHIDES: CONDENSATION OF ETHYLENE MERCAPTAN WITH DI- AND TRICHLORACETIC ACIDS.¹

By Gopāl Chandra Chakravarti and Jogendra Mohan Saha.

The interesting physical and chemical properties possessed by triethylene tri- and tetrasulphides (Rây, *J. C. S.*, 1920, **117**, 1090; 1922, **121**, 1207) and benzylidene diethylenetri- and tetrasulphides (Rây, *J. C. S.*, 1924, **125**, 1141) led the present authors to undertake a more detailed investigation of a further series of cyclic polysulphides and their derivatives. It was anticipated that the reaction between dichloroacetic acid and dithioethylene glycol would take the following course:—



resulting in the formation of the polysulphide (I). When, however, a mixture of equimolecular quantities of the acid and the mercaptan was either heated on the water-bath or gently boiled on the sand-bath, a compound with the composition, $\text{C}_5\text{H}_{10}\text{S}_6$, was isolated. The reaction can evidently be expressed in the following manner:—

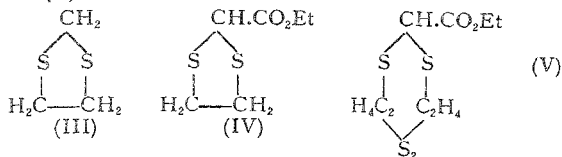


No reaction takes place if benzene is used as the solvent. But when dichloroacetic acid and ethylene mercaptan are heated in xylene solution three isomeric compounds are obtained: one melting at 192–194°, another melting at 83–84° and the third, a liquid, all having the empirical formula $\text{C}_3\text{H}_6\text{S}_2$, which is the cyclic polysulphide (III).

¹ Reprinted from the *Journal of the Indian Chemical Society*, 1928, **5**, 453.

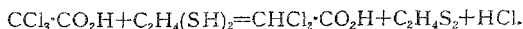
It is extremely probable that the above compounds represent different polymerides of (III).

Ethyl dichloracetate and potassium dithioethylene glycol gave rise to two different oily products which conform to the formulae (IV) and (V).



The compound (V) was formed in small quantities only. Attempts were therefore made to convert compound (IV) successively into compounds (I) and (II) by the usual methods of hydrolysis and heating. But all attempts to obtain the latter failed owing probably to the difficulty in identifying the degradation products. The investigations of Ray (*loc. cit.*) and others (Fromm and Engler, *Ber.*, 1925, 58, 1916, etc.) show that many of the cyclic polysulphides can exist in several polymeric forms. The failure to identify the product of hydrolysis and heating of compound (IV) as any of the compounds (III) must be ascribed to the production of other polymers. Even the simplest compound ethylene disulphide has been obtained in four or five polymeric forms (*vide* Experimental). The expected compound (I) was however obtained by the interaction of potassium dichloracetate and potassium dithioethylene glycol in alcoholic solution.

Trichloroacetic acid reacted with ethylene mercaptan under various conditions. No cyclic polysulphide containing the acid residue was formed in any of these reactions, the trichloroacetic acid molecule only functioning as the oxidising agent by converting the mercaptan into various polymeric disulphides, except in one case only when a crystalline compound, m.p. 95-96° identical with the compound (II) was formed. The formation of this compound goes to show that trichloroacetic acid is first reduced to dichloroacetic acid which then reacts with the mercaptan to give rise to the compound (II) thus:



EXPERIMENTAL.

Interaction of Ethylene Mercaptan and Dichloroacetic Acid.—Six grams of the mercaptan (2 mols.) and 9 grams of the acid (1 mol.) were heated together either on a water-bath or gently boiled on a sand-bath for several hours. Copious evolution of hydrochloric acid, carbon dioxide and sulphuretted hydrogen took place. The dark

violet mass solidified on cooling and was well-washed with dilute caustic alkali and then with water. The alkaline wash water on acidification gave a very scanty green precipitate, insufficient for purification and analysis. The brown residue was extracted three or four times with hot alcohol. The filtrate on concentration gave a crop of brownish needle-shaped crystals of pentamethylene tetrasulphide (II) which were recrystallised from alcohol until they became white, m.p. 96° (Found: S, 65.8; C, 29.83; H, 4.52. $C_5H_{10}S_4$ requires, S, 64.6; C, 30.3; H, 5.1 per cent.). The residue was then successively and separately extracted with acetone, benzene and nitrobenzene. The products obtained by evaporating the solvents were found to be polymers of ethylene disulphide.

Interaction of Ethylene Mercaptan and Dichloroacetic Acid in Xylene Solution.—Four grams of the mercaptan (2 mols.) and 6 grams of the acid (1 mol.) were heated together in 30 c.c. of xylene for about 29 hours. Evolution of hydrogen chloride, carbon dioxide and sulphuretted hydrogen took place. The solution was concentrated on the water-bath to about 10 c.c. and cooled. A granular crystalline precipitate was obtained. This was filtered, washed with cold alcohol and repeatedly crystallised from hot xylene. Fine yellow granular crystals of trimethylene disulphide (III), m.p. $192-194^{\circ}$ soluble in benzene were obtained (Found: C, 34.3; H, 6.4. $C_3H_6S_2$ requires C, 33.96; H, 5.6 per cent.).

The filtrate after the separation of the yellow substance was dissolved in benzene and well washed with dilute caustic alkali and water. It was then filtered, dried with fused calcium chloride, again filtered and then evaporated. An oil mixed with a crystalline substance was obtained. The oil was extracted with a small quantity of ether leaving the white crystalline residue. After filtration the ether was driven off and the oil again extracted with a small quantity of ether. Finally on evaporation the ethereal solution gave a slightly brown, heavy oil with a sweet odour (Found: C, 34.2; H, 4.6; S, 61.38. $C_3H_6S_2$ requires C, 33.96; H, 5.6; S, 60.38 per cent.).

The white crystalline mass mentioned above was repeatedly crystallised from large amounts of ether in which it is very sparingly soluble. White granular crystals, m.p. $83-84^{\circ}$ were obtained (Found: C, 33.51; H, 4.98. $C_3H_6S_2$ requires C, 33.96; H, 5.6 per cent.).

In the above reaction the yield of the yellow product was the largest whilst the other two were formed in small quantities only.

Interaction of Ethyl Dichloroacetate and Monopotassium Ethylene Mercaptan.—The potassium salt (9 gms.), the ester (5.5 gms.) and

50 c.c. of anhydrous alcohol were refluxed together for about 5 hours. The solution was filtered hot from the solid precipitate of potassium chloride, evaporated to dryness and the residue extracted with benzene. The benzene solution was first shaken with dilute caustic alkali and then with water, filtered, dried, again filtered and the benzene removed. The oil thus obtained was repeatedly extracted with cold alcohol or ether. The residual oil was dissolved in benzene, filtered and evaporated to dryness when a brownish thick odourless oil was left. This is ethyl diethylene tetrasulphido-acetate (V) (Found: S, 47·27; C, 34·35; H, 5·94. $C_8H_{14}O_2S_4$ requires S, 47·41; C, 35·55; H, 5·19 per cent.).

The ethereal solution was evaporated to dryness and the residue extracted with a small quantity of ether leaving some insoluble oily and solid matters. The solution was evaporated and the previous process repeated several times until at last a transparent thick oil, ethyl ethylene disulphido-acetate (IV), with a pleasant odour was obtained (Found: C, 39·8; H, 5·89; S, 35·34. $C_6H_{10}O_2S_2$ requires C, 40·4; H, 5·6; S, 36·0 per cent.).

This oil was formed in larger amount in comparison with the previous one. It was dissolved in absolute alcohol and boiled with the calculated quantity of alcoholic potash for about two hours. The whole mass was evaporated to dryness and the residue dissolved in water and acidified with dilute hydrochloric acid. The turbid liquid was extracted with benzene and the benzene extract evaporated to dryness. The percentage of sulphur in this acid shows that it is most probably ethylene-disulphido-acetic acid (I), with which its properties correspond (Found: S, 41·95. $C_4H_6O_2S_2$ requires S, 42·66 per cent.).

Interaction of Potassium Dichloracetate and Monopotassium Ethylene Mercaptan.—Potassium dichloracetate (4·25 gms.), potassium mercaptide (4·75 gms.) and anhydrous alcohol (50 c.c.) were refluxed together for about an hour and filtered hot from the precipitate of potassium chloride. The filtrate was evaporated to dryness and the solid residue dissolved in water, filtered and acidified with concentrated hydrochloric acid in the cold and the turbid solution extracted with benzene. The benzene solution was well washed with water, filtered, dried and again filtered and evaporated to dryness. The oil thus obtained was purified by a repetition of the processes of extraction with a small amount of ether, filtration and evaporation—every time leaving some brown amorphous residue. A heavy oil (I) of pungent odour, insoluble in petroleum ether was obtained. It is strongly acid to litmus and decomposes alkali carbonates and bicarbonates (Found: C, 32·37; H, 4·7. $C_4H_6O_2S_2$ requires C, 32·00; H, 4·00 per cent.).

The oily acid was neutralised by the required quantity of pure caustic potash solution, the solution evaporated to dryness and the

residue crystallised from alcohol. The *potassium salt* was obtained as a colourless mass (Found: K, 19.63. $C_4H_5O_2S_2K$ requires K, 20.0 per cent.).

Interaction of Ethyl Trichloracetate and Ethylene Mercaptan.—The mercaptan (10 gms.) and the ester (10 gms.) were gently heated together for several hours on the sand-bath. Copious evolution of hydrochloric acid and sulphuretted hydrogen was noticed. The cold solid mass after washing with dilute alkali and water, was separated into different fractions by treatment with alcohol, chloroform, xylene and nitrobenzene. The products obtained from these solvents were amorphous and found to be polymerised ethylene disulphide. The ester was subsequently heated with the monopotassium salt of the mercaptan and also with its disodium salt in alcoholic and in benzene solutions—but only the polymers of ethylene disulphide were obtained. Next the monopotassium salt was shaken in the cold; ethylene disulphide was the only product.

Interaction of Trichloroacetic Acid and Ethylene Mercaptan.—The mercaptan (10 gms.), the acid (9 gms.) and xylene (40 c.c.) were heated together for about 22 hours (benzene was first employed but no reaction ensued even on continued boiling) on the sand-bath. Evolution of large quantities of hydrochloric acid, carbon dioxide and sulphuretted hydrogen gases took place. The solution was evaporated to dryness and well washed with dilute alkali and then with water. The alkaline filtrate on acidification yielded no precipitate. The residue was refluxed with alcohol, filtered and the solution concentrated. Fine needle-shaped crystals with a slight greenish tinge were obtained. These were purified by repeated crystallisation from alcohol. White needles, m.p. 95–96° identical with the compound (II) derived from dichloroacetic acid and ethylene mercaptan were obtained (*vide supra*). The residue after extraction with alcohol was separated into three fractions by refluxing with benzene, xylene and nitrobenzene respectively, but the products obtained from these solutions were all amorphous compounds, identical with the polymers of ethylene disulphide.

In conclusion, the authors take this opportunity of expressing their gratefulness to Sir P. C. Rây for his kind interest and help in this investigation.

Chemical Laboratory,
University College of Science and Technology,
Calcutta.
Department of Organic Chemistry,
Indian Institute of Science,
Bangalore.

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