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## LXIX.—Chloroiodoacetic Acid.

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IODINE monochloride acts vigorously on  $\alpha\beta$ -dichlorovinyl ethyl ether with evolution of heat. The solution becomes dark violet and iodine separates. If the ether is kept cool, and the monochloride is added very gradually, but little iodine is set free, and the mixture, on standing exposed to the air, emits a colourless, acrid, inflammable vapour containing ethyl chloride. At the same time crystals of chloroiodoacetic acid are formed on the sides of the containing vessel. The product of the action appears to be chloroiodoacetyl chloride,

## $CHCl:CCl\cdot OEt + ICl = CHClI\cdot COCl + EtCl,$

which is converted into the acid by the absorption of water from the air. If air is excluded, and the mixture left for some time, the acid chloride is produced in good yield, and although it cannot be purified it can be used, in the crude form, for the preparation of the acid and its derivatives.

Chloroiodoacetic Acid.—Iodine monochloride (1 mol.) was added as above to  $\alpha\beta$ -dichlorovinyl ethyl ether (1 mol.), and the mixture kept in a sealed vessel for three weeks. It was then heated at 50° to expel ethyl chloride and, after cooling, filtered through glass wool to remove solid iodine. Water (1 mol.) was added in small quantities at a time and the mixture left over-night. It solidified almost completely, the yield of crude chloroiodoacetic acid being 60 per cent. of the calculated. The acid was purified by crystallisation from light petroleum. Thus obtained, it forms colourless, lustrous leaflets melting at 90° (Found : Cl = 15.50, 15.32; I = 57.50, 57.15; equivalent = 217.9; M = 223.7. C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>ClI requires Cl = 16.06; I = 57.54 per cent.; M = 220.4).

The acid is not perceptibly hygroscopic, although it dissolves readily in water and the ordinary organic solvents. When dry, it does not change on exposure to the air. But its solutions are very sensitive to light. Colourless solutions in light petroleum or benzene turn violet almost immediately when exposed to bright sunlight. The salts of the ordinary metals are all soluble in water. The *barium* salt could only be crystallised from very concentrated solution (Found : Ba = 24.19.  $C_4H_4O_4Cl_2I_2Ba$  requires Ba = 23.84 per cent.).

Chloroiodoacetamide is formed on treating a solution of the crude chloroiodoacetyl chloride described above with dry ammonia. It crystallises from water or benzene in brilliant white needles melting at 140° (Found: N = 6.51; Cl = 16.00; I = 57.20. Cale., N = 6.37; Cl = 16.19; I = 57.89 per cent.). It is evidently identical with the amide obtained by Willstätter and Hottenroth from impure ethyl chloroiodoacetate and ammonia (*Ber.*, 1904, 37, 1786).

Chloroiodoacetanilide is similarly prepared by the action of aniline on the chloride in light petroleum solution. It crystallises from water or benzene in white needles melting at 142° (Found : N = 4.82; Cl = 11.93; I = 42.94. C<sub>8</sub>H<sub>7</sub>ONCII requires N = 4.74; Cl = 12.00; I = 42.98 per cent.).

Esters of chloroiodoacetic acid can be obtained from the above chloride, or, in this case, if the alcohol is added to a freshly prepared mixture of dichlorovinyl ethyl ether and iodine monochloride, a violent reaction sets in on warming and the ester is formed. Liquid esters could not be isolated in a pure condition, but solid esters can be crystallised out and purified.

Phenyl chloroiodoacetate crystallises from light petroleum in brilliant colourless leaflets melting at 110° (Found : Cl = 11.98; I = 42.78.  $C_8H_6O_2ClI$  requires Cl = 11.97; I = 42.83 per cent.).

The replacement of a chlorine atom in phenyl dichloroacetate by a bromine atom has only a slight effect on melting point and crystalline form (Crompton and Triffitt, T., 1921, 119, 1874). When the bromine is replaced by iodine, the melting point rises from  $46.5^{\circ}$  to  $110^{\circ}$ . Also, phenyl chlorobromoacetate and chloroiodoacetate do not form mixed crystals. This is shown by the melting points of their mixtures :

Molecular percentage of chlorobromoacetate.	М. р.	Molecular percentage of chlorobromoacetate.	М. р.
100	46.5°	$62 \cdot 2$	75. <sup>7</sup> °
90.0	42.8	50.0	87.5
88.2	<b>42</b> ·0	37.1	96.0
82.0	42.6	28.0	102.5
80.0	47.9	7.5	107.6
78.8	52.0	0	110

These numbers give a melting point curve of the usual type, the eutectic mixture, containing 82.9 per cent. of the chlorobromo-acetate, melting at  $39.2^{\circ}$ .

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