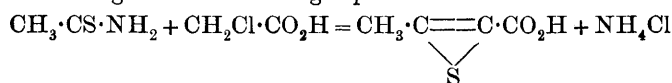


XLVI.—*Synthesis of $\alpha\beta$ -Thiocrotonic Acid.*

By PRAFULLA CHANDRA RÂY AND MANIK LAL DEY.

MONOCHLOROACETIC acid and thioacetamide have been found to interact in acetone solution with the production of *$\alpha\beta$ -thiocrotonic acid* according to the following equation:



E X P E R I M E N T A L.

Molecular proportions of thioacetamide and monochloroacetic acid are separately dissolved in the minimum quantity of anhydrous acetone, the solutions mixed, and set aside. In the course of twenty-four hours a precipitate of ammonium chloride is noticed, which increases day by day, and after about a week the ammonium chloride is filtered off.

The filtrate is now freed from acetone by evaporation at the ordinary temperature when a heavy, orange-yellow oil of an unpleasant odour remains with a few crystals of ammonium chloride. The oil is dissolved in ether, the solution filtered and evaporated, and the oil allowed to crystallise in a desiccator.

It takes about three months to obtain a good crop of crystals, but occasionally they appear earlier. The crystals are purified by recrystallisation first from acetone and then from alcohol. The first crop of crystals obtained in this way were pure, had a faint yellow tint, and melted sharply at 135° ; when the ethereal solution was evaporated slowly, transparent, rhombic plates were obtained.

The acid is fairly soluble in water, readily so in alcohol, acetone, or ether, and sparingly so in chloroform. Its solution rapidly

decolorises bromine water and alkaline permanganate solution, thus proving its unsaturated character.

The *barium* salt forms shining, rhombic plates, the *lead* salt white, needle-shaped crystals, and the *silver* salt is obtained as a faintly yellow, gelatinous precipitate.

Attempts to analyse the acid met with no success; thus when mixed with concentrated nitric acid in a sealed tube for the purpose of estimating sulphur, it explodes violently. Fusion with sodium carbonate and nitrate is also attended with explosion. The barium, silver, and lead salts were therefore analysed.

Barium salt :

0.1238 gave 0.0800 BaSO_4 . Ba = 37.99.

0.1118 „ 0.1460 BaSO_4 . S = 17.94.

$\text{C}_8\text{H}_6\text{O}_4\text{S}_2\text{Ba}$ requires Ba = 37.23; S = 17.44 per cent.

Lead salt :

0.1682 gave 0.1368 CO_2 and 0.0514 H_2O . C = 22.10; H = 3.40.*

0.0628 „ 0.0432 PbSO_4 . Pb = 46.97.

	Found.	Calc. for $\text{C}_8\text{H}_6\text{O}_4\text{S}_2\text{Pb}$.
Pb	46.97	47.17
C	22.10	22.05
H*	3.40	1.38

$\text{C}_8\text{H}_6\text{O}_4\text{S}_2\text{Pb}$ requires C = 22.05; H = 1.38; Pb = 47.17 per cent.

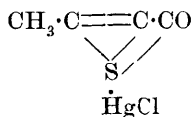
Silver salt :

0.1250 gave 0.0610 Ag. Ag = 48.80.

$\text{C}_4\text{H}_3\text{O}_2\text{SAg}$ requires Ag = 48.43 per cent.

The formula of the compound is thus fully established.

Mercury Salt.—With mercuric chloride the acid forms a compound containing an atom of chlorine, to which the constitutional formula



must be assigned.

I. 0.0790 gave 0.0524 HgS . Hg = 57.17.

II. 0.0828 „ 0.0553 HgS . Hg = 57.57.

0.0920 „ 0.0620 BaSO_4 . S = 9.26.

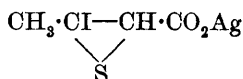
0.0812 „ 0.0339 AgCl . Cl = 10.24.

$\text{C}_4\text{H}_3\text{O}_2\text{ClSHg}$ requires Hg = 57.06; S = 9.13; Cl = 10.13 per cent.

* Several samples of organic mercury compounds had been previously analysed in the combustion tube and hence traces of mercury vapour were carried into the calcium chloride tube, which increased the apparent percentage of hydrogen.

512 RÂY AND DEY : SYNTHESIS OF $\alpha\beta$ -THIOCROTONIC ACID.*Action of Hydriodic Acid.*

The concentrated aqueous solution of the acid was repeatedly treated with concentrated hydriodic acid and evaporated to dryness on the water-bath so as completely to remove every trace of the free halogen acid. The residue was dissolved in water, and on treatment with silver nitrate solution it gave a copious, pale yellow precipitate of *silver β -iodo- $\alpha\beta$ -thiobutyrate* :



0.0256 gave 0.0174 AgI.* Ag=31.23; I=36.73.

$\text{C}_4\text{H}_4\text{O}_2\text{ISAg}$ requires Ag=30.77; I=36.18 per cent.

Molecular Conductivity and Dissociation Constant.

The conductivity of the acid and of its barium salt at different dilutions was determined. The dissociation constant of the acid and the degree of dissociation of the salt were calculated from the data.

<i>Acid.</i> $t = 24^\circ$.			<i>Barium Salt.</i> $t = 25.3^\circ$.		
\mathcal{S} in litres.	μ (equiva- lent con- ductivity).	K .	\mathcal{S}	μ (equiva- lent con- ductivity).	α .
60	42.6	0.000020	200	94	0.75
120	58	0.000019	600	102	0.81
240	77	0.000018	1,200	108	0.86
480	101	0.000017	2,200	117	0.93
960	132	0.000016	4,200	122	0.97
∞	410 mean	0.000018	10,200	126	1.00

K for crotonic acid=0.000002; as a general rule, the substitution of sulphur for hydrogen in organic acids increases the dissociation constant. Thus, in the present instance the value of K for the thio-compound is considerably higher.

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* By Carius's method, without addition of silver nitrate.