XXXII.—On the Formation of *Ethyl*ic Cyanacetoacetate.

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FIFTY grams (1 mol.) of pure ethyl^{ic} monochloracetoacetate boiling at 195—197° were poured into a suitable flask containing 40 grams (2 mols.) of finely ground potassium cyanide and about 700 c.c. 99·5 per cent. alcohol. As the action takes place slowly in the cold, it is advisable to allow the flask to stand a few hours with frequent shaking before completing the reaction by digesting for an hour or so on a water-bath. The potassium cyanide is replaced by a dense precipitate of potassium chloride, which contains but traces of the former.

The alcoholic solution, now deep-brown in colour, and smelling very strongly of hydrocyanic acid, was filtered from the potassium chloride, and the alcohol distilled off on a water-bath. The distillate contained large quantities of hydrocyanic acid, much larger than could be expected had the chlorine simply been displaced by cyanogen, and its occurrence due to decomposition or some secondary reaction.

The residue in the retort deposited indistinct crystals on cooling; these were thoroughly freed from the mother-liquor by pressing them between filter-paper, washed with cold alcohol, which removed a good deal of the brown colouring matter, and twice recrystallised from strong alcohol. The substance was now free from chlorine and consisted of microscopic needles aggregated in nodular groups.

A complete analysis of this compound, which was not perfectly white, yielded the results in I.

After recrystallising six times, lastly from 90° per cent. alcohol, very long, slender needles were obtained, consisting of pure *potussio*-cyanacetoacetate of ethyl (II).

I. 0·172 gram substance burnt with CuO, PbCrO₄, and copper spiral gave 0·067 gram H₂O and 0·2791 gram CO₂.

0·177 gram substance, after ignition and moistening with H₂SO₄, produced 0·0855 gram K₂SO₄.

0·3055 gram substance burnt with CuO and copper spiral gave 23·3 c.c. moist nitrogen at 24·5° and 742 mm.

II. 0·1875 gram substance on combustion gave 0·0695 gram H₂O and 0·2991 gram CO₂.

0·135 gram substance produced 0·0615 gram K₂SO₄.

	Calculated for $\text{CH}_2(\text{CN})\cdot\text{CO}\cdot\text{CHK}\cdot\text{COOEt}$.		Found.	
			I.	II.
C ₇	84	43·52	44·25	43·50
H ₈	8	4·14	4·32	4·11
N	14	7·25	8·34	—
O ₃	48	24·89	—	—
K	39	20·20	21·65	20·41
	193	100·00		

The formation of this salt was quite an unexpected result; it probably takes place in two stages: first, the production of ethylic potassio-monochloracetoacetate, with evolution of hydrocyanic acid, ethylic monochloracetoacetate having strongly acid properties; and then secondly, the ethylic potassio-monochloracetoacetate is acted on by another molecule of potassium cyanide, according to the following equations:—

Ethylic potassiocyanacetoacetate crystallises from 90 per cent. alcohol in long, colourless needles, which have a bitter taste. It is insoluble in ether and benzene; neither of these liquids remove the brown colouring matter from which it is very difficult to purify the salt.

The yield is a very poor one; from 50 grams of ethylic monochloracetoacetate, one or two grams of pure salt can be obtained; in fact, it seems to decompose by simply dissolving in alcohol, in which it is moderately soluble, for the alcoholic solution always becomes brown, even if the salt be nearly colourless to begin with.

Action of Dilute Acids on Ethylic Potassiocyanacetoacetate.

Five grams of pure ethylic potassiocyanacetoacetate dissolved in cold water were acidified with dilute hydrochloric acid, and the colourless oil which separated was removed by shaking out with ether. After drying by calcium chloride, the ethereal solution was allowed to remain over sulphuric acid and lime in a vacuum until all ether and traces of hydrochloric acid were absorbed. A slightly yellow-coloured oil now remained, which is decomposed by distillation.

An analysis showed it to be pure *ethylic cyanacetoacetate*.

0·1685 gram substance after combustion with CuO and copper gave 0·0915 gram H₂O and 0·3335 gram CO₂.

	Calculated for $\text{CH}_2(\text{CN})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COOEt.}$	Found.
C.....	54.19	53.97
H.....	5.80	6.03

Ethyllic cyanacetoacetate is a colourless liquid which cannot be distilled under the ordinary pressure. During the winter months, it solidified to a mass of fine, silky needles melting at 26.5° . Once melted, it will not resolidify, unless cooled to near the freezing point. A drop shaken with water and added to ferric chloride gives a red coloration.

It is insoluble in water, but dissolves in alcohol and ether. The products of its decomposition with alkalis have not been thoroughly examined, but acetic acid is undoubtedly produced.

Action of Potassium Cyanide on Ethyllic Dichloracetoacetate.

Fifty grams of pure ethylic dichloracetoacetate were poured into a litre flask containing 50 grams of potassium cyanide and about 600 c.c. 99.5 per cent. alcohol. The reaction, just as with the monochloracetoacetate, takes place slowly at the ordinary temperature; after standing some time with frequent shaking, the mixture was digested on the water-bath. Little or no potassium chloride separated, but on cooling a large quantity of a salt crystallised out in shining laminæ, containing chlorine, but no nitrogen, and which gave no oily drops on acidifying with dilute hydrochloric acid.

After twice recrystallising from strong alcohol, the substance gave the following analytical results:—

- I. 0.2280 gram substance burnt with CuO and PbCrO_4 gave 0.0170 gram H_2O and 0.1180 gram CO_2 .
- II. 0.193 gram substance ignited with lime finally produced 0.3345 gram AgCl.
- III. 0.278 gram substance, after ignition and treating with sulphuric acid, produced 0.1475 gram K_2SO_4 .

	Calculated for $\text{CHCl}_2\cdot\text{COOK.}$		Found.		
	I.	II.	I.	II.	III.
C_2	24	14.37	14.11	—	—
H.....	1	0.60	0.82	—	—
Cl_2	71	42.51	—	42.82	—
O_2	32	19.17	—	—	—
K.....	39	23.35	—	—	23.78
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	167	100.00			

The salt was therefore *potassium dichloracetate*; it agreed in properties with Wallach's description of this salt (*Ber.*, 1873, 114).

It was certainly to be expected that potassium cyanide would behave towards ethylic dichloracetoacetate in a manner analogous to that which it did with the monochlorinated derivative—if not both atoms of chlorine, the displacement of at least one was expected—but no such action appears to have taken place, even to a small extent; this is borne out by the fact that the yield of potassium dichloracetate is almost the theoretical.

The reaction which occurs may be represented by the following equation:—

I am not aware that any such case as this has been previously described; that is, one in which two haloïd derivatives of ethylic acetoacetate react with the same substance in such a widely different way. It would be interesting to ascertain whether other substances, sodium ethylate, for example, act similarly.

It is necessary to state that the ethylic monochloracetoacetate was prepared by passing chlorine into well-cooled ethylic acetoacetate until 100 grams had gained 30 grams in weight, the pure substance being easily isolated by fractional distillation, after removing the dissolved hydrogen chloride by washing with water and desiccating with calcium chloride.

The ethylic dichloracetoacetate I employed was made by saturating ethylic acetoacetate with chlorine, the flask being kept cool; after removing the hydrogen chloride as above, subsequent rectification yielded the pure substance, boiling at 205—210°.

Geuther's Laboratory,
University of Jena, September, 1886.