LXIII.—*On the Synthetical Production of New Acids of the Pyruvic Series.*

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PART I. *Propionylformic Acid.*

DR. CLAISEN showed some time ago that the cyanides of the acid radicles could, under favourable circumstances, be converted into corresponding acids in the same way as the cyanides of alcohol-radicles, benzoyl cyanide being the one used for experiment.

* The results of this paper give a general confirmation to these or similar formulæ.

Later on, Claisen (*Ber.*, **10**, 429, 844, 1663) and Shadwell (*Ber.*, **13**, 6) proved that acetyl cyanide reacts in the same way. We therefore thought that it would be interesting to follow up this reaction with homologous fatty acid cyanides, *e.g.*, to produce propionylformic acid from propionyl cyanide.

These reactions are interesting theoretically, as other ketonic acids exist which are partly stable and partly unstable. Take for example the three normal ketonic acids of the formula $C_5H_8O_3$:—

Acetopropionic acid.....	$COOH.CH_2.CH_2(CO.CH_3)$	stable.
Propionylacetic acid.....	$COOH.CH_2(CO.CH_2CH_3)$	unstable.
Butyrylformic acid	$COOH(CO.CH_2.CH_2CH_3)$	stable.

The general method employed was that of Claisen and Shadwell, substituting propionyl chloride for the acetyl chloride used by them.

The great difficulty we found was to get a better method for making the acid cyanide; and in spite of numerous experiments, we had to fall back upon Hübner's (*Annalen*, **120**, 334) method, which consists in heating the acid chloride (in this case propionyl chloride) with silver cyanide in closed tubes for an hour at 100° . We found that 12 grams of propionyl chloride and 8 grams of silver cyanide gave the best yield. The contents of all the tubes used was then transferred to a large flask, and the whole was distilled off over a sand-bath into a fractioning flask. The liquid was then accurately fractionated. The propionyl cyanide came over between 100 — 115° . This, when repeatedly fractionated, gave the pure cyanide, which boiled at 108 — 109° . The following are results obtained by analysis :—

	Theory.		Found.	$\left\{ \begin{array}{l} 0.2401 \text{ gram substance gave } \left\{ \begin{array}{l} 0.513 \text{ CO}_2 \\ 0.1289 \text{ H}_2\text{O} \end{array} \right. \\ 0.3198 \text{ gram substance gave } 0.513 \text{ gram AgCN, corresponding to } 0.0536 \text{ nitrogen} \end{array} \right.$
C ₄ ..	48	57.83	58.27	
H ₃ .	5	6.02	5.96	
N..	14	16.87	16.76	
O..	16	19.28	—	
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	83	100.00		

The nitrogen was determined in the form of silver cyanide. On sealing up propionyl cyanide with a few drops of nitric acid, silver nitrate and water, the silver cyanide is precipitated quantitatively.

On fractionating the residue, a polymeric cyanide distils over at a temperature of about 100° higher than the cyanide: of this we shall speak hereafter.

Propionylformic Amide, $CH_3.CH_2.CO.CONH_2$.

To prepare this compound, a number of small test-tubes provided with well-fitting corks were each charged with 2 grams of the cyanide

and 1 gram of hydrochloric acid of sp. gr. 1·23. This is approximately one molecular proportion of cyanide to one of water contained in the acid. The test-tubes were then left for two hours in iced water. By that time the liquids were thoroughly mixed, and hydrochloric acid gas was given off violently, very often blowing the cork out. The mass then became semi-solid, and was placed on to seven or eight watch-glasses, and these were left over lime for several days. The mass, consisting of crystallised soda amide and ammonium chloride, was fractionally sublimed, the amide subliming at a much lower temperature than ammonium chloride. When pure it fuses at 116—117°.

When analysed it gave the following results:—

- (1.) 0·1003 gram substance gave 0·174 CO₂ and 0·065 H₂O.
- (2.) 0·1052 " 0·183 CO₂ and 0·069 H₂O.
- (3.) 0·1505 " 0·2629 CO₂ and 0·097 H₂O.
- (4.) 0·151 " 0·1433 Pt.

			Found.		
			I.	II.	III.
C ₄	48	Theory. 77·53	47·31	47·44	47·64
H ₇	7	6·93	7·20	7·28	7·16
N.....	14	13·86	13·46	—	—
O ₂	32	31·68	—	—	—
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Instead of preparing our acid from the amide as Claisen and Shadwell did, we produced it directly from the cyanide, thereby getting a much larger yield. 36 grams of cyanide were brought together with hydrochloric acid of sp. gr. 1·23, in portions of 5 grams of cyanide to 2·5 of acid (approximately one molecular proportion of cyanide to one of water), and the mixture was left to stand for two hours in iced water till the conversion was complete. To each portion was then added 2·5 grams more hydrochloric acid of the same specific gravity, so that each molecular proportion of cyanide was brought into contact with two of water. After standing for a little while the semi-solid mass was transferred into a flask provided with an inverted condenser, and so much hydrochloric acid of sp. gr. 1·1 added as to convert all the ammonia into ammonium chloride. The vessels were then rinsed out with a little distilled water, and the water added to the rest. The whole mixture was then boiled for two or three hours on the water-bath. On cooling, ammonium chloride separated out.

At the end of three hours enough water was added to dissolve the ammonium chloride, and the liquid was then shaken up for some time

with small portions of ether. The ethereal solution was then dried over calcium chloride and the ether boiled off. The residue consisted of propionylformic acid and a little propionic acid. Propionic acid boils at 57° under a pressure of 25 mm., whereas propionylformic acid boiled at $70-80^{\circ}$. When pure, its boiling point at the same pressure is $74-78^{\circ}$. Between $70-80^{\circ}$ we obtained 18° of our acid.

Propionylformic acid is an oily liquid, having a characteristic burnt smell; its sp. gr. is 1.12. It does not solidify at -15° .

When analysed it gave the following results:—

- (1.) 0.313 gram substance gave 0.5382 CO_2 and 0.178 H_2O .
- (2.) 0.3595 ,, 0.6191 CO_2 and 0.2004 H_2O .

		Theory.	Found.	
			I.	II.
C ₄	48	47.06	46.89	46.96
H ₆	6	5.88	6.31	6.19
O ₃	48	47.06	—	—
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		100.00		

The theoretical values for propionic acid are, $\text{C } 48.64$, $\text{H } 8.11$, from which it can be seen that we obtained our acid in a very pure condition.

It dissolves in water, alcohol, and ether, in all proportions. When diluted and treated warm with silver carbonate, it gives a beautifully crystalline silver salt, $\text{CH}_3\text{CH}_2\text{CO.COOAg}$, which is moderately soluble in cold water. The prismatic crystals always form at right angles to one another.

The following are two silver determinations:—

- (1.) 0.1961 gram substance gave 0.1014 Ag.
- (2.) 0.2083 ,, 0.1077 Ag.

			Found.			
			I.	II.		
C ₄	}	101	Theory.	48.33	—	—
H ₅						
O ₃						
Ag		108		51.67	51.70	51.70
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		209		100.00		

An aqueous solution of the acid when treated with barium carbonate gives a characteristic barium salt of the form $(\text{C}_4\text{H}_5\text{O}_3)_2\text{Ba} + \text{OH}_2$. Between $160-170^{\circ}$ it decomposes.

The following analyses prove its constitution:—

Dried at 100°.		Theory.	Found.	
			I.	II.
$[C_4H_5O_3]_2$	202	59·59	—	—
Ba.....	137	40·41	40·42	40·48
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	339	100·00		

Water estimation.		Theory.	Found.	
			I.	II.
$[C_4H_5O_3]_2Ba$	339	94·96	—	—
OH_2	18	5·04	4·77	—
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	357	100·00		

This salt is of the same form as the corresponding barium propionate, but the latter contains 48·41 of barium, and is very soluble in water, whereas barium propionylformate is only moderately soluble.

By treating the calcium salt with mercurous nitrate, a crystalline mercurous propionylformate is formed, which, however, is extremely unstable.

Propionylformic acid does not give an insoluble basic salt when treated with barium hydrate. This reaction affords less characteristic distinction between the behaviour of propionylformic acid and pyruvic acid under the same circumstances.

Reduction of Propionylformic Acid.

Just as pyruvic acid is converted by hydrogen into acetic acid, so may propionylformic acid be reduced by the action of nascent hydrogen to normal and hydroxybutyric acid. Perfectly pure crystals of this acid were obtained melting at 42—43°.

On the whole the acid is very stable, thereby differing greatly from its isomeride *aceto-acetic acid*, which can exist only in the form of an ether.

Note on the Polymeride Dipropionyl Dicyanide.

If in the distillation of propionyl cyanide, the residue be subjected to accurate fractional distillation, an oily liquid comes over between 200—210°. When perfectly pure it boils at 208°. Curiously enough it cannot be solidified at -15°, although its homologue diacetyl dicyanide is a crystalline solid at the ordinary temperature. We had so little that we could not study its reactions.

The following were the analytical results:—

0·1844 gram substance gave 0·3925 CO_2 .

0·1054 H_2O .

0·2492 gram substance gave 0·292 Pt.

PERKIN ON THE ACTION OF NITRIC ACID

		Theory.	Found.
C ₄	48	57·83	58·05
H ₅	5	6·02	6·35
N.....	14	16·87	16·62
O.....	16	19·28	—
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	93	100·00	

The vapour-density cannot be determined according to Victor Meyer's method, as the substance decomposes when heated to the temperature required. Hofmann's method had to be used; the mean of many determinations gave a result which left no doubt as to the compound in question being the double cyanide.

In our next paper we hope to be able to publish some interesting reactions of these polymeric cyanides, as we have since obtained them in much larger quantities.