LXXI.—*Preparation of the Acyl Derivatives of the Aldehyde-cyanohydrins. Part II.*

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IN a previous communication (Trans., 1909, **95**, 1403) a method was described for the preparation of acyl derivatives of aldehyde-cyanohydrins, which consisted in shaking an aqueous solution of potassium cyanide with the required aldehyde, and gradually adding the acid chloride to the cooled mixture.

With one exception the compounds investigated were derived from aromatic aldehydes, and further experiments have been carried out with those of the aliphatic series. The reaction has been found

to be quite general with these aldehydes, and theoretical yields of the compounds in question have been obtained by the action of benzoyl chloride on acetaldehyde, isovaleraldehyde, and heptaldehyde. In each case the resulting acyl derivatives are oils of high boiling point, which can be distilled without decomposition under diminished pressure.

An attempt was also made to carry out the reaction with acid chlorides of the aliphatic series, but although small amounts of the corresponding acyl derivatives are formed, they are not sufficiently stable to be isolated in a state of purity.

A number of corresponding experiments were then carried out with aliphatic and aromatic ketones, but with the exception of acetone it was not found possible to isolate the desired derivatives.

A series of investigations was made to determine the action of different reagents on the acylaldehyde-cyanohydrins. When dissolved in absolute alcohol and saturated with ammonia gas, the main reaction consists in the elimination of the acyl group with formation of the amide, which is invariably contaminated with oily matter.

On boiling with an aqueous solution of potassium hydroxide, all these compounds lose the acyl group with the formation of the potassium salt and liberation of the cyanohydrin, the latter, in presence of the alkali, giving rise to potassium cyanide and the corresponding aldehyde, which in several cases undergoes condensation.

Towards hydrochloric acid these compounds are fairly stable, but are decomposed when heated with this reagent in sealed tubes at 100—110°.

Only one derivative was fully investigated, namely, carbethoxymandelonitrile, which gave mandelamide after heating for a short time, but further heating gave rise to a mixture of mandelic acid and its ester.

EXPERIMENTAL.

Benzoyl-lactonitrile, $\text{BzO}\cdot\text{CHMe}\cdot\text{CN}$.

This was prepared by the interaction of acetaldehyde, aqueous potassium cyanide, and benzoyl chloride. The heavy oil which separated was extracted with ether, the ethereal solution washed with dilute potassium hydroxide solution, and dried. After removing the ether, a good yield of oil was obtained, which could be distilled without decomposition, even under the ordinary pressure. It boils at 198—200°/125 mm. or 269—270°/760 mm.:

0.4274 gave 29.4 c.c. N_2 (moist) at 16° and 758 mm. $\text{N} = 7.99$.

$\text{C}_{10}\text{H}_9\text{O}_2\text{N}$ requires $\text{N} = 8.00$ per cent.

α -Benzoyloxyisohexonitrile, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OBz}) \cdot \text{CN}$.

This was obtained in the same manner as the compound just described by the interaction of aqueous potassium cyanide, *iso*-valeraldehyde, and benzoyl chloride. It is an almost colourless oil, boiling at $247\text{--}250^\circ/200$ mm.:

0.5284 gave 29.4 c.c. N_2 (moist) at 20° and 761 mm. $\text{N} = 6.37$.

$\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{N} = 6.45$ per cent.

 α -Benzoyloxyoctonitrile, $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{OBz}) \cdot \text{CN}$.

This compound was prepared from heptaldehyde and benzoyl chloride; it is a colourless oil, boiling at $256\text{--}257^\circ/110$ mm.:

0.501 gave 24.6 c.c. N_2 (moist) at 15° and 757 mm. $\text{N} = 5.72$.

$\text{C}_{15}\text{H}_{19}\text{O}_2\text{N}$ requires $\text{N} = 5.71$ per cent.

Benzoyloxyisobutyronitrile, $\text{BzO} \cdot \text{CMe}_2 \cdot \text{CN}$.

Prepared from acetone and benzoyl chloride in the presence of aqueous potassium cyanide. A very small yield of colourless oil, boiling at $185\text{--}190^\circ/70\text{--}80$ mm., was obtained after extracting with ether and drying. After several days the oil solidified to a mass of colourless, crystalline plates, melting at $35\text{--}36^\circ$:

0.6005 gave 37.4 c.c. N_2 (moist) at 16° and 755 mm. $\text{N} = 7.2$.

$\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}$ requires $\text{N} = 7.4$ per cent.

m-Nitrobenzoyloxyisobutyronitrile.

Prepared from *m*-nitrobenzoyl chloride, acetone, and potassium cyanide. A good yield of pale yellow crystals was obtained, and, after recrystallisation from alcohol, these melted at $75\text{--}76^\circ$:

0.214 gave 23.00 c.c. N_2 (moist) at 17° and 749 mm. $\text{N} = 12.2$.

$\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_2$ requires $\text{N} = 11.9$ per cent.

Ethyl-carbonatoisobutyronitrile, $\text{CO}_2\text{Et} \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CN}$.

A very small yield of this derivative was obtained by the interaction of acetone, aqueous potassium cyanide, and ethyl chloroformate. It is a colourless oil, boiling at $140\text{--}142^\circ/100$ mm.:

0.332 gave 26.6 c.c. N_2 (moist) at 21° and 765 mm. $\text{N} = 9.1$.

$\text{C}_7\text{H}_{11}\text{O}_3\text{N}$ requires $\text{N} = 8.91$ per cent.

Action of Butyryl Chloride on Benzaldehyde in presence of Aqueous Potassium Cyanide.

In this reaction a very small yield of an oil was obtained, which boiled at $200^{\circ}/80$ mm. It appeared to be partly decomposed during distillation. An analysis showed it to be in all probability impure butyrylmandelonitrile:

0.2207 gave 0.561 CO_2 and 0.130 H_2O . $\text{C} = 69.3$; $\text{H} = 6.5$.

$\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C} = 70.9$; $\text{H} = 6.4$ per cent.

Reactions of Acylaldehyde-cyanohydrins: Action of Ammonia.

Benzoylmandelonitrile.—Five grams of this nitrile were dissolved in absolute alcohol, and the solution saturated with ammonia. After twelve hours the solution was evaporated, when a crystalline solid, mixed with oily matter, was obtained. When crystallised from benzene, the substance melted at 127° , and its reactions and analysis showed it to consist of benzamide.

Benzoyl-p-methoxymandelonitrile and *Benzoyl-lactonitrile*.—When treated with ammonia, as described above, both these compounds gave benzamide.

Cinnamoylmandelonitrile.—In this case the reaction product was contaminated with a considerable amount of resinous matter, and only a small amount of cinnamide could be isolated.

Action of Hydrochloric Acid on Carbethoxymandelonitrile.

A small quantity of the above substance was heated in a sealed tube for one and a-half hours at 110° . When cool, there was considerable pressure in the tube, and colourless crystals had separated, which, after crystallisation from alcohol, melted at 134 — 135° , and gave the reactions of mandelamide.

In a second experiment the heating was prolonged for five hours, when ammonium chloride was found to be present in almost theoretical amount. In addition, mandelic acid and its ester were identified, the latter giving mandelic acid on hydrolysis with potassium hydroxide.

Action of Potassium Hydroxide.

Benzoylmandelonitrile.—Five grams of the compound, crystallised from alcohol, were heated under a reflux condenser for five hours with 10 c.c. of 15 per cent. aqueous potassium hydroxide. On cooling, the product was extracted with ether, and 2.5 grams of an oil were obtained, which solidified after some time. On crystallisation, first from alcohol and finally from boiling water, it

melted at 134° , and analysis showed it to be benzoin. The residue was distilled in a current of steam, and the distillate contained traces of ammonia and some benzaldehyde.

After removal of the benzaldehyde, the liquid remaining was found to contain potassium cyanide, and on acidifying with dilute hydrochloric acid, benzoic acid was precipitated.

Several similar experiments were made, and it appears that the proportion of benzoin to benzaldehyde formed depends on the concentration of the potassium hydroxide solution.

Benzoyl-p-tolylglycollonitrile.—When treated as described in the previous case, 5 grams of benzoyl-*p*-tolylglycollonitrile gave 2.5 grams of a compound, which corresponded very closely with the benzoyl derivative of *p*-toluoin, and not to *p*-toluoin, as was expected. After crystallisation from alcohol it melted at 122 – 123° (Beilstein gives the melting point of benzoyl-*p*-toluoin as 119° , whereas *p*-toluoin melts at 88 – 89°). The analysis leaves little doubt that the substance is actually benzoyl-*p*-toluoin, but it is not easy to see how it is formed in this reaction:

0.1980 gave 0.5822 CO_2 and 0.1066 H_2O . $\text{C}=80.15$; $\text{H}=5.9$.

0.510, in 24.87 benzene, gave $\text{E}=0.155^{\circ}$. $\text{M.W.}=353$.

$\text{C}_{23}\text{H}_{20}\text{O}_3$ requires $\text{C}=80.23$; $\text{H}=5.8$ per cent. $\text{M.W.}=345$.

After removal of this substance, potassium cyanide, traces of ammonia, potassium benzoate, and *p*-tolualdehyde were identified in the solution.

Cinnamoylmandelonitrile and *Carbethoxymandelonitrile*.—Both these compounds gave benzoin, but from compounds derived from anisaldehyde no anisoin could be isolated from the products of the reaction with potassium hydroxide.

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