

CCXV.—*The Condensation of Ketones and Aldehydes
with the Sodium Derivative of Ethyl Cyanoacetate.
Part II.*

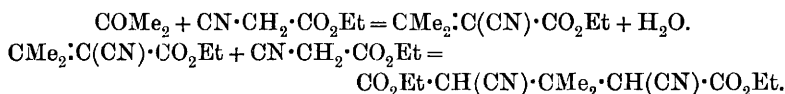
By HENRY DENT GARDNER, jun., and WALTER NORMAN HAWORTH.

IN a previous communication by one of us (Haworth, this vol., 480), the condensation of cyclic ketones with ethyl sodiocyanoacetate, first studied by Harding, Haworth, and Perkin (Trans., 1908, **93**, 1944), was extended to the more general cases of aldehydes and ketones, such as phenylacetaldehyde and acetophenone, in order to discover in

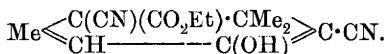
what direction this condensation might be useful for further synthetic work. The results which were obtained at that time seemed to make it desirable that simpler cases should be investigated, and the present communication is the outcome of experiments in this direction.

Komppa (*Ber.*, 1900, **33**, 3530) has studied the condensation of acetone with ethyl cyanoacetate, using a trace of piperidine as the condensing agent, and by a process which extended over many weeks he succeeded in isolating two definite products.

The reaction proceeded in two stages:

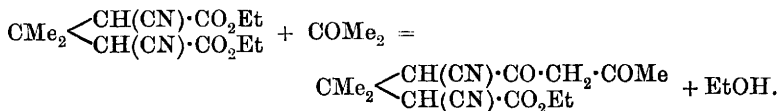


We have discovered that the condensation proceeds in quite an unexpected direction if sodium ethoxide is employed in the place of piperidine. When acetone is condensed with ethyl sodiocyanoacetate, the reaction is of a complicated character, the final product being *ethyl 2:6-dicyano-1:1:5-trimethyl-Δ^{2:4}-cyclohexadien-3-ol-6-carboxylate*,

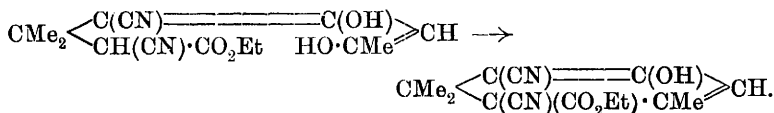


This substance, which melts at 135°, gives a green coloration in alcoholic solution with ferric chloride, and dissolves readily in sodium carbonate, the increased acidity being probably due to the close proximity of the cyano- to the hydroxy-group.

The course of the reaction may be expressed by assuming that the first product is ethyl *αα'*-dicyano-*ββ*-dimethylglutarate, which was obtained as stated above by Komppa. The presence of sodium ethoxide in our experiments had the effect of inducing a secondary condensation with an extra molecule of acetone to take place:

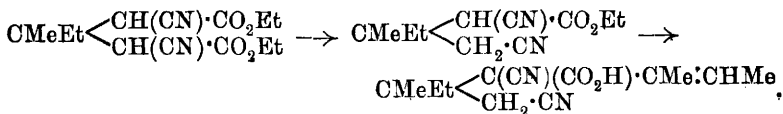


The latter substance contains four reactive hydrogen atoms, and in contact with hydrochloric acid undergoes tautomeric change, with the elimination of water and the formation of a six-membered ring:

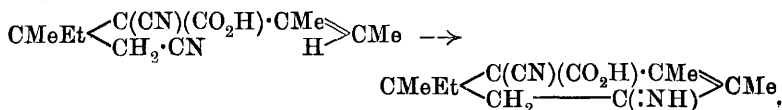


Striking confirmation of this view of the mechanism of the reaction was obtained from the condensation of ethyl cyanoacetate with methyl ethyl ketone. In this case the substitution of an ethyl group for one of the methyl groups in acetone, modified the result to some extent by

introducing the factor of steric hindrance, which was responsible for the loss of a carbethoxy-group in the form of ethyl carbonate. As before, the initial stage is evidently the formation of ethyl $\alpha\alpha'$ -dicyano- β -methyl- β -ethylglutarate, which then reacts with another molecule of the ketone, hydrolysis taking place under the influence of sodium ethoxide :

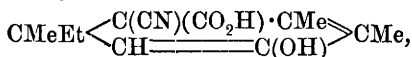


This open-chain compound subsequently condenses to a six-membered ring with formation of an imino-group :



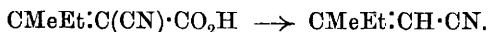
It is important to observe that this is another instance of the production of an alicyclic compound by the formation of the imino-grouping, which in the case of a five-membered ring has been so elegantly worked out by Dr. J. F. Thorpe (this vol., 685). We are indebted to his researches on the imino-compounds for the elucidation of the constitution of this and other compounds met with in this investigation.

The above imino-compound, 6-imino-3-cyano-1:2:4-trimethyl-4-ethyl- Δ^1 -cyclohexene-3-carboxylic acid, is yellow and melts at 108°. It dissolves readily in cold concentrated hydrochloric acid, and on digestion is converted into 3-cyano-1:2:4-trimethyl-4-ethyl- $\Delta^{1:5}$ -cyclohexadien-6-ol-3-carboxylic acid,



which is a liquid boiling at 193°/18 mm.

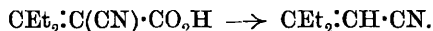
By a slight variation of the conditions, a simpler condensation product was subsequently obtained, namely, α -cyano- β -methyl- β -ethylacrylic acid, which on distillation is decomposed with elimination of carbon dioxide and formation of β -methyl- β -ethylacrylonitrile :



When this nitrile is hydrolysed under the conditions described in the experimental part of this paper (p. 1962), it yields β -methyl- β -ethylacrylic acid.

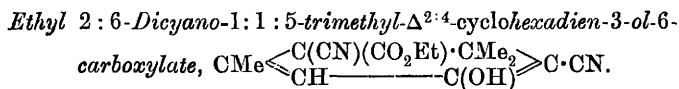
The constitution of the acid was controlled by oxidation with permanganate, when methyl ethyl ketone was recovered from the products and identified by its boiling point and the behaviour of its semicarbazone.

From a similar condensation of diethyl ketone with ethyl cyanoacetate, α -cyano- β -diethylacrylic acid was isolated, and this readily passes with loss of carbon dioxide into the corresponding β -diethylacrylonitrile:



The condensation has also been carried out with other homologues of acetone, namely, methyl propyl ketone and methyl hexyl ketone, with results which are exactly analogous to those described above; these are given in detail in the experimental part of this paper.

EXPERIMENTAL.



A good yield of this acid was obtained under the following conditions: Sodium (4.6 grams), dissolved in ethyl alcohol, was mixed with ethyl cyanoacetate (22.6 grams), and, after the separation of the white sodium derivative, acetone (11 grams) was added to the mixture. The white sodium derivative immediately dissolved, forming a clear yellow solution, which, on heating for an hour on the water-bath, deposited a yellow sodium salt. The product was cooled, dissolved in water, acidified with hydrochloric acid, and extracted with ether. The extract was washed several times with water, and afterwards with sodium carbonate, which dissolved the chief product of the reaction. This alkaline solution was acidified with excess of mineral acid, when an oil was deposited which, on keeping overnight, crystallised to a hard cake.

In another experiment, this oil was extracted with ether, and, after evaporation, was left to solidify in an open basin, but crystallisation did not take place even after the introduction of a crystal of the solid substance; it could only be induced to solidify by leaving it in contact with hydrochloric acid for several hours. The agency of hydrochloric acid is therefore necessary to complete the last stage of the synthesis. The substance was recrystallised from a mixture of benzene and light petroleum, or, better, from dilute methyl alcohol, from which it separates in colourless needles melting at 135°.

Owing probably to the strongly negative character of the hydroxy-group due to the proximity of a cyano-group, the compound dissolves readily in cold sodium carbonate, forming a deep yellow solution, which also decolorises permanganate instantly. It is readily soluble in benzene or alcohol, and in solution of the latter solvent it gives a deep green coloration with ferric chloride. It is sparingly soluble in water or light petroleum:

0.1220 gave 0.2880 CO₂ and 0.0680 H₂O. C = 64.4; H = 6.2.

0.1333 „ 13.6 c.c. N₂ at 18° and 755 mm. N = 11.6.

C₁₄H₁₆O₃N₂ requires C = 64.6; H = 6.1; N = 10.8 per cent.

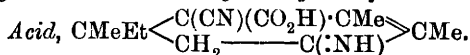
The *benzoyl* derivative crystallises from methyl alcohol in colourless needles, melting at 116°, and containing one molecule of water of crystallisation. This derivative dissolves in the ordinary organic solvents, but is insoluble in cold alkali, and gives no coloration with ferric chloride :

0.1123 gave 0.2700 CO₂ and 0.0600 H₂O. C = 65.6; H = 5.9.

0.1080 „ 7.0 c.c. N₂ at 18° and 752 mm. N = 7.4.

C₂₁H₂₀O₄N₂·H₂O requires C = 66.0; H = 5.8; N = 7.3 per cent.

6-*Imino-3-cyano-1:2:4-trimethyl-4-ethyl-Δ¹-cyclohexene-3-carboxylic*



In preparing the above acid, sodium (11.5 grams), dissolved in absolute ethyl alcohol, was mixed with ethyl cyanoacetate (56.5 grams), and as soon as the white sodium compound had separated, methyl ethyl ketone (36 grams) was introduced into the very hot mixture, which was then heated for two hours on the water-bath. The white sodium compound first dissolved, forming a clear yellow solution, from which a bulky, yellow precipitate gradually separated. After cooling, the product was dissolved in water, acidified with very dilute hydrochloric acid, and extracted with ether. The ethereal solution was washed until free from alcohol and shaken with dilute sodium carbonate solution; the slight residue remaining in the ether consisted of unchanged ketone and ethyl carbonate along with some neutral oils, the investigation of which is not yet complete. The sodium carbonate extract was acidified with dilute hydrochloric acid, the solution during the process being kept in violent agitation, until the oil suddenly became solid. This was immediately collected, well washed, and spread on porous porcelain, and, when quite dry, [recrystallised from benzene, from which solvent it separated in light yellow needles, melting and decomposing at 108° :

0.1411 gave 0.3444 CO₂ and 0.0991 H₂O. C = 66.5; H = 7.8.

0.1516 „ 16.6 c.c. N₂ at 12° and 762 mm. N = 13.0.

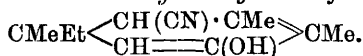
C₁₃H₁₈O₂N₂ requires C = 66.6; H = 7.7; N = 12.0 per cent.

A titration with *N*/10-sodium hydroxide gave the following results :

0.2698 required 0.0454 NaOH, whereas the same weight of a monobasic acid, C₁₃H₁₈O₂N₂, requires 0.0461 NaOH.

6-*Imino-3-cyano-1:2:4-trimethyl-4-ethyl- Δ^1 -cyclohexene-3-carboxylic acid* is soluble in benzene or alcohol, but sparingly so in light petroleum; it decomposes slowly in contact with the air. Its solution in alcohol becomes deep brown on the addition of ferric chloride. It also dissolves at once in concentrated hydrochloric acid, which effects the hydrolysis of the imino-group.

3-*Cyano-1:2:4-trimethyl-4-ethyl- $\Delta^{1:5}$ -cyclohexadien-6-ol*,



The imino-compound just described was dissolved in cold concentrated hydrochloric acid, and, after twelve hours, the solution was diluted by adding twice its volume of water and digested for two hours in a reflux apparatus; carbon dioxide was evolved and an oily layer appeared on the top of the liquid. This was extracted with ether, evaporated, and distilled under diminished pressure, when almost the whole passed over at 193–194°/18 mm. as a colourless oil. The product was now insoluble in cold sodium carbonate, although it dissolved slightly on boiling; the oil dissolved at once in potassium hydroxide when sufficiently dilute, forming a yellow solution, but the potassium salt is only sparingly soluble in concentrated alkali:

0.1002 gave 0.2780 CO₂ and 0.0782 H₂O. C = 75.6; H = 8.7.

0.1136 „ 7.5 c.c. N₂ at 18° and 758 mm. N = 7.6.

C₁₂H₁₇ON requires C = 75.4; H = 8.9; N = 7.3 per cent.

The substance is an oil with an odour resembling that of a nitrile; its solution in alcohol gives a dark red coloration with ferric chloride. It readily forms a *benzoyl* derivative, but as this showed no signs of crystallising it was distilled under diminished pressure, when it boiled constantly at about 250°/40 mm., and gave the following numbers on analysis:

0.1177 gave 0.3307 CO₂ and 0.0749 H₂O. C = 76.7; H = 7.1.

C₁₉H₂₁O₂N requires C = 77.3; H = 7.1 per cent.

The benzoyl derivative is insoluble in alkalis, and does not give a coloration with ferric chloride.

The *carbonate* of the hydroxy-acid was also prepared by leading a stream of carbonyl chloride into an aqueous solution of the potassium salt. An oil was precipitated, which was extracted with ether, and, as it did not solidify, was distilled under 25 mm. pressure, when it passed over at 260° as a viscid, colourless liquid:

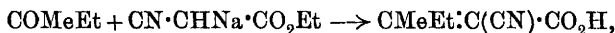
0.1203 gave 0.3228 CO₂ and 0.0866 H₂O. C = 73.2; H = 8.0.

C₅H₃₂O₃N₂ requires C = 73.5; H = 7.8 per cent.

β -Methyl- β -ethylacrylonitrile, CMeEt:CH:CN.

By a modification of the method employed in the condensation of equimolecular quantities of methyl ethyl ketone and ethyl sodiocyanoacetate described above (p. 1959), an oily mixture was obtained which could not be crystallised; it is explained below that this was due to the course of the initial reaction having proceeded in a rather different direction. In the former preparation care was taken to bring together the reacting substances in such a way as to produce as vigorous a reaction as possible at the beginning; but if on the other hand the reagents are allowed to cool before mixing, and the initial stage of the condensation is thus rendered less violent, the oil which is precipitated from the sodium carbonate solution by mineral acid does not crystallise.

Subsequent investigation showed that the course which the reaction follows under these conditions is:



whilst at the same time a small quantity of 6-imino-3-cyano-1:2:4-trimethyl-4-ethyl- Δ^1 -cyclohexene-3-carboxylic acid (p. 1959) is also formed. This was demonstrated by submitting the oily mixture of acids to fractional distillation under diminished pressure; the process is accompanied by the elimination of carbon dioxide and the formation of an oil possessing the disagreeable odour of a nitrile, which passed over at 95—105°/100 mm. in the first instance. A further small fraction was collected at 180°/150 mm. The lower boiling fraction consisted of *β -methyl- β -ethylacrylonitrile*, which was further purified by repeated distillation, and then analysed:

0.1308 gave 17.1 c.c. N_2 at 16° and 743 mm. $\text{N} = 14.9$.

$\text{C}_6\text{H}_9\text{N}$ requires $\text{N} = 14.7$ per cent.

β -Methyl- β -ethylacrylonitrile is a colourless, mobile liquid, which distils at 101°/100 mm.

The higher boiling fraction gradually solidified, and, after draining on porous porcelain, was recrystallised from benzene, from which solvent it separates in long needles melting at 184°. The investigation of this substance is not yet complete; it seems to possess a high molecular weight and a rather complex constitution:

0.1789 gave 0.4647 CO_2 and 0.0929 H_2O . $\text{C} = 70.8$; $\text{H} = 5.8$.

0.1211 „ 16.6 c.c. N_2 at 16° and 756 mm. $\text{N} = 15.9$.

After the fractionation a considerable residue remained behind in the flask, which was found to have crystallised; this on purification melted at 108°, and was identified as the iminocarboxylic acid of this melting point.

β -Methyl- β -ethylacrylic Acid, $\text{CMeEt}\cdot\text{CH}\cdot\text{CO}_2\text{H}$.

The hydrolysis of β -methyl- β -ethylacrylonitrile is best carried out by digesting it for twenty-four hours with 20 per cent. alcoholic sulphuric acid, when, on cooling, crystals of ammonium sulphate separate out. The product was poured into water, extracted with ether, the ethereal solution well washed with water, and then evaporated. The residual oil was digested for a few minutes with methyl-alcoholic potash, then poured into water, and the neutral portion extracted with ether. The aqueous solution was acidified, when an oil separated, which was dissolved in ether, and the ethereal solution was dried and evaporated; the residue distilled at 208° under the ordinary pressure:

0.1143 gave 0.2640 CO_2 and 0.0900 H_2O . $\text{C} = 63.0$; $\text{H} = 8.8$.

$\text{C}_6\text{H}_{10}\text{O}_2$ requires $\text{C} = 63.2$; $\text{H} = 8.8$ per cent.

A titration with $N/10$ -sodium hydroxide gave the following result: 0.2042 required 0.0720 NaOH , whereas the same weight of a monobasic acid, $\text{C}_6\text{H}_{10}\text{O}_2$, requires 0.0717 NaOH .

β -Methyl- β -ethylacrylic acid is a colourless, mobile liquid, possessing an odour characteristic of olefinic acids; it is sparingly soluble in water, and a solution of its sodium salt instantly decolorise permanganate.

The *anilide* is a colourless substance melting at 93 — 94° :

0.0800 gave 5.4 c.c. N_2 at 20° and 752 mm. $\text{N} = 7.6$.

$\text{C}_{12}\text{H}_{15}\text{ON}$ requires $\text{N} = 7.4$ per cent.

Oxidation.—About 5 grams of the acid were dissolved in excess of dilute sodium carbonate in presence of powdered ice, and a 1 per cent. solution of potassium permanganate was slowly added. As soon as the oxidation was complete, the product was subjected to steam distillation, when an oil having the odour of a ketone passed over and was salted out from the distillate and extracted with ether. After removal of the ether, an oil, boiling at about 80° , remained, which was easily identified as methyl ethyl ketone by its general properties and by the melting point of its semicarbazone.

5-Imino-2-cyano-1 : 3-dimethyl-6-ethyl-3-propyl- Δ^6 -cyclohexene-

2-carboxylic Acid, $\text{CMePr} \begin{array}{c} \text{C}(\text{CN})(\text{CO}_2\text{H})\cdot\text{CMe} \\ \text{CH}_2\text{---}\text{C}(\text{:NH}) \end{array} \text{CEt}$.

A hot solution of sodium (5.7 grams) in alcohol was treated with ethyl cyanoacetate (28 grams), and, after the separation of ethyl sodio-cyanoacetate, methyl propyl ketone (21.5 grams) was quickly added to the hot mixture. The reaction proceeded as before, and the product was worked up as described in the previous cases. The amount of

neutral oil formed was too small to investigate; the acid separated from the sodium carbonate extract as an oil, which, on stirring, soon solidified. It was collected, washed, drained on a porous tile, and then recrystallised from benzene, in which solvent it is almost insoluble in the cold; it separates in glistening leaflets, melting and decomposing at 113—114°:

0.1672 gave 0.4226 CO₂ and 0.1290 H₂O. C = 68.9; H = 8.6.

0.1504 „ 13.7 c.c. N₂ at 13° and 746 mm. N = 10.6.

C₁₅H₂₂O₂N₂ requires C = 68.7; H = 8.4; N = 10.7 per cent.

A titration with *N*/10-sodium hydroxide gave the following results: 0.3160 required 0.0479 NaOH, whereas the same weight of a monobasic acid, C₁₅H₂₂O₂N₂, requires 0.0482 NaOH.

The imino-acid decomposes slowly on exposure to the air; it is readily soluble in alcohol or hot benzene, but only sparingly so in light petroleum. Concentrated hydrochloric acid dissolves it at once, effecting the hydrolysis of the imino-group and the production of the corresponding hydroxy-acid. The addition of ferric chloride to a little of the acid dissolved in alcohol causes the precipitation of a brown substance.

β-Methyl-β-propylacrylonitrile, CMePr·CH·CN.

By moderating the conditions of the experiment described above, so as to produce a less energetic reaction, an oily mixture of acids, similar in constitution to that obtained under parallel conditions in the case of methyl ethyl ketone (p. 1961), was precipitated from the sodium carbonate solution. The oil was dissolved in ether as before, and the oily residue, after evaporation, was slowly distilled under diminished pressure, when almost the whole passed over between 90° and 100°/30 mm. The initial product of the condensation is doubtless α-cyano-β-methyl-β-propylacrylic acid, which readily passes on distillation into *β-methyl-β-propylacrylonitrile*. This is a light, colourless oil, possessing the pungent odour characteristic of nitriles, and boiling at 95—96°/30 mm.:

0.1530 gave 17.4 c.c. N₂ at 12° and 748 mm. N = 13.2.

C₇H₁₁N requires N = 12.8 per cent.

β-Methyl-β-propylacrylic Acid, CMePr·CH·CO₂H.

The nitrile just described was readily hydrolysed by digesting it for eighteen hours with 20 per cent. alcoholic sulphuric acid, and subsequently treating the ester thus formed with methyl-alcoholic potash (see p. 1962). On acidifying the solution of the potassium salt, an oil was obtained which distilled at 222—225° under ordinary pressure. This acid is a mobile, colourless liquid, having the odour of fatty acid

a solution of its sodium salt decolorised permanganate instantly; it also combines freely with bromine in a chloroform solution:

0.1265 gave 0.3019 CO_2 and 0.1058 H_2O . $\text{C} = 65.1$; $\text{H} = 9.3$.

$\text{C}_7\text{H}_{12}\text{O}_2$ requires $\text{C} = 65.6$; $\text{H} = 9.4$ per cent.

β -Methyl- β -hexylacrylonitrile and β -Methyl- β -hexylacrylic Acid,
 $\text{C}_6\text{H}_{13} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{H}$.

Sodium (4.6 grams), dissolved in alcohol, was mixed with ethyl cyanoacetate (22.6 grams), and to the hot solution methyl hexyl ketone (26 grams) was added, and the product worked up as described in previous cases (p. 1959). In this example, no solid acid was isolated in the first instance, so that the oil was subjected to fractional distillation under 100 mm. pressure, when carbon dioxide was eliminated, and a large fraction of oil was collected at about 130° . A considerable residue remained behind in the flask, and a portion of this afterwards solidified (see below). The distillate was further purified, and, on analysis, gave numbers agreeing with the formula of *β -methyl- β -hexylacrylonitrile*:

0.1220 gave 9.8 c.c. N_2 at 15° and 762 mm. $\text{N} = 9.4$.

$\text{C}_{10}\text{H}_{17}\text{N}$ requires $\text{N} = 9.3$ per cent.

This nitrile was digested for eighteen hours with 20 per cent. alcoholic sulphuric acid, and the resulting ester treated with methyl-alcoholic potash. On acidifying the alkaline solution after adding water, an oily acid was obtained which distilled constantly at $158^\circ/20$ mm. *β -Methyl- β -hexylacrylic acid* is a colourless oil, possessing an olefinic odour, and when dissolved in sodium carbonate it decolorises permanganate at once:

0.1560 gave 0.4030 CO_2 and 0.1502 H_2O . $\text{C} = 70.4$; $\text{H} = 10.7$.

$\text{C}_{10}\text{H}_{18}\text{O}_2$ requires $\text{C} = 70.6$; $\text{H} = 10.6$ per cent.

To determine its basicity, the acid was titrated with $N/10$ -sodium hydroxide: 0.1860 required 0.0431 NaOH , whereas the same weight of a monobasic acid, $\text{C}_{10}\text{H}_{18}\text{O}_2$, requires 0.0435 NaOH .

5-Imino-2-cyano-1:3-dimethyl-6-amyl-3-hexyl- Δ^6 -cyclohexene-2-

carboxylic Acid, $\text{C}_6\text{H}_{11} \cdot \text{CMe} \begin{array}{c} \text{C}(\text{CN})(\text{CO}_2\text{H}) \cdot \text{CMe} \\ \text{CH}_2 \text{---} \text{C}(\text{NH}) \end{array} \text{C} \cdot \text{C}_5\text{H}_9$.

It is mentioned above that the residue remaining in the flask after the distillation of the product obtained from the condensation of methyl hexyl ketone partly solidified, and this solid was found to be an acid. It was further purified by dissolving in sodium carbonate and reprecipitating with mineral acid, when a solid separated. This was collected and drained on porous porcelain, and then recrystallised from methyl alcohol, from which solvent it

separates in almost colourless leaflets, melting and decomposing at 136—137°. The analytical results indicate that it is an iminocyclohexenecarboxylic acid, analogous to those previously described on p. 1959, and, like these, it is unstable towards permanganate

0.1181 gave 0.3165 CO₂ and 0.1009 H₂O. C=73.1; H=9.5.

0.1172 „ 8.5 c.c. N₂ at 15° and 760 mm. N=8.4.

C₂₁H₃₄O₂N₂ requires C=72.8; H=9.8; N=8.1 per cent.

Hydrochloric acid effects the hydrolysis of the imino-group, forming the corresponding hydroxycarboxylic acid.

α-Cyano-ββ-diethylacrylic Acid, C₈H₁₁O₂N·CO₂H.

Ethyl sodiocyanoacetate was prepared by treating ethyl cyanoacetate (28 grams) with sodium (5.7 grams) dissolved in alcohol, adding diethyl ketone (21.5 grams) to the hot mixture, and boiling the whole for two hours on the water-bath. The reaction proceeded rather more slowly than in experiments with other ketones, and the yield of oil obtained from the sodium carbonate solution was much smaller. The product was worked up exactly as in other cases, and, after some days, the oily acid deposited large crystals, which were pressed on a porous tile and, when free from oil, recrystallised from light petroleum, from which the substance separated in colourless, elongated prisms melting at 55°. *α-Cyano-ββ-diethylacrylic acid* is sparingly soluble in light petroleum, very soluble in benzene, ethyl acetate, or alcohol.

A titration showed it to be monobasic: 0.1374 required 0.0360 NaOH, whereas the same weight of a monobasic acid, C₈H₁₁O₂N, requires 0.0359 NaOH.

0.1474 gave 0.3431 CO₂ and 0.0964 H₂O. C=63.4; H=7.2.

0.1448 „ 11.2 c.c. N₂ at 13° and 758 mm. N=9.1.

C₈H₁₁O₂N requires C=62.7; H=7.2; N=9.1 per cent.

The above cyano-acid is decomposed on distillation with elimination of carbon dioxide and formation of *ββ-diethylacrylonitrile*, which is a colourless oil distilling at 90°/25 mm. We were unable through lack of material to prepare the corresponding *ββ-diethylacrylic acid* by hydrolysis of the nitrile:

0.1644 gave 19.0 c.c. N₂ at 16° and 745 mm. N=13.1.

C₇H₁₁N requires N=12.8 per cent.

We desire to express our indebtedness to Prof. W. H. Perkin for the interest he has taken in this investigation.

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