CLXIV.—*Some Alkyl Derivatives of Glutaconic Acid and of 2 : 6-Dihydroxypyridine.*

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THE reactive nature of the remaining hydrogen atom in the sodium compound of ethyl cyanoacetate has formed the subject of a number of previous communications, and in one of them (Trans., 1900, **77**, 923) it was suggested that this activity could be explained on the assumption that the sodium compound reacts in its enolic form, whereas the corresponding sodium derivative of ethyl malonate, which does not appear to be nearly so reactive, reacts in the ketonic form.

In the present communication, further experimental evidence is adduced which again illustrates the remarkable difference between the two sodium compounds. If the sodium derivative of ethyl malonate is boiled in alcoholic solution with ethyl acetoacetate for several hours, no condensation takes place, but if the ethyl sodiomalonate is replaced by the sodium compound of ethyl cyanoacetate, a 60 per cent. yield of a condensation product is obtained after heating for only twenty minutes.

On investigation, this condensation product proved to be ethyl α -cyano- β -methylglutaconate, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, and its mode of formation can be represented by either equation I, II, or III :

In equation I, the mobile hydrogen atom of ethyl sodiocyanoacetate forms an additive product with ethyl acetoacetate, water being subsequently eliminated to form the derivative of glutaconic acid; in equation II, the sodium derivative reacts directly with ethyl acetoacetate in its enolic form; and in equation III sodium hydroxide is eliminated.

It is difficult to decide between the first two equations, but for certain reasons we are inclined to think that equation II is the true representation of the course of this reaction.

If equation I were correct, it would be expected that ethyl dimethylacetoacetate would form a condensation product with ethyl sodiocyanoacetate in accordance with the equation,

it was, however, found that on condensing these two substances together only a small quantity of an oil with a high boiling point was obtained which was too small for further investigation.

That equation III does not represent the course of the reaction is shown by the fact that the sodium compound of ethyl acetoacetate, although reacting to a certain extent with ethyl cyanoacetate to form the above condensation product, gives only a small yield, and at the same time other products are formed, from which it is difficult to separate pure ethyl α -cyano- β -methylglutaconate.

So long as one of the methylene hydrogen atoms in ethyl acetoacetate remains unsubstituted, that is, so long as it is capable of reacting in an enolic form, it possesses the power of combining with ethyl sodiocyanoacetate in the foregoing manner.

The glutaconic acid derivative is produced in the first stage of the condensation, and its formation is usually complete after heating the

condensation mixture for twenty to thirty minutes on the water-bath, after this time it slowly disappears and is replaced by products of higher boiling point, which are under investigation.

Alkyl derivatives of ethyl sodiocyanoacetate, for example, ethyl sodiomethylecyanoacetate, do not react with ethyl acetoacetate or its monoalkyl derivatives to form condensation products.

Condensation of Ethyl Sodiocyanoacetate with Ethyl Acetoacetate.

Formation of Ethyl α -cyano- β -methylglutaconate,

This substance is most conveniently prepared in the following manner: 23 grams of sodium are dissolved in 70 grams of alcohol and mixed with 113 grams of ethyl cyanoacetate, 130 grams of ethyl acetoacetate being subsequently added. The white sodium compound of ethyl cyanoacetate, which is in the first instance precipitated, immediately dissolves on the addition of the ethyl acetoacetate, and the solution becomes deep yellow. The mixture is then heated on the water-bath for half an hour, after which time the contents of the flask will have become almost solid owing to the separation of the sodium compound of the above ethyl salt. Care must be taken that the length of time during which the mixture is heated does not exceed a half, or at most three-quarters of an hour, since the above sodium salt re-dissolves on further heating, being transformed into products of higher molecular weight.

The partially solid contents of the flask are now mixed with water, when a clear solution is obtained which, on acidifying with dilute hydrochloric acid, deposits an oil; this is extracted by means of ether, the ethereal solution being washed with water and with sodium carbonate solution, dried, and the ether evaporated. The oil which then remains is fractionated under diminished pressure and the fraction passing over at 170—172°/25 mm. is collected.

0.2044 gave 0.4390 CO_2 and 0.1301 H_2O . $\text{C} = 58.57$; $\text{H} = 7.07$.

$\text{C}_{11}\text{H}_{15}\text{O}_4\text{N}$ requires $\text{C} = 58.6$; $\text{H} = 6.7$ per cent.

Ethyl α -cyano- β -methylglutaconate, prepared in this way, is a colourless oil, and is obtained in quantities representing 60 per cent. of the theoretical. The more volatile fraction consists of almost pure ethyl acetoacetate and can be used again for another condensation.

The sodium carbonate extract from the ethereal solution gave a small quantity of oil on acidifying. This, which evidently consists of the hydrogen ethyl salt, $\text{CO}_2\text{H} \cdot \text{CH}(\text{CN}) \cdot \text{CMe} : \text{CH} \cdot \text{CO}_2\text{Et}$, was extracted, and without being further purified, distilled under the ordinary pressure, when carbon dioxide was eliminated and ethyl γ -cyano- β -methylcrotonate,

$\text{CH}_2(\text{CN})\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, passed over at 250° as a colourless, mobile oil. [View Online](#)

0.2113 gave 0.4836 CO_2 and 0.1337 H_2O . $\text{C} = 62.42$; $\text{H} = 7.03$.

$\text{C}_8\text{H}_{11}\text{O}_2\text{N}$ requires $\text{C} = 62.7$; $\text{H} = 7.2$ per cent.

Hydrolysis of Ethyl α -Cyano- β -methylglutaconate.

- (1) *With Hydrochloric Acid.* Formation of Ethyl 4-Methyl-2:6-dihydroxy-pyridine-5-carboxylate, $\text{N} \begin{smallmatrix} \text{C}(\text{OH})\cdot\text{C}(\text{CO}_2\text{Et}) \\ \text{C}(\text{OH})\text{---CH} \end{smallmatrix} \text{CMe}$, 4-Methyl-2:6-dihydroxypyridine, $\text{N} \begin{smallmatrix} \text{C}(\text{OH})\cdot\text{CH} \\ \text{C}(\text{OH})\cdot\text{CH} \end{smallmatrix} \text{CMe}$, and of β -Methylglutaconic Acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$.

Ethyl 4-Methyl-2:6-dihydroxypyridine-5-carboxylate.—Ethyl α -cyano- β -methylglutaconate slowly dissolves on boiling in a Geissler flask with concentrated hydrochloric acid, and if when all has passed into solution the liquid is cooled, a crystalline substance separates. This, when collected, dried on a porous plate, and recrystallised from glacial acetic acid, is obtained in the form of large, colourless prisms which melt at 218° .

0.2135 gave 0.4300 CO_2 and 0.1123 H_2O . $\text{C} = 54.91$; $\text{H} = 5.80$.

$\text{C}_9\text{H}_{11}\text{O}_4\text{N}$ requires $\text{C} = 54.8$; $\text{H} = 5.6$ per cent.

Ethyl 4-methyl-2:6-dihydroxypyridine-5-carboxylate gives in alcoholic solution a deep purple colour with ferric chloride. It is readily soluble in concentrated hydrochloric acid, and on standing the solution deposits the *hydrochloride* in the form of long, feathery needles, which on warming give off hydrogen chloride, regenerating the ethyl salt. It is instantly dissociated by cold water.

The ethyl salt is insoluble in aqueous sodium carbonate, but dissolves slowly in caustic alkalis, the solution depositing a sparingly soluble alkali salt on standing. It is insoluble in water, but appreciably soluble in hot alcohol.

The *isonitroso-derivative (oxime)*, $\text{CMe} \begin{smallmatrix} \text{C}(\text{CO}_2\text{Et})\text{---CO} \\ \text{C}(\text{NOH})\text{---CO} \end{smallmatrix} \text{NH}$, is formed by dissolving the pyridine derivative in glacial acetic acid and pouring the solution into water containing a slight excess of sodium nitrite. Yellow needles separate which can be freed from unchanged ethyl salt by washing with concentrated hydrochloric acid, in which they are insoluble. Recrystallised from absolute alcohol, they melt and blacken at 160° .

0.2165 gave 0.3769 CO_2 and 0.0895 H_2O . $\text{C} = 47.52$; $\text{H} = 4.59$.

$\text{C}_9\text{H}_{10}\text{O}_5\text{N}_2$ requires $\text{C} = 47.8$; $\text{H} = 4.4$ per cent.

The oxime dissolves in a solution of sodium carbonate, forming a violet-red solution, from which a sodium salt is slowly deposited in the form of green plates. It gives in neutral solution a deep greenish-blue coloration with ferrous sulphate.

4-Methyl-2:6-dihydroxypyridine.—When ethyl 4-methyl-2:6-dihydroxypyridine-5-carboxylate is boiled in a flask fitted with a reflux condenser with concentrated hydrochloric acid until a test portion on dilution with water no longer immediately deposits any crystalline precipitate of unchanged ethyl ester, it is completely hydrolysed to 4-methyl-2:6-dihydroxypyridine, the same compound being also formed on boiling ethyl α -cyano- β -methylglutaconate for twelve hours with the concentrated acid. Although the hydrochloride of this compound slowly separates from the cooled product of hydrolysis on standing, yet it was found more convenient to isolate the free pyridine derivative in the following way. The strongly acid product was first made alkaline with ammonia and then acidified with acetic acid, when the deep blue solution thus obtained almost instantly deposited a crystalline precipitate which was found to be complete after standing half an hour. On investigation, this proved to be the pyridine derivative, which, when recrystallised from water, in which it is fairly soluble, is obtained in the form of needles containing one molecule of water of crystallisation which melt at 194° .

0.2116 gave 0.3927 CO_2 and 0.1247 H_2O . $\text{C} = 50.62$; $\text{H} = 6.55$.

$\text{C}_6\text{H}_7\text{O}_2\text{N}, \text{H}_2\text{O}$ requires $\text{C} = 50.3$; $\text{H} = 6.2$ per cent.

A specimen dried in an air-bath at 110° gave the following result on analysis:

0.1163 lost 0.0145 on heating to constant weight. $\text{H}_2\text{O} = 12.46$.

$\text{C}_6\text{H}_7\text{O}_2\text{N}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 12.58$ per cent.

The anhydrous pyridine derivative is best prepared by crystallising this hydrate from absolute alcohol, from which solvent it separates in the form of small, glistening plates.

0.2224 gave 0.4680 CO_2 and 0.1144 H_2O . $\text{C} = 57.38$; $\text{H} = 5.71$.

$\text{C}_6\text{H}_7\text{O}_2\text{N}$ requires $\text{C} = 57.6$; $\text{H} = 5.6$ per cent.

The water of crystallisation does not, however, affect the melting point, and both the hydrated and anhydrous compounds melt at 194° ; the water is therefore evidently eliminated from the former without causing it to become liquid.

4-Methyl-2:6-dihydroxypyridine boils at 305° (765 mm.) without undergoing appreciable decomposition, and possesses both acid and basic properties. It dissolves in alkaline carbonates and in caustic alkalis, forming salts which contain one equivalent of the metal.

0.2310 requires 18.4 c.c. of normal NaOH solution.

$C_6H_7O_2N$ (monobasic) requires 18.5 c.c.

There are indications that a disodium salt is formed on dissolving the pyridine derivative in excess of caustic soda, but we were unable to prepare it sufficiently pure for analysis; from the foregoing analysis, it is evident that it must possess an alkaline reaction.

The pyridine derivative slowly reduces an ammoniacal solution of silver nitrate in the cold, and on warming a mirror of metallic silver is immediately produced. In alcoholic solution, it gives a deep reddish-violet colour with ferric chloride, which disappears on boiling. When exposed to the air, the dihydroxypyridine slowly oxidises, forming a soluble blue compound; this change is more rapid when the ammonium salt is exposed to the action of air at 100°. It behaves as a meta-dihydric phenol, and gives a blue fluorescent phthalein when fused with phthalic anhydride; it, moreover, combines with diazo-salts, forming yellow colouring matters. These products are still under investigation.

4-Methyl-2:6-dihydroxypyridine withstands prolonged boiling with concentrated hydrochloric acid, and can be fused with caustic potash without undergoing change; it is formed in the complete hydrolysis of ethyl α -cyano- β -methylglutaconate to the extent of about 80 per cent. of the theoretical quantity.

Towards concentrated mineral acids, it behaves as a mono-acid base; the salts formed are, however, unstable in aqueous solution.

The *hydrochloride*, $C_6H_7O_2N \cdot HCl$, separates from a solution of the dihydroxypyridine in concentrated hydrochloric acid in the form of long, colourless needles.

0.2101 gave 0.1837 AgCl. $Cl = 21.69$.

$C_6H_7O_2N \cdot HCl$ requires $Cl = 21.9$ per cent.

It is soluble in cold water, but is almost immediately dissociated, the free dihydroxypyridine separating from the solution.

The *sulphate* separates from a solution of the base in 50 per cent. sulphuric acid in the form of long, silky needles. Like the hydrochloride, it is dissociated by cold water.

The *dibenzoyl* derivative, $C_6H_5O_2N(COPh)_2$, is best prepared by the Schotten-Baumann method, which consists in dissolving the dihydroxypyridine in dilute (10 per cent.) sodium hydroxide solution, adding excess of benzoyl chloride, and stirring until the odour of benzoyl chloride ceases to be apparent. The solid residue is then filtered and recrystallised from absolute alcohol, from which solvent it separates in the form of microscopic needles melting at 94°.

0.2053 gave 0.5436 CO_2 and 0.0860 H_2O . $C = 72.21$; $H = 4.65$.

$C_{20}H_{15}O_4N$ requires $C = 72.1$; $H = 4.5$ per cent.

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The isonitroso-derivative (*oxime*), $\text{CMe} \begin{array}{c} \text{CH} \text{---} \text{CO} \\ \diagdown \quad \diagup \\ \text{C}(\text{:NOH}) \cdot \text{CO} \end{array} \text{NH}$, is formed as a yellow, crystalline precipitate on pouring a solution of the pyridine derivative in aqueous caustic soda containing excess of sodium nitrite into dilute acetic acid. Recrystallised from water, it forms small, yellow prisms which melt and blacken at 178° .

0.1583 gave 0.2721 CO_2 and 0.0587 H_2O . $\text{C} = 46.88$; $\text{H} = 4.12$.

$\text{C}_6\text{H}_6\text{O}_3\text{N}_2$ requires $\text{C} = 46.7$; $\text{H} = 3.9$ per cent.

The oxime dissolves in aqueous sodium carbonate, forming a magenta-red solution from which the sodium salt is slowly deposited in the form of red needles. With ferrous sulphate, in neutral solution, it gives an intense green coloration, the liquid, on standing, yielding a green precipitate.

β -Methylglutaconic Acid.

This acid, which is only formed to the extent of about 5 per cent. of that theoretically possible from the amount of ethyl α -cyano- β -methylglutaconate hydrolysed, can be obtained from the mother liquors on evaporating them to dryness and extracting the residue with ether. Since, however, the liquor contained free acetic acid, the residue was heated on the water-bath until the odour of the acid was no longer apparent, when hydrochloric acid was added and the product again evaporated to dryness; this was found to be necessary, since acetic acid does not completely decompose the alkali salt of the glutaconic acid.

On extraction with ether, a solid acid was obtained which, after recrystallising from concentrated hydrochloric acid, melted sharply at 149° , giving off water at 180° with formation of the anhydride; the acid crystallises in the form of small, lustrous plates.

0.2216 gave 0.4086 CO_2 and 0.1196 H_2O . $\text{C} = 50.3$; $\text{H} = 5.9$.

$\text{C}_6\text{H}_8\text{O}_4$ requires $\text{C} = 50.0$; $\text{H} = 5.6$ per cent.

β -Methylglutaconic acid instantly decolorises a solution of permanganate in sodium hydrogen carbonate solution.

The silver salt, $\text{C}_6\text{H}_6\text{O}_4\text{Ag}_2$, is formed as a white, insoluble precipitate when the calculated quantity of a solution of silver nitrate is added to a neutral solution of the ammonium salt of the acid.

0.3121 gave 0.1876 Ag on ignition. $\text{Ag} = 60.11$.

$\text{C}_6\text{H}_6\text{O}_4\text{Ag}_2$ requires $\text{Ag} = 60.2$ per cent.

The anhydride, $\text{CMe} \begin{array}{c} \text{CH}_2 \text{---} \text{CO} \\ \diagdown \quad \diagup \\ \text{CH} \cdot \text{CO} \end{array} \text{O}$, is best prepared by boiling the

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acid with excess of acetyl chloride until hydrogen chloride ceases to be evolved. On evaporating the acetyl chloride, the anhydride remains as an oil which quickly solidifies. Recrystallised from light petroleum (b. p. 40—60°) it is obtained in the form of fine, colourless needles which melt at 86°.

0.2118 gave 0.4426 CO₂ and 0.0876 H₂O. C = 57.00; H = 4.59.

C₆H₆O₃ requires C = 57.1; H = 4.8 per cent.

The conversion of the acid into the anhydride by this means is complete and no trace of unchanged acid is mixed with the anhydride. On boiling the anhydride with sodium carbonate solution for a short time it passes into solution, and, on acidifying and extracting, the original acid melting at 149° is obtained.

The *anilic acid*, CONHPh·CH₂·CMe·CH·CO₂H, is prepared by adding a solution of the anhydride in benzene to a benzene solution of aniline; no precipitate is formed on standing, and the product must be isolated by evaporating off the benzene and rubbing the residue with dilute hydrochloric acid. The solid produced in this way crystallises from benzene in the form of glistening plates which melt at 143°.

0.2132 gave 0.5150 CO₂ and 0.1093 H₂O. C = 65.88; H = 5.69.

C₁₂H₁₃O₃N requires C = 65.7; H = 5.9 per cent.

The anilic acid dissolves in a solution of sodium carbonate.

Transformation of β-Methylglutaconic Acid into 4-Methyl-2:6-Dihydroxypyridine.

In order to bring about this change, β-methylglutaconic acid was converted into its ammonium salt by adding ammonia to a solution of the acid in water and evaporating to dryness. The dried ammonium salt was then distilled under 500 mm. pressure, when an oil passed over at 270—275° which rapidly solidified. Recrystallised from absolute alcohol, it was obtained in the form of small plates melting at 194°, and was in every way identical with 4-methyl-2:6-dihydroxypyridine already described.

- (2) *With Sulphuric Acid. Formation of Ethyl α-Carbethoxy-β-methylglutaconamide*, CONH₂·CH(CO₂Et)·CMe·CH·CO₂Et, *and of Ethyl 4-Methyl-2:6-dihydroxypyridine-5-carboxylate.*

When ethyl α-cyano-β-methylglutaconate is treated with an equal volume of concentrated sulphuric acid and the solution allowed to become as hot as it will, it is rapidly transformed into ethyl 4-methyl-2:6-dihydroxypyridine-5-carboxylate, already described. This transformation

is complete after one hour, and the pyridine derivative can be isolated by adding water and filtering. If, however, the ethyl ester is mixed with twice its volume of concentrated acid and the mixture allowed to stand (without cooling) for fifteen minutes, the above amide is obtained as a white precipitate on pouring the product into water. The substance prepared in this way always, however, contains traces of the pyridine derivative, but it can be freed from this by washing with concentrated hydrochloric acid, in which the amide is insoluble. The product purified in this way crystallises from glacial acetic acid in the form of small, transparent prisms, which melt at 181° with evolution of gas, resolidify a few degrees higher, and then melt again at 218° :

0.1492 gave 0.2978 CO_2 and 0.0909 H_2O . $\text{C} = 54.43$; $\text{H} = 6.77$.

$\text{C}_{11}\text{H}_{17}\text{O}_5\text{N}$ requires $\text{C} = 54.3$; $\text{H} = 7.0$ per cent.

The amide gives no colour with ferric chloride, and is insoluble in strong mineral acids. It is insoluble in cold alkalis, but dissolves on warming, undergoing at the same time partial hydrolysis.

Conversion of Ethyl α -Carbethoxy- β -methylglutaconamide into Ethyl 4-Methyl-2:6-dihydroxypyridine-5-carboxylate.

Ten grams of the amide were heated in a flask fitted with a condenser in an oil-bath at 190° until the evolution of gas had ceased, the gas formed being removed from the flask by means of a current of air. When the contents of the flask had completely solidified, the distillate was tested and found to consist of nearly pure alcohol. The solid residue was recrystallised from glacial acetic acid and found to be ethyl 4-methyl-2:6-dihydroxypyridine-5-carboxylate, melting at 218° .

(3) With Alcoholic Potash. Formation of 4-Methyl-2:6-dihydroxypyridine and of Malonic Acid.

Ethyl α -cyano- β -methylglutaconate is quickly hydrolysed by alcoholic potash, being almost entirely converted into 4-methyl-2:6-dihydroxypyridine; at the same time, however, there is formed a small quantity of malonic acid, but no trace of β -methylglutaconic acid. Ethyl α -carbethoxy- β -methylglutaconamide behaves in the same way, and the method adopted in the case of either of these compounds was as follows.

Ten grams were added to a solution containing one and a half times the calculated quantity of potash dissolved in methyl alcohol, and heated on the water-bath until the odour of ammonia which is first noticed ceases to be apparent. When the ethyl ester is first added to the alcoholic potash, a deep red solution is formed; this colour, on heating, gradually disappears, and when all the ammonia has been evolved the

solution is colourless. It was evaporated to dryness and the residue made strongly acid with hydrochloric acid and again evaporated to dryness. In order to effect the complete conversion of the pyridine into its hydrochloride, and thus prevent its being extracted by ether, this process was again repeated, hydrochloric acid being added and the mixture once more evaporated to dryness. The residue was then extracted with ether and the extracted acid spread on a porous plate; it melted at 132° and gave acetic acid on distillation.

0.2221 gave 0.2801 CO_2 and 0.0739 H_2O . $\text{C} = 34.39$; $\text{H} = 3.69$.

$\text{C}_3\text{H}_4\text{O}_4$ requires $\text{C} = 34.6$; $\text{H} = 3.8$ per cent.

The quantity of this acid formed is very small, about 2 grams being obtained from 20 grams of ethyl ester. No trace of β -methylglutaconic acid could be found accompanying the malonic acid, and it is evident that it is not formed under these experimental conditions.

The residue left after the extraction with ether consisted of the hydrochloride of 4-methyl-2:6-dihydroxypyridine mixed with inorganic salts. The free pyridine derivative was isolated by dissolving the mixture in water, making alkaline with ammonia, and then acidifying with acetic acid, when it slowly separated from the solution.

(4) *With Aqueous Potash. Formation of the Potassium Compound*
 $\text{CO}_2\text{Et} \cdot \text{CK}(\text{CN}) \cdot \text{CMc} \cdot \text{CH} \cdot \text{CO}_2\text{Et}$.

When ethyl α -cyano- β -methylglutaconate is added to cold aqueous caustic potash, it almost instantly dissolves, forming a clear, yellow solution, from which a copious precipitate of the above potassium compound separates on standing. The best method for preparing this compound in large quantities was found to be as follows: 100 grams of ethyl α -cyano- β -methylglutaconate were added quickly, with constant stirring, to 500 c.c. of an aqueous solution containing 150 grams of caustic potash. The ethyl ester dissolved without appreciable rise of temperature, and almost immediately the contents of the beaker became nearly solid owing to the separation of the potassium compound. This was filtered at the pump, washed with a little cold alcohol, and dried on a porous plate. For the purposes of analysis, a small quantity was recrystallised from alcohol, from which solvent it separated in the form of small needle clusters, usually of a lemon-yellow colour.

0.2413 gave 0.0791 K_2SO_4 . $\text{K} = 14.69$.

$\text{C}_{11}\text{H}_{14}\text{O}_4\text{NK}$ requires $\text{K} = 14.8$ per cent.

The potassium compound melts at high temperature to a red liquid.

It dissolves in water without undergoing decomposition, and on acidifying the solution the original ethyl ester is immediately precipitated.

Formation of Ethyl α -Cyano- $\alpha\beta$ -dimethylglutaconate, $\text{CO}_2\text{Et}\cdot\text{CMe}(\text{CN})\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, from the Potassium Compound.

In order to prepare this ethyl ester, 100 grams of the potassium compound, formed as described above, were mixed with cold absolute alcohol in a flask fitted with a condenser and treated with excess of methyl iodide, the whole being heated on the water-bath for two hours. Water was then added and the oil which separated extracted by means of ether. On evaporating the ether from the dried solution, an oil was obtained which on distillation under diminished pressure passed over constantly at 167° (25 mm.) as a colourless oil :

- I. 0.2066 gave 0.4552 CO_2 and 0.1384 H_2O . $\text{C} = 60.08$; $\text{H} = 7.43$.
 II. 0.1743 „ 0.3877 CO_2 and 0.1169 H_2O . $\text{C} = 60.3$; $\text{H} = 7.4$.
 $\text{C}_{12}\text{H}_{17}\text{O}_4\text{N}$ requires $\text{C} = 60.2$; $\text{H} = 7.1$ per cent.

The same ethyl ester can be also prepared by treating the sodium compound formed in the condensation of ethyl sodiocyanoacetate with ethyl acetoacetate directly with excess of methyl iodide, but it was found that by this means the conversion was not quite complete, small quantities of unchanged ethyl ester always accompanying the methylated product. This impurity cannot be removed by fractional distillation, and when the pure methylated ethyl ester is desired it is better to produce it through the potassium compound in the manner described above ; if, however, the ethyl ester is required for the production of further alkylated products, the second method will be found to yield a compound sufficiently pure for the purpose, and the latter process in this case is to be recommended, since the inevitable loss entailed in working through the pure potassium compound is not then experienced. An analysis of the product prepared by direct methylation gave the following figures :

- 0.2061 gave 0.4527 CO_2 and 0.1339 H_2O . $\text{C} = 59.89$; $\text{H} = 7.21$.
 $\text{C}_{12}\text{H}_{17}\text{O}_4\text{N}$ requires $\text{C} = 60.2$; $\text{H} = 7.1$ per cent.
 $\text{C}_{11}\text{H}_{15}\text{O}_4\text{N}$ „ $\text{C} = 58.6$; $\text{H} = 6.7$ „

Accordingly, the quantity of unchanged ethyl ester is extremely small.

Pure ethyl α -cyano- $\alpha\beta$ -dimethylglutaconate does not dissolve in cold aqueous caustic potash ; if, however, some unchanged ethyl α -cyano- β -methylglutaconate is present, the ethyl ester becomes partially solid owing to the formation of the potassium compound.

Hydrolysis of Ethyl α -Cyano- $\alpha\beta$ -dimethylglutaconate.

(1) *With Hydrochloric Acid.* Formation of 4:5-dimethyl-2:6-dihydroxypyridine, $\text{CMe} \begin{smallmatrix} \text{CMe} \cdot \text{C}(\text{OH}) \\ \text{CH} - \text{C}(\text{OH}) \end{smallmatrix} \text{N}$, and of $\alpha\beta$ -Dimethylglutaconic Acid, $\text{CO}_2\text{H} \cdot \text{CHMe} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CO}_2\text{H}$.

$\alpha\beta$ -Dimethylglutaconic Acid.—A considerable difference was noticed between the behaviour of ethyl α -cyano- $\alpha\beta$ -dimethylglutaconate towards hydrochloric acid and that of ethyl α -cyano- β -methylglutaconate already described.

When ethyl α -cyano- $\alpha\beta$ -dimethylglutaconate was boiled in a Geissler flask with concentrated hydrochloric acid, it slowly passed into solution, and after heating for three hours had completely dissolved.

On cooling, crystals separated which were collected, dried, and recrystallised from water. On examination they proved to be, not the pyridine derivative, but the above acid, which, when recrystallised from water, formed large, feather-like crystals which melted at 145° with immediate conversion into the anhydride. The acid, when dissolved in a solution of sodium hydrogen carbonate, instantly decolorised a solution of permanganate.

0.2059 gave 0.4041 CO_2 and 0.1201 H_2O . $\text{C} = 53.52$; $\text{H} = 6.48$.

$\text{C}_7\text{H}_{10}\text{O}_4$ requires $\text{C} = 53.2$; $\text{H} = 6.3$ per cent.

The *silver* salt, $\text{C}_7\text{H}_8\text{O}_4\text{Ag}_2$, is obtained as a white, amorphous precipitate on adding a solution of the calculated quantity of silver nitrate to a neutral solution of the ammonium salt of the acid.

0.2074 gave 0.1714 CO_2 , 0.0432 H_2O , and 0.1203 Ag . $\text{C} = 22.54$; $\text{H} = 2.31$; $\text{Ag} = 58.00$.

$\text{C}_7\text{H}_8\text{O}_4\text{Ag}_2$ requires $\text{C} = 22.64$; $\text{H} = 2.15$; $\text{Ag} = 57.94$ per cent.

The *anhydride*, $\text{CMe} \begin{smallmatrix} \text{CHMe} \cdot \text{CO} \\ \text{CH} - \text{CO} \end{smallmatrix} \text{O}$, is formed either by boiling the acid with acetyl chloride until hydrochloric acid ceased to be evolved, or by boiling it with acetic anhydride, in both cases the excess of the reagent being eliminated by evaporation in an evacuated desiccator over caustic potash. The anhydride which remained showed no tendency to solidify, and it was therefore subjected to distillation under diminished pressure, when the pure anhydride passed over at 163° (25 mm.) as a colourless, mobile oil which did not show any tendency to become solid even when cooled in a mixture of ice and salt. It must therefore be assumed that under ordinary conditions this compound is a liquid.

0.2057 gave 0.4510 CO₂ and 0.1036 H₂O. C = 59.79; H = 5.59. [View Online](#)

C₇H₈O₃ requires C = 60.0; H = 5.7 per cent.

The anhydride gives the acid from which it was derived on boiling with sodium carbonate solution and acidifying.

The *anilic acid*, CONHPh·CHMe·CMe·CH·CO₂H, is formed on adding a benzene solution of aniline to a solution of the anhydride in the same solvent and boiling. On cooling, the anilic acid separates as a white, insoluble precipitate, soluble in aqueous sodium carbonate. It is sparingly soluble in benzene, but separates from a large quantity of this solvent in the form of small needles which melt at 139°; it is better recrystallised from benzene containing a little alcohol.

0.2199 gave 0.5380 CO₂ and 0.1256 H₂O. C = 66.72; H = 6.34.

C₁₃H₁₅O₃N requires C = 66.9; H = 6.4 per cent.

The quantity of αβ-dimethylglutaconic acid formed in this way is about 35 per cent. of the theoretical amount possible from the ethyl ester hydrolysed.

4:5-Dimethyl-2:6-dihydroxypyridine.

This compound is formed in about the same quantities as αβ-dimethylglutaconic acid by the hydrolysis of ethyl α-cyano-αβ-dimethylglutaconate with hydrochloric acid, and was isolated in the following way.

After filtering the acid from the product of hydrolysis, the strongly acid filtrate was diluted with water and a solution of caustic soda added until only a faintly acid reaction was shown to litmus. An oil separated which solidified on scratching; this was collected, spread on a porous plate, and recrystallised from absolute alcohol, the pyridine derivative being in this way obtained in the form of small, colourless needles which melted at 189°.

0.1928 gave 0.4266 CO₂ and 0.1153 H₂O. C = 60.34; H = 6.64.

C₇H₉O₂N requires C = 60.4; H = 6.5 per cent.

4:5-Dimethyl-2:6-dihydroxypyridine is sparingly soluble in hot water, but can be recrystallised from this solvent if a sufficient quantity is used. The product prepared in this way does not, however, contain water of crystallisation. In alcoholic solution, it gives a deep red coloration with ferric chloride. The solid base does not exhibit any tendency to oxidise in the air, and combines with phthalic anhydride to form a blue, fluorescent dyestuff, and with the diazotised *p*-nitroaniline to form a yellow colouring matter. It reacts as a monobasic acid and as a monoacid base, the salts formed in the latter case being

unstable in aqueous solution. It reduces an ammoniacal solution of silver nitrate on warming, forming a mirror of metallic silver.

The *hydrochloride*, $C_7H_9O_2N, HCl$. The pyridine derivative dissolves instantly in concentrated hydrochloric acid, and, on standing, the solution deposits the hydrochloride in the form of slender needles which dissolve in cold water, but the solution immediately deposits the free base.

0.1825 gave 0.1478 AgCl. $Cl = 20.10$.

$C_7H_9O_2N, HCl$ requires $Cl = 20.2$ per cent.

The *dibenzoyl* derivative, $C_7H_7O_2N(Ph \cdot CO)_2$, is best prepared by the Schotten-Baumann method by dissolving the pyridine derivative in dilute (10 per cent.) caustic soda solution and adding excess of benzoyl chloride. After stirring until the odour of benzoyl chloride is no longer apparent, the solid residue which remains is recrystallised from glacial acetic acid, when the benzoyl derivative is obtained in the form of small, glistening prisms which melt at 179° .

0.2301 gave 0.6107 CO_2 and 0.0979 H_2O . $H = 72.36$; $H = 4.83$.

$C_{21}H_{17}O_4N$ requires $C = 72.6$; $H = 4.9$ per cent.

The *isonitroso*-derivative (*oxime*), $CMe \begin{smallmatrix} \text{---CO} \\ \diagup \quad \diagdown \\ C(\text{:NOH}) \cdot CO \end{smallmatrix} NH$, is formed on pouring a solution of the pyridine derivative in caustic soda containing excess of sodium nitrite into dilute acetic acid. On mixing the solutions, a deep red coloration is produced, and on standing the oxime slowly separates as a light yellow, crystalline precipitate. It crystallises from dilute alcohol in the form of small, yellow needles which melt and blacken at $167\text{--}169^\circ$.

0.2118 gave 3.3875 CO_2 and 0.0934 H_2O . $C = 49.89$; $H = 4.90$.

$C_7H_8O_3N_2$ requires $C = 50.0$; $H = 4.8$ per cent.

The oxime dissolves in aqueous sodium carbonate forming a magenta-red solution, and gives in neutral solution an intense blue coloration with ferrous sulphate.

Transformation of $\alpha\beta$ -Dimethylglutaconic Acid into 4:5-Dimethyl-2:6-dihydroxypyridine.

This transformation is effected by distilling the ammonium salt of the acid, which was prepared by evaporating a solution of the acid made alkaline with ammonia, to dryness on the water-bath. The solid residue on distillation under 500 mm. pressure gave an oil which passed over at $265\text{--}270^\circ$ and immediately became solid. Recrystallised from absolute alcohol, it formed small, colourless plates which

melted at 189°, and which were in every way identical with the dimethyldihydroxypyridine already described.

(2) *With Sulphuric Acid.*

When ethyl α -cyano- $\alpha\beta$ -dimethylglutaconate is mixed with an equal volume of concentrated sulphuric acid, but little heat is generated, and if the solution is allowed to stand for twelve hours and then poured into water the ethyl salt is recovered unchanged. It is evident, therefore, that there is no tendency to form the pyridine derivative under these conditions.

(3) *With Alcoholic Potash. Formation of 4:5-Dimethyl-2:6-dihydroxypyridine.*

When ethyl α -cyano- $\alpha\beta$ -dimethylglutaconate is boiled for five hours in a Geissler flask with a solution containing one and a half times the calculated quantity of potash dissolved in methyl alcohol, no ammonia is evolved, and the product, on evaporating free from alcohol, acidifying, and extracting with ether, gave a solid residue which, when recrystallised from alcohol, melted at 189° and consisted entirely of 4:5-dimethyl-2:6-dihydroxypyridine.

Condensation of Ethyl Sodicyanoacetate with Ethyl Methylacetoacetate. Formation of Ethyl α -Cyano- $\beta\gamma$ -dimethylglutaconate,
 $\text{CO}_2\text{Et} \cdot \text{CH}(\text{CN}) \cdot \text{CMe} : \text{CMe} \cdot \text{CO}_2\text{Et}.$

In order to effect this condensation, 23 grams of sodium were dissolved in twelve times its weight of alcohol and the solution mixed first with 113 grams of ethyl cyanoacetate and then with 144 grams of ethyl methylacetoacetate, the whole being heated on the water-bath for half an hour.

On adding the ethyl methylacetoacetate, the sodium derivative of ethyl cyanoacetate slowly dissolves and is replaced by the gelatinous sodium compound of the condensation product. This is decomposed on the addition of dilute acid, and an oil separates which can be extracted by means of ether, the ethereal solution being washed with water and with sodium carbonate solution, dried, and the ether evaporated, the oil which remained being then fractionated under diminished pressure. In this way, the pure ethyl salt was obtained as a moderately viscid oil which boiled at 168° (25 mm.).

0.2270 gave 0.5018 CO_2 and 0.1472 H_2O . C = 60.29; H = 7.2.

$\text{C}_{12}\text{H}_{17}\text{O}_4\text{N}$ requires C = 60.2; H = 7.11 per cent.

Ethyl α -cyano- $\beta\gamma$ -dimethylglutaconate dissolves in strong caustic potash solution in much the same way as ethyl α -cyano- β -methylglutaconate, but the gelatinous potassium salt which is formed is difficult to purify sufficiently for analysis.

Hydrolysis of Ethyl α -Cyano- $\beta\gamma$ -dimethylglutaconate.

(1) *With Hydrochloric Acid. Formation of $\beta\gamma$ -Dimethylglutaconic Acid,*
 $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CO}_2\text{H}.$

The ethyl salt was boiled in a Geissler flask with excess of concentrated hydrochloric acid, when the oil slowly dissolved with considerable effervescence. When all had passed into solution, the product was cooled and the solid which separated filtered and recrystallised from water. In this way, it was obtained in the form of feather-like crystals melting at 145° .

0.2010 gave 0.3901 CO_2 and 0.1207 H_2O . $\text{C} = 52.93$; $\text{H} = 6.67$.

$\text{C}_7\text{H}_{10}\text{O}_4$ requires $\text{C} = 53.2$; $\text{H} = 6.3$ per cent.

$\beta\gamma$ -Dimethylglutaconic acid is in every way identical with $\alpha\beta$ -dimethylglutaconic acid already described. The two acids have the same melting point and the same crystalline form, and a mixture of the two, prepared by evaporating a mixture of their respective solutions to dryness, shows no alteration of the melting point. They both form liquid anhydrides which boil at the same temperature, and give in benzene solution with aniline the same anilic acid, melting at 139° .

The quantity of acid formed in this hydrolysis is very much greater than that from an equal quantity of ethyl α -cyano- $\alpha\beta$ -dimethylglutaconate under similar conditions, representing as it does about 75 per cent. of that theoretically possible; it was not surprising, therefore, to find that the pyridine derivative is not formed at all in this hydrolysis.

On adding alkali to the hydrochloric acid filtrate of the acid until only a faintly acid reaction remained, although the solution became cloudy, showing that some formation of the pyridine derivative had probably taken place, yet the quantity was not sufficient for identification.

4:5-Dimethyl-2:6-dihydropyridine, melting at 189° , was, however, readily prepared from the acid by distilling its ammonium salt in the manner already described in the case of the $\alpha\beta$ -acid.

- (2) *With Sulphuric Acid. Formation of Ethyl 3:4-Dimethyl-2:6-dihydroxypyridine-5-carboxylate*, $\text{CMe} \begin{array}{c} \text{C}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{OH}) \\ \text{CMe} \longrightarrow \text{C}(\text{OH}) \end{array} \text{N}$.

On treating ethyl α -cyano- β - γ -dimethylglutaconate with an equal volume of concentrated sulphuric acid, considerable heat is generated, and if after standing (without cooling) for twelve hours the product is poured into water, the above compound separates as a yellow, crystalline precipitate.

Recrystallised from hot alcohol, it forms long needles, usually slightly yellow in colour, which melt at 187° .

0.2349 gave 0.4888 CO_2 and 0.1266 H_2O . $\text{C} = 56.75$; $\text{H} = 5.98$.

$\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}$ requires $\text{C} = 56.9$; $\text{H} = 6.1$ per cent.

The pyridine derivative is soluble in concentrated acids, forming unstable salts; it is insoluble in alkaline carbonates, but dissolves in caustic alkalis. It does not react with nitrous acid, and gives a transient red colour in alcoholic solution with ferric chloride. On boiling with hydrochloric acid in a Geissler flask, it is completely hydrolysed after heating for three hours, forming 4:5-dimethyl-2:6-dihydroxypyridine, melting at 189° .

The *hydrochloride* slowly separates in the form of colourless needles on dissolving the pyridine derivative in concentrated hydrochloric acid and allowing the solution to stand. It is immediately dissociated by cold water.

- (3) *With Alcoholic Potash. Formation of 4:5-Dimethyl-2:6-dihydroxypyridine.*

On boiling ethyl α -cyano- β - γ -dimethylglutaconate with a solution containing one and a half times the calculated quantity of potash dissolved in methyl alcohol for five hours, no appreciable quantity of ammonia is evolved, and on evaporating the solution free from alcohol, rendering slightly acid, and extracting with ether, an extract is obtained which solidifies on cooling and when crystallised from absolute alcohol forms small, colourless needles which melt at 189° .

0.2115 gave 0.4671 CO_2 and 0.1201 H_2O . $\text{C} = 60.23$; $\text{H} = 6.29$.

$\text{C}_7\text{H}_9\text{O}_2\text{N}$ requires $\text{C} = 60.4$; $\text{H} = 6.5$ per cent.

This substance is in every respect the same as the dimethyldihydroxypyridine prepared from ethyl α -cyano- $\alpha\beta$ -dimethylglutaconate, and by the distillation of the ammonium salt of $\alpha\beta$ -dimethylglutaconic acid, not only are the melting points and crystalline forms of the two compounds the same, but the hydrochlorides separate from their solutions

in concentrated hydrochloric acid in the same characteristic form, and, moreover, the benzoyl derivatives of the two substances melt at the same temperature.

Further Methylation of Ethyl α -Cyano- $\alpha\beta$ -dimethylglutaconate.

Formation of Ethyl α -Cyano- $\alpha\beta\gamma$ -trimethylglutaconate,

This ethyl ester was prepared in the following way: 48 grams of ethyl α -cyano- $\alpha\beta$ -dimethylglutaconate were mixed with a solution of 4.6 grams of sodium dissolved in alcohol. The mixture became dark coloured and a considerable amount of heat was generated. As quickly as possible, 30 grams of methyl iodide were added through a condenser tube and the whole heated on the water-bath for three hours. Water was then added, and the oil which separated extracted with ether. On evaporating the ether from the dried solution, an oil remained, which, on distilling under diminished pressure, boiled constantly at 160—161° (25 mm.), passing over as a colourless oil.

0.2150 gave 0.4855 CO_2 and 0.1512 H_2O . $\text{C} = 61.58$; $\text{H} = 7.81$.

$\text{C}_{18}\text{H}_{19}\text{O}_4\text{N}$ requires $\text{C} = 61.7$; $\text{H} = 7.5$ per cent.

In this experiment, there is always formed a small quantity of ethyl γ -cyano- $\alpha\beta\gamma$ -trimethylcrotonate, the production of which in large quantities is described in the next paragraph.

Further Methylation of Ethyl α -Cyano- $\alpha\beta\gamma$ -trimethylglutaconate.

Formation of Ethyl γ -Cyano- $\alpha\beta\gamma$ -trimethylcrotonate,

and of Ethyl Carbonate.

The object of this experiment was to introduce another methyl group into the molecule of ethyl α -cyano- $\alpha\beta\gamma$ -trimethylglutaconate; it was found, however, that instead of the methyl group entering, the compound quantitatively split off a carboxyl group as ethyl carbonate, being at the same time transformed into the above derivative of crotonic acid.

Twenty-five grams of ethyl α -cyano- $\alpha\beta\gamma$ -trimethylglutaconate were mixed with a solution of 2.3 grams of sodium dissolved in alcohol, and the mixture, which became warm and dark coloured, allowed to stand for half an hour at the ordinary temperature. Methyl iodide was then added and the solution heated on the water-bath for two hours, when water was introduced and the oil which separated extracted by means of ether. On drying the solution and evaporating the ether, an oil remained which was first fractionated under diminished pressure, care being taken to condense the more volatile portion. In this

way, two fractions were obtained, which were subsequently fractionated under the ordinary pressure. The more volatile portion passed over at 126° (750 mm.), and was found to consist of pure ethyl carbonate.

0.1934 gave 0.3597 CO₂ and 0.1501 H₂O. C = 50.98; H = 8.66.

C₅H₁₀O₃ requires C = 50.9; H = 8.5 per cent.

It was identified by conversion into carbamide on heating in a sealed tube with ammonia at 180° for four hours.

The less volatile fraction passed over at 245° (750 mm.) as a clear, mobile oil smelling strongly of bracken, and was found to consist of ethyl γ -cyano- $\alpha\beta\gamma$ -trimethylcrotonate.

0.2132 gave 0.5163 CO₂ and 0.1587 H₂O. C = 66.03; H = 8.27.

C₁₀H₁₅O₂N requires C = 66.2; H = 8.3 per cent.

The conversion is quantitative, a practically theoretical yield of the crotonic acid derivative being obtained.

Hydrolysis of Ethyl α -Cyano- $\alpha\beta\gamma$ -trimethylglutaconate and of Ethyl γ -Cyano- $\alpha\beta\gamma$ -trimethylcrotonate.

(1) *With Hydrochloric Acid. Formation of 3:4:5-Trimethyl-2:6-dihydroxypyridine*, $\text{CMe} \begin{smallmatrix} \text{CMe} \cdot \text{C}(\text{OH}) \\ \text{CMe} \cdot \text{C}(\text{OH}) \end{smallmatrix} \text{N}$, *and of $\alpha\beta\gamma$ -Trimethylglutaconic Acid*, CO₂H·CHMe·CMe·CMe·CO₂H.

3:4:5-Trimethyl-2:6-dihydroxypyridine.—Both ethyl α -cyano- $\alpha\beta\gamma$ -trimethylglutaconate and ethyl γ -cyano- $\alpha\beta\gamma$ -trimethylcrotonate yield the same products on hydrolysis, the only difference between them being in the length of time during which the process must be prolonged in order to complete the reaction.

On boiling either of these ethyl esters in a Geissler flask with concentrated hydrochloric acid, the derivative of crotonic acid naturally passes first into solution, the glutaconic derivative, owing to the presence of an additional carbethoxyl group, taking longer to hydrolyse. The reaction is, however, in each case finished when all the oil has passed into solution. On cooling, a large quantity of crystals separated; these were collected and found to consist of a hydrochloride readily dissociated by cold water. On boiling with water, the substance dissolved, and on cooling 3:4:5-trimethyl-2:6-dihydroxypyridine separated in the form of small, colourless plates melting at 180°.

0.2280 gave 0.5217 CO₂ and 0.1522 H₂O. C = 62.40; H = 7.41.

C₈H₁₁O₂N requires C = 62.7; H = 7.1 per cent.

The pyridine derivative can also be recrystallised from alcohol, in which case it is unnecessary to use so much of the solvent. It gives

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a transient red colour in alcoholic solution with ferric chloride, and behaves as a monobasic acid and as a monoacid base, the salts formed in the latter case being dissociated by cold water. It does not react with phthalic anhydride to form a phthalein, neither does it combine with diazotised *p*-nitroaniline to form a colouring matter. It does not exhibit any tendency to oxidise in the air, but reduces an ammoniacal solution of silver nitrate, forming on warming a mirror of metallic silver.

The *hydrochloride*, $C_8H_{11}O_2N \cdot HCl$, separates from a solution of the pyridine in concentrated hydrochloric acid in the form of long, slender needles; it is dissociated by cold water.

0.2111 gave 0.1598 AgCl. $Cl = 18.78$.

$C_8H_{11}O_2N \cdot HCl$ requires $Cl = 18.9$ per cent.

The *dibenzoyl* derivative, $C_8H_9O_2N(COPh)_2$, is formed by dissolving the pyridine derivative in 10 per cent. caustic soda solution, adding excess of benzoyl chloride, and stirring until the odour of benzoyl chloride is no longer apparent. The solid which then remains crystallises from glacial acetic acid in the form of long, spear-like needles which melt at 188° .

0.1996 gave 0.5329 CO_2 and 0.0987 H_2O . $C = 72.81$; $H = 5.49$.

$C_{22}H_{19}O_4N$ requires $C = 73.1$; $H = 5.3$ per cent.

$\alpha\beta\gamma$ -Trimethylglutaconic Acid.

The filtrate from the pyridine derivative was evaporated to dryness. On adding water to the residue, an oil remained undissolved, and since it was found that this oil still contained some unhydrolysed product it was mixed with hydrochloric acid and again heated in a Geissler flask for three hours, when, on cooling, a further quantity of the hydrochloride of 3 : 4 : 5-trimethyl-2 : 6-dihydropyridine separated. This was filtered off and the filtrate extracted with ether. On evaporating the dried ethereal solution, an oil remained, which became partially solid on standing; this solid, however, dissolved on adding water, leaving an oil undissolved, which passed into solution on boiling, but separated as an oil on cooling. It was purified by dissolving in hot water, cooling, and gradually adding sufficient concentrated hydrochloric acid during the process to prevent the separation of oil. On standing, a large quantity of crystals separated, which were collected and purified by recrystallisation from water. *$\alpha\beta\gamma$ -Trimethylglutaconic acid* prepared in this way forms small needles, which melt at 127° with immediate formation of the anhydride.

0.1817 gave 0.3709 CO_2 and 0.1173 H_2O . $C = 55.67$; $H = 7.17$.

$C_8H_{12}O_4$ requires $C = 55.8$; $H = 7.0$ per cent.

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The *silver* salt, $C_8H_{10}O_4Ag_2$, is obtained as a white precipitate on adding a solution of the calculated quantity of silver nitrate to a neutral solution of the ammonium salt of the acid.

0.2621 gave 0.1463 Ag. $Ag = 55.82$.

$C_8H_{10}O_4Ag_2$ requires $Ag = 55.8$ per cent.

The *anhydride*, $CMe \begin{array}{c} \diagup CHMe \cdot CO \\ \diagdown CMe - CO \end{array} O$, is best prepared by boiling the acid with excess of acetic anhydride on the sand-bath for half an hour. On evaporating the solution in an evacuated desiccator over caustic potash, a crystalline residue remains, which separates from light petroleum (b. p. 60—80°) in the form of large prisms melting at 119°.

0.2002 gave 0.4588 CO_2 and 0.1138 H_2O . $C = 62.50$; $H = 6.31$.

$C_8H_{10}O_3$ requires $C = 62.3$; $H = 6.5$ per cent.

The hydrochloric acid residues from the acid gave an oil on dilution with water, from which a further quantity of the acid was separated on repeating the process already described.

Ultimately a product was obtained from which no more acid could be extracted. It was an oil insoluble in cold water, but dissolves on heating and separates as an oil again on cooling. An attempt was made to purify it by distillation, since it was thought that it might be the unsaturated monobasic acid formed by the elimination of carbon dioxide during the process of hydrolysis. It was found, however, that the liquid distilled constantly at 190° (30 mm.), and that the distillate, which immediately solidified, consisted of pure 3:4:5-trimethyl-2:6-dihydroxypyridine melting at 180°.

Transformation of $\alpha\beta\gamma$ -Trimethylglutacetic Acid into 3:4:5-Trimethyl-2:6-dihydroxypyridine.

This transformation was effected by distilling the ammonium salt of the acid under slightly diminished pressure. The ammonium salt prepared by evaporating a solution of the acid in dilute ammonia to dryness was distilled under 500 mm. pressure; the pyridine derivative passed over at 260° as a yellow oil which instantly solidified.

Recrystallised from alcohol, it formed small needles which melted at 180°, and which were in every way identical with the 3:4:5-trimethyl-2:6-dihydroxypyridine already described.

Esterification of $\alpha\beta\gamma$ -Trimethylglutaconic Acid. Attempt to Introduce another Methyl Group.

In the first place, in order to see whether another methyl group could be introduced into ethyl γ -cyano- $\alpha\beta\gamma$ -trimethylcrotonate, it was treated with the theoretical quantity of sodium dissolved in alcohol and then with excess of methyl iodide, the mixture being heated on the water-bath until a test portion dissolved in water gave a neutral reaction. On extracting the product in the usual way, the oil obtained was found to boil at 245° (750 mm.) and to give figures on analysis corresponding with the ethyl ester, showing therefore that no methyl group had been introduced.

0.2584 gave 0.6262 CO_2 and 0.1965 H_2O . $\text{C} = 66.09$; $\text{H} = 8.4$.

$\text{C}_{10}\text{H}_{15}\text{O}_3\text{N}$ requires $\text{C} = 66.2$; $\text{H} = 8.3$ per cent.

$\text{C}_{11}\text{H}_{17}\text{O}_3\text{N}$ „ $\text{C} = 67.7$; $\text{H} = 8.7$ „

An attempt was then made to esterify ethyl γ -cyano- $\alpha\beta\gamma$ -trimethylcrotonate by treating it with alcohol and sulphuric acid. The ethyl ester was mixed with three times its volume of absolute alcohol and an equal volume of concentrated sulphuric acid and the mixture heated on the water-bath for three hours, when the product was poured into water and the oil which separated extracted with ether. On drying and evaporating the ether, an oil remained which became solid on cooling. It was spread on a porous plate and then recrystallised from dilute alcohol, from which solvent it separated in the form of large plates which melted at 190° .

0.2050 gave 0.5002 CO_2 and 0.1506 H_2O . $\text{C} = 66.54$; $\text{H} = 8.16$.

$\text{C}_{10}\text{H}_{15}\text{O}_3\text{N}$ requires $\text{C} = 66.2$; $\text{H} = 8.3$ per cent.

The compound contains nitrogen, and gives in alcoholic solution a deep reddish-violet colour with ferric chloride. It was not further investigated, but is probably 3 : 4 : 5-trimethyl-2-hydroxy-6-ethoxypyridine,

$\text{CMe} \begin{matrix} \text{CMe} \cdot \text{C}(\text{OEt}) \\ \text{CMe} - \text{C}(\text{OH}) \end{matrix} \text{N}$. Since the ethyl salt of $\alpha\beta\gamma$ -trimethylglutaconic acid could not be prepared in this way, its formation was effected by the direct esterification of the acid, and for this purpose the silver salt was found most convenient. This salt, which was prepared by the method already described, was thoroughly dried and suspended in dry ether in a flask fitted with a reflux condenser, the requisite quantity of ethyl iodide being added through the condenser tube. The mixture was then heated on the water-bath for five hours.

The contents of the flask were then filtered, the ether evaporated, and the residue distilled under diminished pressure.

Ethyl $\alpha\beta\gamma$ -trimethylglutaconate prepared in this way is a colourless, mobile oil boiling at 125—127° (25 mm.).

0.2147 gave 0.4994 CO₂ and 0.1685 H₂O. C = 63.43; H = 8.72.

C₁₂H₂₀O₄ requires C = 63.2; H = 8.8 per cent.

The pure ethyl salt was then treated with the calculated quantity of sodium dissolved in alcohol, and methyl iodide in slight excess added to the solution, the whole being heated on the water-bath until neutral. On adding water and extracting with ether, an oil was obtained on evaporating the ether which boiled at the same temperature as ethyl $\alpha\beta\gamma$ -trimethylcrotonate, and on analysis gave numbers corresponding with this compound.

0.2071 gave 0.4810 CO₂ and 0.1623 H₂O. C = 63.34; H = 8.70.

C₁₂H₂₀O₄ requires C = 63.2; H = 8.8 per cent.

C₁₃H₂₂O₄ „ C = 64.4; H = 9.1 „

It is evident, therefore, that it is not possible to introduce another methyl group into this substance by this means.

Further Methylation of Ethyl α -Cyano- $\beta\gamma$ -dimethylglutaconate. Formation of Ethyl α -Cyano- $\alpha\beta\gamma$ -trimethylglutaconate, 3:4:5-Trimethyl-2:6-dihydropyridine, and $\alpha\beta\gamma$ -Trimethylglutaconic Acid.

Ethyl α -cyano- $\beta\gamma$ -dimethylglutaconate,

can be directly methylated by treating the product of the condensation between ethyl sodiocyanoacetate and ethyl methylacetoacetate with methyl iodide, and in this case, when the production of the ethyl cyano-salt is required in large quantities, the direct method is to be recommended, since the production of ethyl γ -cyano- $\alpha\beta\gamma$ -trimethylcrotonate is thereby prevented. The product of the condensation of molecular proportions of ethyl sodiocyanoacetate and ethyl methylacetoacetate was treated directly with methyl iodide in slight excess and the mixture heated for a further three hours on the water-bath. On working up the product, an oil was obtained which boiled at 160—161° (25 mm.).

0.2158 gave 0.4857 CO₂ and 0.1501 H₂O. C = 61.38; H = 7.72.

C₁₃H₁₉O₄N requires C = 61.7; H = 7.5 per cent.

Since this ethyl ester gave, on hydrolysis with hydrochloric acid, 3:4:5-trimethyl-2:6-dihydropyridine melting at 180° and $\alpha\beta\gamma$ -trimethylglutaconic acid melting at 127°, the former giving a benzoyl derivative melting at 188° and the latter an anhydride melting at 119°, there could be no doubt that it was identical with the ethyl

α -cyano- $\alpha\beta$ -trimethylglutaconate prepared by the methylation of ethyl α -cyano- $\alpha\beta$ -dimethylglutaconate.

Another method of producing ethyl α -cyano- $\alpha\beta$ -trimethylglutaconate consists in treating pure ethyl α -cyano- β -dimethylglutaconate with sodium ethoxide and methyl iodide, and although by this method the pure ethyl ester is obtained, yet the yield is diminished owing to the formation of ethyl γ -cyano- $\alpha\beta$ -trimethylcrotonate in the manner already described.

Pure ethyl α -cyano- $\alpha\beta$ -trimethylglutaconate prepared in this way boils at 160—161° (25 mm.), and gave the following numbers on analysis:

0.2103 gave 0.4769 CO₂ and 0.1402 H₂O. C = 61.85; H = 7.41.

C₁₃H₁₉O₄N requires C = 61.7; H = 7.5 per cent.

On hydrolysis with hydrochloric acid, 3:4:5-trimethyl-2:6-dihydroxypyridine melting at 180° and $\alpha\beta$ -trimethylglutaconic acid melting at 127° were produced.

Treatment of the Potassium Compound CO₂Et·CK(CN)·CMe·CH·CO₂Et with Ethyl Iodide. *Formation of Ethyl α -Cyano- β -methyl- α -ethylglutaconate*, CO₂Et·CEt(CN)·CMe·CH·CO₂Et.

Fifty grams of the well-dried potassium compound prepared in the manner described on page 1694 were suspended in cold alcohol and treated with a slight excess of ethyl iodide in a Geissler flask, the mixture being heated on the water-bath for three hours. On pouring the product into water, an oil separated which was extracted with ether, the ether after drying was evaporated, and the residual liquid fractionated under diminished pressure. In this way, ethyl α -cyano- β -methyl- α -ethylglutaconate is obtained as a fairly viscid oil which boils at 163° (25 mm.).

0.2171 gave 0.4934 CO₂ and 0.1504 H₂O. C = 61.98; H = 7.69.

C₁₃H₁₉O₄N requires C = 61.7; H = 7.5 per cent.

The yield of ethyl ester from potassium compound is practically theoretical. It may also be prepared by the direct ethylation of the condensation product formed in the interaction of ethyl sodiocyanoacetate and ethyl acetoacetate, but the remarks made in respect to the production of ethyl α -cyano- $\alpha\beta$ -dimethylglutaconate by similar means apply also in this case, the product formed always containing some unchanged ethyl α -cyano- β -methylglutaconate.

Hydrolysis of Ethyl α-Cyano-β-methyl-α-ethylglutaconate.

(1) *With Hydrochloric Acid.* Formation of β-Methyl-α-ethylglutaconic Acid, $\text{CO}_2\text{H}\cdot\text{CHEt}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, and 4-Methyl-5-ethyl-2:6-dihydroxypyridine, $\text{CMe}\begin{smallmatrix} \text{CEt}\cdot\text{C}(\text{OH}) \\ \text{CH}\cdot\text{C}(\text{OH}) \end{smallmatrix}\text{N}$.

β-Methyl-α-ethylglutaconic acid.—On boiling the ethyl ester in a Geissler flask with concentrated hydrochloric acid, the oil gradually dissolved, and after heating for twelve hours all had passed into solution.

The product on cooling deposited a large quantity of crystals which were collected and recrystallised from water, when the above acid was obtained in the form of plates melting at 164° , with immediate formation of the anhydride.

0.2216 gave 0.4542 CO_2 and 0.1410 H_2O . $\text{C} = 55.90$; $\text{H} = 7.07$.

$\text{C}_8\text{H}_{12}\text{O}_4$ requires $\text{C} = 55.8$; $\text{H} = 7.0$ per cent.

The acid in alkaline solution instantly decolorises a solution of permanganate.

The silver salt, $\text{C}_8\text{H}_{10}\text{O}_4\text{Ag}_2$, is formed as a white, insoluble precipitate on adding a solution containing the calculated quantity of silver nitrate to a neutral solution of the ammonium salt of the acid.

0.3120 gave 0.1740 Ag. $\text{Ag} = 55.77$.

$\text{C}_8\text{H}_{10}\text{O}_4\text{Ag}_2$ requires $\text{Ag} = 55.8$ per cent.

The anhydride, $\text{CMe}\begin{smallmatrix} \text{CHEt}\cdot\text{CO} \\ \text{CH}\cdot\text{CO} \end{smallmatrix}\text{O}$, is best produced by boiling the acid with excess of acetyl chloride until the evolution of hydrogen chloride ceases. On evaporating the excess of acetyl chloride and acetic acid formed by placing the solution in an evacuated desiccator over potash, a viscid liquid remains which solidifies on scratching. Recrystallised from light petroleum (b. p. $40\text{--}50^\circ$), it is obtained in the form of lustrous plates which melt at 53° .

0.1945 gave 0.4461 CO_2 and 0.1137 H_2O . $\text{C} = 62.55$; $\text{H} = 6.49$.

$\text{C}_8\text{H}_{10}\text{O}_3$ requires $\text{C} = 62.3$; $\text{H} = 6.5$ per cent.

The anhydride on boiling with a solution of sodium carbonate slowly dissolves, and, on acidifying, the acid melting at 164° , from which it was derived, is precipitated.

The anilic acid, $\text{CONHPh}\cdot\text{CHEt}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, was prepared by adding a benzene solution of aniline to a solution of the anhydride in the same solvent and boiling. On cooling, a solid separated which was recrystallised from benzene, and in this way obtained in the form of small, clustered needles which melted at 129° .

0.2205 gave 0.5518 CO₂ and 0.1333 H₂O. C = 68.25; H = 6.71. [View Online](#)

C₁₄H₁₇O₃N requires C = 68.0; H = 6.9 per cent.

The anilic acid instantly dissolves in a solution of sodium carbonate.

4-Methyl-5-ethyl-2:6-dihydroxypyridine.

On adding caustic soda solution to the strongly acid mother liquor obtained after the filtration of the above acid until the solution showed only a faintly acid reaction, an oil was precipitated which solidified on scratching. It was filtered and, after spreading on a porous plate, recrystallised from absolute alcohol, when the above pyridine derivative was obtained in the form of small prisms which melted at 175°.

0.2210 gave 0.5050 CO₂ and 0.1474 H₂O. C = 62.3; H = 7.4.

C₈H₁₁O₂N requires C = 62.6; H = 7.2 per cent.

Like the other pyridine derivatives already described, this compound is both a monobasic acid and a monoacid base, the salts formed in the latter case being dissociated by water. It combines with phthalic anhydride forming a blue, fluorescent phthalein, and with diazotised *p*-nitroaniline forming a yellow colouring matter. It gives, in alcoholic solution, a deep red coloration with ferric chloride, and is not oxidised on exposure to the air. It reduces an ammoniacal solution of silver nitrate on warming, forming a mirror of metallic silver.

The *hydrochloride*, C₈H₁₁O₂N.HCl, separates from a solution of the pyridine derivative in concentrated hydrochloric acid in the form of small prisms which dissolve in cold water, but the solution immediately deposits the free base.

0.2099 gave 0.1585 AgCl. Cl = 18.73.

C₈H₁₁O₂N.HCl requires Cl = 18.9 per cent.

The *dibenzoyl* derivative, C₈H₉O₂N(COPh)₂, is best formed by dissolving the pyridine derivative in dilute caustic soda solution, and, after adding excess of benzoyl chloride, stirring until the odour of the chloride is no longer apparent. The solid which remained was recrystallised from dilute alcohol and thus obtained in the form of needles which melted at 87°.

0.1466 gave 0.3930 CO₂ and 0.0710 H₂O. C = 73.11; H = 5.38.

C₂₂H₁₉O₄N requires C = 73.1; H = 5.3 per cent.

The *isonitroso*-derivative (*oxime*), CMe<math display="block">\begin{array}{c} \text{CEt} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(\text{NOH}) \cdot \text{CO} \end{array}\text{>NH, is produced when a solution of the dihydroxypyridine in caustic soda containing excess of sodium nitrite is poured into dilute acetic acid. The oxime

is not precipitated at once, but separates after the solution [View Online](#) has stood for some time. Recrystallised from dilute alcohol, it forms small, yellow prisms which melt at 95°.

0.2309 gave 0.4453 CO₂ and 0.1195 H₂O. C=52.60; H=5.75.

C₈H₁₀O₃N₂ requires C=52.7; H=5.5 per cent.

It dissolves in sodium carbonate solution with a magenta-red colour and gives in neutral solution a deep green lake with ferrous sulphate.

Transformation of α-Methyl-β-ethylglutaconic Acid into 4-Methyl-5-ethyl-2:6-dihydroxypyridine.

This transformation was effected in the manner already described in the case of the other pyridine derivatives. The pure, well-dried ammonium salt of the acid was distilled under 500 mm. pressure, when an oil passed over at 265—267° which solidified on cooling, and, when recrystallised from absolute alcohol, formed small prisms melting at 175°, which were in every way identical with the 4-methyl-5-ethyl-2:6-dihydroxypyridine described above.

(2) *With Sulphuric Acid.*

On adding ethyl α-cyano-β-methyl-α-ethylglutaconate to an equal volume of concentrated sulphuric acid, no appreciable amount of heat is developed, and after allowing to stand for three days the solution, on pouring into water, gave an oil which, on investigation, proved to be the unchanged ethyl ester.

(3) *With Alcoholic Potash. Formation of 4-Methyl-5-ethyl-2:6-dihydroxypyridine.*

On boiling the ethyl salt with a solution containing 1½ times the calculated quantity of potash dissolved in methyl alcohol, only a small amount of ammonia is evolved. The mixture was heated on the water-bath for four hours, when the alcohol was evaporated off and the residue, when rendered slightly acid with hydrochloric acid, extracted by means of ether. The ethereal solution on evaporating gave a solid residue which, on investigation, proved to be 4-methyl-5-ethyl-2:6-dihydroxypyridine melting at 175°.

During the above hydrolysis, it was noticed that the odour of ethyl acetate was apparent, evidently caused by the partial decomposition of the ethyl ester. Since, however, the yield of the pyridine derivative in this experiment represented about 70 per cent. of that theoretically possible, the quantity formed could not have been very considerable. On fusing the ethyl salt with caustic potash, the quantity of ethyl

acetate generated was much larger, and although the residue on extraction in the manner already described gave a quantity of the pyridine derivative, yet it was noticed that on acidifying the strong caustic potash solution obtained by dissolving the fused mass in water the odour of butyric acid was quite apparent.

*Condensation of Ethyl Sodicyanoacetate with Ethyl Ethylacetoacetate.
Formation of Ethyl α -Cyano- β -methyl- γ -ethylglutaconate,
 $\text{CO}_2\text{Et}\cdot\text{CH}(\text{CN})\cdot\text{CMe}\cdot\text{CEt}\cdot\text{CO}_2\text{Et}$.*

In order to effect this condensation, 23 grams of sodium were dissolved in twelve times its weight of alcohol, mixed with 113 grams of ethyl cyanoacetate, and 158 grams of ethyl ethylacetoacetate added. On heating on the water-bath, the white sodium derivative of ethyl cyanoacetate slowly passed into solution, and was replaced by the gelatinous sodium compound of the condensation product. The mixture was heated for three-quarters of an hour, when dilute hydrochloric acid was added, and the oil which separated extracted by means of ether. The ethereal solution, after washing with water and sodium carbonate solution, was dried and the ether evaporated, when an oil was obtained, which, on fractionation under diminished pressure, passed over as a clear, rather viscid liquid at 163° (25 mm.).

0.2128 gave 0.4823 CO_2 and 0.1493 H_2O . $\text{C} = 61.81$; $\text{H} = 7.79$.

$\text{C}_{13}\text{H}_{19}\text{O}_4\text{N}$ requires $\text{C} = 61.65$; $\text{H} = 7.51$ per cent.

The yield is about 60 per cent. of that theoretically possible.

Hydrolysis of Ethyl α -Cyano- β -methyl- γ -ethylglutaconate.

(1) *With Hydrochloric Acid. Formation of β -Methyl- γ -ethylglutaconic Acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CEt}\cdot\text{CO}_2\text{H}$.*

The ethyl ester dissolved slowly when boiled in a Geissler flask with concentrated hydrochloric acid, and after heating on a sand-bath for twelve hours all the oil had disappeared. The product on cooling deposited a large quantity of crystals, which, on purifying by recrystallisation from water, formed small plates melting at 164° with immediate formation of the anhydride.

0.2157 gave 0.4410 CO_2 and 0.1320 H_2O . $\text{C} = 55.76$; $\text{H} = 6.79$.

$\text{C}_8\text{H}_{12}\text{O}_4$ requires $\text{C} = 55.8$; $\text{H} = 7.0$ per cent.

There can be no doubt that this acid is identical with β -methyl- α -ethylglutaconic acid prepared as previously described. Not only do the two acids crystallise in the same forms and melt at the same

temperature, but on mixing equal portions of the two, the mixture melts at the same temperature as either component.

Moreover, the two anhydrides made from the acids by means of acetyl chloride have the same crystalline form, and both melt at 53°, and the anilic acids from these anhydrides are without doubt identical.

On distilling the ammonium salt of the acid it is transformed into 4-methyl-5-ethyl-2:6-dihydroxypyridine melting at 175°, which is in every way identical with the dihydroxypyridine prepared by the hydrolysis of ethyl α -cyano- β -methyl- α -ethylglutaconate.

Just as in the analogous hydrolysis of ethyl α -cyano- β -dimethylglutaconate, the above acid appeared to be the sole product formed by the hydrolysis, and on rendering the filtrate from the acid nearly neutral with caustic soda no precipitation of the pyridine derivative took place.

(2) *With Sulphuric Acid. Formation of Ethyl 4-Methyl-3-ethyl-2:6-dihydroxypyridine-5-carboxylate*, $\text{CMe} \begin{array}{c} \text{C}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{OH}) \\ \text{CEt} \text{---} \text{C}(\text{OH}) \end{array} \text{N}$.

On treating ethyl α -cyano- β -methyl- γ -ethylglutaconate with an equal volume of concentrated sulphuric acid, considerable heat is developed, and if, after the mixture has been allowed to stand without cooling for twelve hours, it is poured into water, the above ethyl ester separates as a white, colourless precipitate. Recrystallised from absolute alcohol, it forms large needles, usually slightly yellow in colour, which melt at 134°.

0.1979 gave 0.4269 CO_2 and 0.1165 H_2O . $\text{C} = 58.83$; $\text{H} = 6.54$.

$\text{C}_{11}\text{H}_{15}\text{O}_4\text{N}$ requires $\text{C} = 58.6$; $\text{H} = 6.7$ per cent.

The *hydrochloride* slowly separates from a solution of the ethyl ester in cold concentrated hydrochloric acid in the form of small needles which are immediately dissociated by cold water.

Ethyl 4-methyl-5-ethyl-2:6-dihydroxypyridine-5-carboxylate is insoluble in alkaline carbonates, but dissolves in caustic alkalis. It gives a transient reddish-violet colour in alcoholic solution with ferric chloride, and on boiling with concentrated hydrochloric acid is completely hydrolysed to 4-methyl-5-ethyl-2:6-dihydroxypyridine.

(3) *With Alcoholic Potash. Formation of 4-Methyl-5-ethyl-2:6-dihydroxypyridine*.

The products formed in the hydrolysis of ethyl α -cyano- β -methyl- γ -ethylglutaconate with $1\frac{1}{2}$ times the calculated quantity of potash dissolved in methyl alcohol are the same as those formed in the analo-

gous hydrolysis of ethyl α -cyano- β -methyl- α -ethylglutaconate already described.

Practically no ammonia is evolved, and on working up the product in the usual way 4-methyl-5-ethyl-2:6-dihydroxypyridine was alone obtained.

0.2091 gave 0.4825 CO_2 and 0.1332 H_2O . $\text{C} = 62.93$; $\text{H} = 7.07$.

$\text{C}_8\text{H}_{11}\text{O}_2\text{N}$ requires $\text{C} = 62.7$; $\text{H} = 7.2$ per cent.

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