CXXIII.—*Reactions Involving the Addition of Hydrogen Cyanide to Carbon Compounds. Part III.*
Action of Potassium Cyanide on Mesityl Oxide.

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It is well known that the ethylenic linking in $\alpha\beta$ -unsaturated ketones, aldehydes, and esters is characterised by an exceptional reactivity, and these compounds are capable of taking up at the carbon double bond, not only agents with which ordinary unsaturated compounds unite, such as the halogens or the halogen hydrides, but also a number of those which otherwise exhibit additive functions only in respect to the carbonyl group, that is to say, agents such as hydroxylamine, sodium hydrogen sulphite, and ammonia. Further, it is frequently the case that the carbonyl group of an $\alpha\beta$ -unsaturated ketone or aldehyde appears devoid of reactivity until addition has first occurred at the ethylenic position, or, if a reactive character is manifested, it is usually less marked than in the corresponding saturated compounds.

Addition in this class of compounds is governed by the law that the negative part of the agent added is taken up at the β -position, hence where an acid or other hydrogen compound is added in two parts, for example, H and NH_2 , H and Cl, H and $\text{NH}\cdot\text{OH}$, H and $\text{CH}(\text{CO}_2\text{Et})_2$, the product contains the hydrogen in the α -position.

Whilst it is too early to discuss in great detail the theory of the addition process in these compounds, it may be worth while to point out that the conditions under which these additions occur are precisely similar to those which are advantageous in the case of simple carbonyl compounds. One very favourable condition appears to be a high concentration of the negative ion of the agent, as is particularly noticeable in the case of hydrogen cyanide addition processes (Trans., 1903,

83, 997). Hence it is natural to surmise that the principle which appears to be one of the governing factors in the simpler cases applies to the other, namely, the formation of a complex negative ion as an initial step. If so, then it should follow that, other things being equal, the greater the affinity of the resulting complex ion for the negative charge, the greater should be the tendency towards the complex formation, or, in other words, the more acidic the character of the compound first formed, the more readily should the synthetical process occur, when this change consists in the addition of a hydrogen compound in the above sense. Now, in accordance with Thiele's theory of such additions, the initial compound is to be regarded as the enol, and therefore a substance of distinctly acidic character:

A simple modification of this gives the ionic view:

Such a modification of Thiele's theory appears likely to afford the basis of a rational explanation of the great difference in reactivity between the groups >C:C< and $\text{>C:\dot{C}:\dot{C}:C<}$, on the one hand, and $\text{>\dot{C}:O}$ and $\text{>C:\dot{C}:\dot{C}:O}$, on the other, for the same assumptions applied to the former class would lead to the formulation of additive products, >CX-CH< and $\text{>CX:\dot{C}:\dot{C}:CH<}$, that is to say, groups of a type with which acidity has not yet been definitely associated.

Of the addition reactions in which these $\alpha\beta$ -unsaturated compounds take part, some have proved of great value as general synthetical methods, in particular those which involve the union of a carbon atom with the β -carbon atom of the unsaturated compound. Such, for example, are the reactions with ethyl malonate and ethyl acetoacetate, which lead to the production of substituted glutaric acids, δ -ketocarboxylic acids, or dihydroresorcinols.

Numerous attempts have probably been made to discover a general method by which the addition of the elements of hydrogen cyanide at the double linking in $\alpha\beta$ -unsaturated ketones, &c., might be brought about, but hitherto with only partial success. Bredt and Kallen (*Annalen*, 1896, 293, 350) were unable to bring about the interaction of $\alpha\beta$ -unsaturated monocarboxylic acids or esters with hydrogen cyanide, but discovered that if the esters of alkylidenemalonate acids were dissolved in dilute alcohol containing potassium cyanide, and the mixture was then treated with acid or warmed at about 80° , so as to

cause partial hydrolysis of the ester and consequent liberation of hydrogen cyanide, the desired additive products were obtained; the efficiency of the method was attributed to a special property of nascent hydrogen cyanide.

In a recent paper (Trans., 1903, 83, 995), the author showed that hydrogen cyanide is much more efficient as an additive reagent when its own salts are present, and described methods of bringing about the addition of that agent at the double linking in an $\alpha\beta$ -unsaturated ketone (phorone) and an $\alpha\beta$ -unsaturated nitrile (benzylidenebenzylcyanide). It was shown also that these compounds actually remove hydrogen cyanide from the alkaline solution of potassium cyanide (*ibid.*, 1003).

The extraordinary ease with which the addition was thus effected naturally led to a more systematic investigation of the reaction, with the result that it proves likely to be an important systematic method, and perhaps may be so developed as to afford a fairly convenient process for preparing γ -ketonic nitriles and acids, 1:2-dinitriles, and substituted succinic acids.

Unfortunately, however, potassium cyanide, which usually must be present in considerable quantity, is only very sparingly soluble in alcohol, except in presence of much water, so that the resulting alkaline solutions tend to cause by-reactions; it is therefore desirable that a considerable number of cases should be somewhat thoroughly investigated, so as to determine the conditions most suitable for the treatment of compounds of different types.

No difficulty was found with phorone or benzylidenebenzyl cyanide, because the products are stable and crystalline very easily, but a number of other cases which have since been attacked have given much trouble. In this paper, some of the results obtained with mesityl oxide, $C(CH_3)_2:CH \cdot CO \cdot CH_3$, are described.

The conversion of acetone into mesitononitrile,

was first effected by Pinner (*Ber.*, 1881, 14, 1072), who saturated the ketone with hydrogen chloride and heated the product with a solution of potassium cyanide.

It is most probable that the process occurs in two stages, the first of which involves the formation of water and mesityl oxide, followed by the interaction of the latter with potassium cyanide and water, thus,

In accordance with this view, it has now been found that mesityl oxide, like phorone (Trans., 1903, 83, 1003), when heated with a dilute

alcoholic solution of potassium cyanide, alone or in presence of free hydrogen cyanide, reacts in the above way, as the solution becomes strongly alkaline, and the product when poured into water and hydrolysed with hydrochloric acid yields mesitonic acid; after 10 minutes' heating on the water-bath, more than half the ketone is converted into mesitononitrile and other substances. If the heating be prolonged, the potassium hydroxide liberated in the reaction hydrolyses the nitrile formed, yielding the corresponding carboxylic acid, so that in one operation the synthesis of a γ -ketonic acid from an $\alpha\beta$ -unsaturated ketone is accomplished,

Not only is it possible so to prepare the γ -ketonic acid, but the reaction proceeds even further. The mononitrile first formed readily affords a somewhat stable cyanohydrin, which is probably formed in appreciable amount in the alkaline solution, because at the end of an operation in which the ketone had been boiled for a considerable time with the cyanide solution, mesitylic acid,

was obtained on acidification, and this must have been formed from the cyanohydrin of mesitononitrile or from mesitonic acid itself.

The constitution of mesitylic acid has already been satisfactorily determined by Pinner (*Ber.*, 1881, 14, 1075, and 1882, 15, 582), who obtained from it *as*-dimethylsuccinamic acid,

by the oxidising action of potassium permanganate in acid solution; moreover, as he found it yielded mesitonic acid when it is heated with sulphuric acid at 150° (*Ber.*, 1882, 15, 585), the constitution of the ketonic acid was scarcely questionable. When mesitonic acid is oxidised with nitric acid, however, it yields dimethylmalonic acid, whilst dimethylsuccinic acid does not appear to have been detected. In order to obtain this acid and at the same time to establish conclusively the view that the ketonic acid contains the group $\cdot\text{CO}\cdot\text{CH}_3$, mesitonic acid, prepared by the new process, was oxidised by means of warm dilute sodium hypobromite. As was to be anticipated, bromoform and *as*-dimethylsuccinic acid were obtained without difficulty.

In agreement with the supposed ketonic nature of mesitonic acid, it yields an oxime, a semicarbazone, and hydrazones, all having well-defined crystalline habits.

The results, taken in conjunction with the work of Bredt and Kallen (*loc. cit.*), and the author's observations on benzyldiene-benzyl cyanide, show that the addition of hydrogen cyanide to unsaturated compounds containing the group $\text{:C}:\dot{\text{C}}\cdot\text{R}$ (where $\text{R} = \cdot\text{CO}\cdot$ or CN) occurs in accordance with the usual rule.

EXPERIMENTAL.

Action of Potassium Cyanide on Mesityl Oxide.

In preliminary experiments made with the object of bringing about the addition of one molecular proportion of hydrogen cyanide to mesityl oxide, the ketone was shaken with an aqueous solution of potassium cyanide containing one molecular proportion of free hydrogen cyanide. Occasionally it occurred that, after some days, the liquid ketone was replaced by a relatively small quantity of a solid, crystalline material, which on examination proved to consist of the cyanohydrin of mesitronitrile, but the yield obtained by this method was exceedingly poor, and various modifications of the method were therefore tried. The results generally tended to show that much of the difficulty arose from the circumstance that the mesitronitrile initially formed reacted much more rapidly with the reagent than did the original mesityl oxide.

As, however, the ketone-cyanohydrins are usually easily broken down by alkali, whilst the γ -cyanoketones are comparatively stable, experiments were next instituted with the object of ascertaining what would be the result if potassium cyanide alone were employed, since in this case the alkali formed by the removal of the elements of hydrogen cyanide from the solution in the initial stage might be expected to prevent the formation of a cyanohydrin. Thus 3.9 grams of the ketone (1 mol.) were dissolved in 25 c.c. of alcohol and warmed on the water-bath with a solution of 5 grams of potassium cyanide (2 mols.) in 15 c.c. of water. Within a few minutes the odour of ammonia was noticed, and at the end of an hour the whole was evaporated on the water-bath to drive off alcohol, the residue being diluted with water and extracted repeatedly with ether. On evaporating the ethereal extracts, practically no residue was obtained; the aqueous liquid was therefore strongly acidified and the extraction with ether repeated, when the ethereal extracts now yielded a considerable residue; this was found to consist of a portion, easily soluble in water, which was mainly mesitonic acid, whilst the less soluble portion was crystalline, and was identical with mesitylic acid. These substances had evidently resulted from the addition of one and two

molecular proportions of hydrogen cyanide to the mesityl oxide, followed by hydrolysis of the products in the alkaline liquid.

The experiments indicated that the addition process in solutions of the concentrations employed was somewhat rapid at the temperature of the water-bath, and it was therefore possible to devise methods for obtaining any one of the products at will. The precise conditions which were finally adopted in each case are given below.

Preparation of Mesitonic Acid, $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$.

In preparing this substance, a solution of mesityl oxide (1 mol.) in six times its weight of boiling alcohol is mixed with a solution of potassium cyanide (2 mols.) in three times its weight of hot water, and the whole heated on the water-bath during 15 minutes. To the cooled liquid is then added an aqueous solution of ferrous sulphate ($\frac{1}{3}$ mol.), which serves the purpose of converting excess of potassium cyanide into ferrocyanide as well as decomposing any cyanohydrin formed. The latter process is completed by raising the whole once more to the boiling point with constant shaking, care being taken that the liquid remains alkaline throughout. After filtration through glass wool, the liquid is diluted largely with water, extracted with ether, the ethereal extract being dried with calcium chloride and evaporated. The liquid residue, which is mainly mesitonitrile, is dissolved in hydrochloric acid (saturated at 0°), the whole being allowed to remain for two days in the cold, after which it evaporated on the water-bath. The oily acid remaining is best purified by dissolving it in ethyl bromide, the solution being dried with calcium chloride. By adding light petroleum to the liquid and allowing the whole to evaporate spontaneously, the product may be obtained without further difficulty in quadrangular plates or magnificent, transparent rhombs which are nearly pure mesitonic acid. The acid is easily obtained in a purified condition by recrystallisation from the same mixture.

0.3003 gave 0.6392 CO_2 and 0.2322 H_2O . $\text{C} = 58.0$; $\text{H} = 8.6$.

$\text{C}_7\text{H}_{12}\text{O}_3$ requires $\text{C} = 58.3$; $\text{H} = 8.3$ per cent.

The acid had all the properties assigned it by Pinner (*Ber.*, 1881, 14, 1072, and 1882, 15, 585); it melted at 75.5 — 76.5° and crystallised by careful evaporation of its solution in a mixture of ethyl bromide and light petroleum in magnificent, transparent rhombs which have one plane of perfect cleavage.

When fused on a microscopic slide beneath a cover-glass, it solidified somewhat rapidly, forming semi-transparent patches which show aggregate extinction. Examination of the mass in convergent, polar-

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ised light reveals, here and there, the interference figure surrounding the bisectrix of a biaxial crystal of very wide axial angle; if, as is probable, this is the obtuse bisectrix, the double refraction is positive in sign and strong.

The following new derivatives of the acid were prepared with the object of more fully characterising the compound.

The *semicarbazone*, $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3):\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, is rapidly deposited on warming an aqueous solution of the acid with semicarbazide acetate; it was purified by crystallisation from dilute ethyl alcohol. On analysis of the material dried at 100° :

0.1982 gave 0.3468 CO_2 and 0.1335 H_2O . $\text{C} = 47.7$; $\text{H} = 7.5$.

$\text{C}_8\text{H}_{15}\text{O}_3\text{N}_3$ requires $\text{C} = 47.7$; $\text{H} = 7.7$ per cent.

The substance is nearly insoluble in petroleum, ethyl acetate, chloroform, carbon disulphide, or water, but dissolves somewhat readily in methyl or ethyl alcohol; it separates slowly from an alcoholic solution in well-defined, glistening octahedra. When heated slowly, the semicarbazone contracts at 140 – 145° , at a higher temperature it swells to an opaque mass, and at 197° is suddenly converted into a clear liquid which rapidly evolves gas, but without darkening in colour.

Crushed fragments of the octahedra, examined in cedar-wood oil by convergent, polarised light, show occasionally the acute bisectrix of a biaxial interference figure of moderate angle. The double refraction is strong and positive in sign.

The *oxime*, $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3):\text{N}\cdot\text{OH}$, was made by warming the acid in aqueous solution with hydroxylamine for a few minutes, and was isolated by rendering the solution faintly acid with hydrochloric acid and extracting with ether. The residue from the dried ethereal extract was triturated with a little dilute alcohol, and slowly became crystalline. After being dried on porous earthenware, it was crystallised from a mixture of ether and ethyl bromide.

0.1829 gave 0.3560 CO_2 and 0.1384 H_2O . $\text{C} = 53.1$; $\text{H} = 8.4$.

$\text{C}_7\text{H}_{13}\text{O}_3\text{N}$ requires $\text{C} = 52.8$; $\text{H} = 8.2$ per cent.

The oxime dissolves readily in methyl or ethyl alcohol, ethyl acetate, benzene, chloroform, or ether, somewhat readily in ethyl bromide, but is only sparingly soluble in boiling light petroleum, in which it fuses to a clear liquid. It separates on spontaneous evaporation of its solution in a mixture of ether and ethyl bromide as transparent, pyramidal crystals which melt at 93 – 94° .

When crushed fragments of the crystals are examined in convergent polarised light, they show occasionally the acute bisectrix of a figure

of moderate angle. The double refraction is positive and strong. After melting between glass slips, the substance solidifies very slowly in numerous isolated, small, spindle-shaped plates.

The *phenylhydrazone*, $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3):\text{N}_2\text{H}\cdot\text{C}_6\text{H}_5$, was prepared by mixing cold dilute aqueous solutions of the acid and phenylhydrazine acetate; it separates rapidly in beautiful, white plates, and may be purified, when dry, by recrystallisation from benzene. On analysis of a specimen dried by exposure over sulphuric acid in a vacuum:

0.1547 gave 0.3782 CO_2 and 0.1045 H_2O . $\text{C} = 66.6$; $\text{H} = 7.5$.

$\text{C}_{13}\text{H}_{18}\text{O}_2\text{N}_2$ requires $\text{C} = 66.6$; $\text{H} = 7.7$ per cent.

The phenylhydrazone is somewhat readily soluble in ethyl acetate, ethyl or methyl alcohol, or in acetone, as well as in hot benzene or chloroform, but dissolves only sparingly in light petroleum; it separates from hot benzene or dilute alcohol in thin, colourless, pearly plates of considerable size, which melt at 135° . The crystals, which probably belong to the orthorhombic system, have straight extinction, and present the appearance of elongated, six-sided plates, and the acute bisectrix of the crystals emerges perpendicularly through the large faces; the double refraction is moderate and positive in sign. When fused on a glass slip beneath a cover glass, it solidifies on cooling, somewhat slowly, to masses of small plates, which are apparently identical in crystallographic character with the crystals from benzene or alcohol.

The phenylhydrazone dissolves in sodium carbonate solution, and is reprecipitated unaltered on acidifying with acetic acid. When exposed to the air and light, however, it rapidly becomes brown, and is finally converted into a dark brown resin.

The *p-nitrophenylhydrazone*,

is easily isolated from even very dilute solutions of the acid on adding the corresponding hydrazine acetate; it may be purified by crystallisation from ethyl acetate or glacial acetic acid.

0.1629 gave 0.3351 CO_2 and 0.0901 H_2O . $\text{C} = 56.1$; $\text{H} = 6.1$.

$\text{C}_{13}\text{H}_{17}\text{O}_4\text{N}_3$ requires $\text{C} = 55.9$; $\text{H} = 6.1$ per cent.

This substance dissolves readily in alcohol and in hot glacial acetic acid, and less readily in ethyl acetate, but is very sparingly soluble in light petroleum, benzene, or chloroform; it separates from hot ethyl acetate or glacial acetic acid in beautiful, six-sided plates, and in flat needles from dilute acetic acid. When heated slowly, it softens above 180° , and melts with effervescence at 190° .

The larger crystals are yellow, probably orthorhombic, plates, which

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show slight dichroism, and have one direction of good cleavage. Crushed fragments, observed in convergent polarised light, occasionally show an axis of a wide-angled biaxial interference figure; the double refraction is very strong. When melted between glass slips, the substance solidifies very slowly when cold, but if kept warm the material crystallises more rapidly, but still incompletely, to a mixture of plates and needles with straight extinction, apparently identical in crystallographic character with the forms described above. Here and there the bisectrix of a crystal emerges perpendicularly to the field, and if, as is probably the case, this is the obtuse bisectrix, the double refraction is positive in sign; the axial dispersion is moderate.

Action of Alkaline Sodium Hypobromite on Mesitonic Acid.

Formation of as-Dimethylsuccinic Acid, $\text{CO}_2\text{H}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

A solution containing 5 grams of mesitonic acid in 100 grams of dilute sodium hydroxide was warmed on the water-bath while a solution of bromine in 10 per cent. sodium hydroxide was added in small quantities, the end of the reaction being ascertained by removing a small portion of the solution 5 minutes after the last addition of hypobromite, and observing whether bromine was liberated on addition of strong hydrochloric acid. An excess of sodium sulphite was then added, the whole evaporated nearly to dryness, strongly acidified with hydrochloric acid, and extracted repeatedly with ether. The dried extracts after evaporation slowly crystallised on cooling, and the product was purified by draining on porous earthenware and crystallising from hot ethyl acetate.

0.1909 gave 0.3413 CO_2 and 0.1071 H_2O . $\text{C} = 49.2$; $\text{H} = 6.7$.

$\text{C}_6\text{H}_{10}\text{O}_4$ requires $\text{C} = 49.3$; $\text{H} = 6.9$ per cent.

0.2028 gram required 27.85 c.c. *N*/10 sodium hydroxide for neutralisation with phenolphthalein as indicator, making the equivalent of the acid 72.8, that is, practically identical with that required for a dibasic acid, $\text{C}_{10}\text{H}_{10}\text{O}_4$, namely, 73.

The identity of the acid with *as*-dimethylsuccinic acid was proved by a thorough examination of its general properties. It formed needles melting at $140\text{--}141^\circ$, and, when boiled with acetyl chloride, it was easily converted into a fusible anhydride. Finally, the anilic acid was prepared by the usual method, and found to consist of flat needles melting at $185\text{--}186^\circ$.

Mesitononitrilecyanohydrin, $\text{CN}\cdot\text{C}(\text{CH}_3)_2\cdot\text{CH}_2\cdot\text{C}(\text{CH}_3)(\text{OH})\cdot\text{CN}$.

In preparing the cyanohydrin of mesitylic nitrile, it was found unnecessary to isolate the intermediate product. The mixture, prepared by heating together 3.9 grams of mesityl oxide dissolved in 25 c.c. of alcohol and 5 grams of potassium cyanide (2 mols.) in 15 c.c. of water during 15 minutes on the water-bath, is cooled and carefully mixed with glacial acetic acid or dilute hydrochloric acid; the introduction of acid is best effected by means of a test-tube drawn out at its centre to a long capillary which reaches to the bottom of the liquid, and the whole is cooled during the operation by a stream of water.

As effectual treatment depends on the presence of the salt of hydrocyanic acid, care must be taken that the liquid remains alkaline, but only faintly so, during about an hour, when a distinct excess of acid is added, an operation which renders the cyanohydrin stable, and the solution is then diluted with an equal bulk of water, when alcohol for the most part is removed by evaporation on the water-bath.

The product is best isolated by saturating the liquid with ammonium sulphate and extracting repeatedly with chloroform. On removal of the latter, the extracted material becomes almost solid, and when drained in the usual way may be purified by recrystallisation from ethyl acetate.

0.1798 gave 26.6 c.c. at 2350° and 769 mm. $N = 18.3$.

$\text{C}_8\text{H}_{12}\text{ON}_2$ requires $N = 18.4$ per cent.

The cyanohydrin is to some extent soluble in water, especially near the boiling point of the latter; it is much less readily soluble in solutions of inorganic salts, and is mostly precipitated from its cold aqueous solution on saturating the latter with ammonium sulphate in the form of nacreous plates or aggregates of flat needles. It is sparingly soluble in light petroleum, more readily so in ether or carbon disulphide, is freely dissolved by chloroform, and to a less marked extent by ethyl acetate. It separates from a mixture of ethyl acetate and light petroleum in slender, flattened needles, which melt sharply at 165—166°. The extinction directions of the crystals in polarised light are about 20° to their length, the double refraction being weak, and the elasticity in the direction of greatest length exceeds that at right angles to it. When melted on a glass slide below a cover-slip, the compound sets rapidly when cold to radiate masses of minute needles; if, however, the crystallisation of the material is started while the mass is cooling slowly, solidification occurs in well-defined, flat plates. The solidified material, when examined in convergent

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polarised light, shows occasionally the bisectrix of a wide-angled interference figure emergent normal to the field; in the probable event of this being the obtuse bisectrix, the double refraction of the crystals is negative in sign.

The cyanohydrin * is distinctly acidic in character, being much more easily soluble in solution of sodium hydroxide than in water; from the resulting solution, it is reprecipitated on addition of an acid and even of sodium hydrogen carbonate.

The dissolution of the compound in cold sodium hydroxide does not appear to decompose it to any very marked extent; thus, if the solution is poured into excess of mineral acid, which would prevent recombination of the constituents, no odour of prussic acid can be detected; if, however, the alkaline solution is heated to boiling, cooled, and the foregoing experiment repeated, hydrocyanic acid was eliminated, and recognised by its odour and by other tests.

Strong mineral acids, such as cold saturated hydrochloric or hydrobromic acid, dissolve the substance without difficulty in the cold; this behaviour is, however, characteristic of nitriles, and is the result of the basic character of the cyano-group (compare J. Walker, *Ber.*, 1901, 34, 4117).

*Hydrolysis of Mesitononitrilecyanohydrin. Formation of
Mesitylic Acid,*

This hydrolysis is easily accomplished by using cold saturated hydrochloric acid, in which case the action requires about 5 days, or more rapidly by warming the compound with ordinary hydrochloric acid on the water-bath for about 12 hours. On evaporation, the product separates in a crystalline form, and may be purified, after drying for some hours at 100°, by crystallisation from acetone. For analysis, the material was dried at 100°.

0.1633 gave 0.3376 CO₂ and 0.1123 H₂O. C = 56.4; H = 7.6.

C₈H₁₃O₃N requires C = 56.2; H = 7.6 per cent.

The compound was acidic in character, and had all the properties of mesitylic acid.

The crystals from acetone are anhydrous and present the appearance of short, rectangular prisms, quite unlike the hydrated needles which are obtained on crystallising the solution from water. An examination of crushed fragments of the crystals in cedar-wood oil by

* An account of experiments on the acidity of this substance is given elsewhere (p. 1212).

convergent polarised light reveals the fact that the crystals are biaxial in character, the axial angle being moderately wide and with weak dispersion. The double refraction is positive in sign.

When melted between glass slips, the acid solidifies quickly, on cooling, in numerous opaque radiate patches.

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