XVII.—*The Formation and Reactions of Imino-Compounds. Part VI. The Formation of Derivatives of Hydrindene from o-Phenylenediacetonitrile.*

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IN a former communication (Trans., 1906, **89**, 1916) attention was drawn to the influence which different groups attached to the carbon atom adjacent to the carbimino-group in an imino-compound exercised on the stable form of this group, and it was mentioned that whereas ethyl 1 : 3-naphthylenediamine-2-carboxylate (I) evidently has the imino-structure, yet when the carbethoxyl group is replaced by carboxyl or by phenyl as in 1 : 3-naphthylenediamine-3-carboxylic acid (II) or 2-phenyl-1 : 3-naphthylenediamine (III) :

the stable form of the compound evidently has the amino-structure.

In the present communication, we deal with a series of imino-compounds in which this influence is very much more clearly defined and in which the nature of the groups attached to the carbon atom adjacent to the carbimino-group materially affects the structure of the compound.

The first member of this series of imino-compounds is β -imino- α -cyanohydrindene (V), which we find can be prepared in quantitative yields when *o*-phenylenediacetonitrile (IV) is warmed in alcoholic solution in the presence of a trace of sodium ethoxide :

The proof of the constitution of this substance is derived from the nature of the products formed from it on hydrolysis. Thus with dilute hydrochloric acid it is hydrolysed at once, forming α -cyano- β -hydrindone (VI), from which, on treatment with caustic alkalis, *o*-phenylenediacetic acid (VII) can be readily obtained :

Moreover, β -imino- α -cyanohydrindene can be hydrolysed to the

corresponding acid (VIII), which is readily transformed by a method described in the experimental portion into β -hydrindone (IX) :

There can be no doubt that the stable form of β -imino- α -cyano-hydrindene (V) has the imino-structure. It is a neutral substance which does not exhibit the slightest tendency to combine with acids ; moreover, it is readily hydrolysed by dilute mineral acids to the corresponding oxygen derivative (VI). Again, when treated with ethyl alcohol and sulphuric acid, it quickly undergoes alcoholysis and is transformed into a substance which is evidently, for reasons which will be given later, 3-cyano-2-ethoxyindene (X) :

All these reactions are characteristic of the imino-group ; if, however, the nitrile group in β -imino- α -cyano-hydrindene is replaced by the carboxyl, carbethoxyl, or carboxyamino-groups, the structure of the molecule is at once changed, and there can be no doubt that these compounds are 2-aminoindene-3-carboxylic acid (XI), ethyl 2-aminoindene-3-carboxylate (XII), and 2-aminoindene-3-carboxamide (XIII) respectively :

The proof of this is as follows : 2-aminoindene-3-carboxylic acid readily forms a salt with concentrated hydrochloric acid which is stable in the presence of the strong mineral acid but is dissociated by water. When boiled with dilute hydrochloric acid, the carboxylic acid is not hydrolysed to the corresponding oxygen derivative, but remains unacted on until carbon dioxide is eliminated, when hydrolysis at once ensues and β -hydrindone is formed. When the acid is boiled for some time with ethyl alcohol and sulphuric acid, the nitrogen group is not eliminated, but etherification alone takes place and ethyl 2-aminoindene-3-carboxylate (XII) is produced. Prolonged boiling with the above reagents fails to produce any change in the nature of the product. When the acid is treated in concentrated hydrochloric acid with nitrous acid, the whole of the nitrogen corresponding with the amino-group is eliminated in the free condition ; owing, however, to the formation of ill-defined by-products, we were unable to isolate 2-hydroxyindene-3-carboxylic acid by means of this reaction. Ethyl 2-aminoindene-3-carboxylate (XII) also forms a well-defined salt with hydrochloric acid which is stable in the presence of strong hydro-

chloric acid but is dissociated by water. When boiled with dilute hydrochloric acid it is hydrolysed to the corresponding acid (XI), but the nitrogen group is not eliminated. When a solution of the ethyl salt in concentrated hydrochloric acid is treated with nitrous acid, the whole of the nitrogen corresponding with the amino-group is evolved in the elemental form, although in this case also the production of complex by-products rendered it impossible for us to isolate ethyl 2-hydroxyindene-3-carboxylate. It is probable that in both these reactions with nitrous acid the hydrogen atoms attached to the α -carbon atom also take part and lead to the formation of compounds of higher molecular complexity; unfortunately, it is impossible to avoid the use of excess of nitrous acid, since the whole of the aminic nitrogen is not evolved when the theoretical quantity is used.

All the above reactions clearly indicate, therefore, that ethyl 2-aminoindene-3-carboxylate and 2-aminoindene-3-carboxylic acid possess an entirely different structure from β -imino- α -cyanohydrindene, and that in the first cases the aminic structure is stable and in the other the iminic. The same difference is also shown by 2-aminoindene-3-carboxamide (XIII), which forms a salt with hydrochloric acid and is hydrolysed by dilute mineral acids to 2-aminoindene-3-carboxylic acid, the amino-group remaining unaltered.

The reactions of the oxygen derivative (α -cyano- β -hydrindone) also indicate that very slight changes in the experimental conditions employed cause it to react in either the ketonic or enolic form. α -Cyano- β -hydrindone (VI) reacts as a true acid, that is, as 3-cyano-2-hydroxyindene (XIV), since it is not only readily soluble in aqueous solution of caustic alkalis and of alkaline carbonates, but is quickly etherified by alkyl sulphates. The salts thus produced are true *O*-derivatives, since on hydrolysis they are rapidly reconverted into the ketone. Thus, when the ketone is treated with methyl sulphate, it is converted into 3-cyano-2-methoxyindene (XV):

and, when treated with ethyl alcohol and sulphuric acid, is transformed into 3-cyano-2-ethoxyindene (XVI). Both these compounds are true *O*-salts, since, on boiling for a short time with dilute hydrochloric acid, they are hydrolysed, forming the alcohol and α -cyano- β -hydrindone. The capacity of the ketone to react in the enolic form is also shown by the fact that it gives an *O*-benzoyl derivative by the Baumann-Schotten method.

On the other hand, α -cyano- β -hydrindone reacts as a true ketone in that it forms a well-defined phenylhydrazone, and, when methylated with sodium methoxide and methyl iodide, leads to the formation of the *C*-methyl derivative, α -cyano- α -methyl- β -hydrindone (XVII) :

Unfortunately for the purposes of direct comparison, we have been unable to obtain this compound in a solid condition. It is a liquid which boils at 187° (25 mm.), that is to say, 8° lower than the *O*-methyl derivative, which boils at 195° (25 mm.). Its constitution is clearly proved by the fact that, on hydrolysis with alcoholic potash, it is completely transformed into *o*-phenyleneaceticpropionic acid (XVIII), and its ketonic nature is also shown by the formation of a well-defined phenylhydrazone with phenylhydrazine.

The formation of the *C*-methyl derivative in the above reaction is complete, and no trace of the *O*-methyl derivative could be detected accompanying it. It is therefore remarkable that ethylation with sodium ethoxide and ethyl iodide in ethyl-alcoholic solution should lead to the formation of the *O*-ethyl derivative, 3-cyano-2-ethoxyindene (XVI), and that none of the *C*-ethyl derivative could be isolated from the product. The compound formed in this reaction is identical with that which is derived from α -cyano- β -hydrindone on treatment with ethyl alcohol and sulphuric acid, since it not only possesses the same melting point and crystalline form as this substance, but on hydrolysis is readily transformed into ethyl alcohol and α -cyano- β -hydrindone. Several experiments were tried with the hope of inducing the ethyl group to enter at the carbon atom, but without success. For example, it was found that the sodium salt of α -cyano- β -hydrindone was very insoluble in both methyl and ethyl alcohol, and it was thought that the formation of the *O*-derivative from the sodium salt and ethyl iodide might have been due to a "constrained reaction" (compare Wislicenus, *Ahrens-Sammlung*, 1897, 249), but on treating the very soluble potassium salt with ethyl iodide under the same conditions, precisely the same result was obtained, and the *O*-ethyl derivative was the sole product formed. Moreover, when the sparingly soluble sodium salt of the ketone was treated with methyl iodide the *C*-methyl derivative was alone formed, and no trace of the *O*-methyl derivative could be isolated.

It is difficult to account for this remarkable difference in behaviour unless it is assumed that it constitutes an instance of steric hindrance, and that the spacial relations of the atoms do not permit of groups of more than a certain size attaching themselves to the α -carbon atom. Arguing on this assumption, it would seem

to supply an explanation for the remarkable fact that such dissimilar groups as carboxyl and carbethoxyl bring about the same change in the molecule of β -iminohydrindene, and cause the compound to react in the amino-form.

Reviewing the evidence in this light, it will be seen that the following groups, when attached to the α -carbon atom of β -hydrindone or its imino-derivative, render the single bond between the α - and β -carbon atoms stable or unstable:

Stable.		Unstable.	
H	CN	H	CO·NH ₂
Me	CN	H	CO ₂ H
		Et	CN
		H	CO ₂ Et

Arguing on the assumption that it is the molecular weights or a function of the molecular weights of the groups in the second list which render it impossible for them to attach themselves to the α -carbon atom, it will be seen that the limit of stability is probably reached with the groups Me and CN, since the molecular weight of these groups (41) is only four units less than of the groups H and CO·NH₂ (45). Experiments are now in progress which it is hoped will throw further light on this point, for if the above view is correct, then the alkylation of β -hydrindone will take place at the carbon atom until an alkyl group such as butyl is introduced, when alkylation will take place at the oxygen.

It should be mentioned that, although when the groups H and CN are attached to the α -carbon atom as in β -imino- α -cyanohydrindene and α -cyano- β -hydrindone the compound reacts both as a ketone and hydroxy-derivative or as an amine or imine, yet, when the aminic structure is stable, as in ethyl 2-aminoindene-3-carboxylate, 2-aminoindene-3-carboxylic acid and 2-aminoindene-3-carboxamide, there is not the slightest evidence that they can react in the iminic form, and it is highly improbable that these compounds are capable of exhibiting tautomerism.

It may also be mentioned that the name steric hindrance is hardly a satisfactory term to apply to a phenomenon of this type, since hindrance implies merely temporary opposition. There are, however, many cases, such as, for example, the non-formation of tetraphenylmethane, in which the formation of the compound is not merely hindered but inhibited by steric conditions. To these reactions, of which we believe the experiments described in the present paper are instances, the term steric inhibition would be better applied.

β -Imino- α -cyanohydrindene does not form a sodium derivative with sodium ethoxide, and cannot, therefore, be alkylated by this means.

The fact is interesting because it has been shown (Trans., 1906, 89, 1912) that ethyl β -imino- α -cyano- γ -phenylbutyrate,

is alkylated with great difficulty, and that only after several treatments with sodium ethoxide and an alkyl iodide can one of the hydrogen atoms marked (*) be replaced by alkyl. It is evident, therefore, that ring formation in the ortho-position entirely destroys the capacity of the methylene group adjacent to the imino-group for forming a sodium derivative. The question therefore arises, what is the mechanism of the reaction by which β -imino- α -cyanohydrindene is formed from *o*-phenylenediacetonitrile? The formation is, as has been already mentioned, quantitative, and takes place with remarkable ease in the presence of a trace of sodium ethoxide. The actual quantity of sodium ethoxide which is sufficient and the rate of the reaction have not as yet been determined, but Mr. A. Holt, jun., has signified his intention of working out these questions in the near future. For the purposes of the preparation it was found that 0.1 gram of sodium ethoxide would convert 10 grams of *o*-phenylenediacetonitrile into 10 grams of β -imino- α -cyanohydrindene in the course of one hour at 80°.

Moreover, the presence of sodium ethoxide is essential to the formation of the hydrindene derivative, since, when an attempt was made to produce it by E. v. Meyer's method for preparing imino-nitriles, that is by treating a solution of the dinitrile in ether with metallic sodium, no trace could be isolated when the ether had been previously carefully freed from the last traces of alcohol, although when very small quantities of alcohol were added to the ether the formation readily took place.

The reaction is, we consider, an instance of true catalysis in which sodium ethoxide plays the part of a catalyst probably in accordance with the scheme

Attempts made to isolate the intermediate imino-ether have so far been unsuccessful because, even at low temperatures, the elimination of alcohol takes place at once with the formation of the hydrindene ring; it is probable that its existence is only momentary.

It has always seemed likely to us that the formation of imino-nitriles could be better represented by a catalytic action such as the above rather than by the equation previously suggested (Trans., 1906, 89, 1906), but no direct evidence could be obtained on this point because the imino-nitriles prepared by us up to the present have

all been capable of reacting with sodium ethoxide to form a sodium derivative, and hence the catalyst in these cases has been rapidly destroyed. It is proposed to institute experiments with the object of ascertaining whether imino-nitriles which do not react with sodium ethoxide can be formed by the action of sodium on a solution of the nitrile in ether which has been entirely freed from alcohol, and it is also hoped that by the aid of the above reaction with sodium ethoxide valuable evidence concerning ring formation will be obtained by the production of alicyclic compounds from straight chain dinitriles.

In a former communication (Trans., 1907, 91, 584), it was suggested that the formation of ethyl 1:3-naphthylenediamine-2-carboxylate from ethyl β -imino- α -cyano- γ -phenylbutyrate by the action of cold concentrated sulphuric acid could be best explained on the assumption that the nitrile first formed an additive product with one molecule of sulphuric acid, and that sulphuric acid was then eliminated from the hydrogen atom in the ortho-position in the benzene ring; the naphthalene derivative being formed thus:

It was also mentioned that in all probability the explanation of the formation of an acid amide by dissolving a nitrile in concentrated sulphuric acid and pouring the product into water is of the same kind:

A good instance of the formation of an amide in this way is given in the present paper, for when *o*-phenylenediacetonitrile is dissolved in concentrated sulphuric acid and the product is poured into water, the amide is produced in almost quantitative yield:

Since the amide is completely converted into *o*-phenylenediacetic acid on warming with potash, this method is probably the best for preparing this acid in quantity.

During a conversation with Dr. F. E. Matthews on this subject, he mentioned that his experiments with certain nitriles pointed to the formation of an additive product from one molecule of the nitrile and two of sulphuric acid, but at that time the compounds investigated

by us furnished no evidence of the formation of this double additive product, for although the formation of the amide could be readily explained by its means:

yet it was difficult to see how the formation of an additive product of this kind could lead to the production of the naphthalene ring in the manner described above.

β -Imino- α -cyanohydrindene is, however, a compound which without doubt forms an additive product with two molecules of sulphuric acid, and we are indebted to Dr. Matthews for a suggestion which has enabled us to explain the curious behaviour of this imino-nitrile with concentrated sulphuric acid.

For some time considerable difficulty was experienced in hydrolysing the nitrile group of β -imino- α -cyanohydrindene without either breaking the hydrindene ring or causing the formation of products of higher molecular weight. As already stated, the imino-nitrile is readily hydrolysed by dilute mineral acids, forming α -cyano- β -hydrindone, but when the action of the hydrolysing agent is prolonged, the ketone condenses with itself and a derivative of bishydrindene is formed. When either the ketone or the imino-compound is treated with alkaline hydrolysing agents, the disruption of the indene ring is rapidly effected and *o*-phenylenediacetic acid is the sole product. An attempt was therefore made to prepare the amide from β -imino- α -cyanohydrindene by dissolving it in concentrated sulphuric acid and pouring the product into water. It was found that the imino-nitrile readily reacted with the strong acid, and that after leaving for half an hour a clear solution could be obtained on pouring a test portion into water. The sulphuric acid solution was therefore poured on ice, when the solid which separated was found to consist almost entirely of the carboxylic acid and to contain only a small quantity (about 2 per cent.) of the amide. We consider that the formation of the acid in this manner is due to the production of an additive product of the imino-nitrile with two molecules of sulphuric acid which subsequently reacts with water, forming the ammonium salt of the acid, thus:

* These formulæ are written in the iminic form for the sake of clearness. The compounds, of course, have the aminic structure.

This ammonium salt is then at once decomposed by the free sulphuric acid present, yielding the free carboxylic acid.

It is, of course, evident that the product formed by water on the sulphuric acid additive product may either pass by rearrangement into the ammonium salt or may eliminate water and pass into the amide, and it is possible that the small quantity of amide produced in the above reaction may have been formed in this way, but for certain reasons we are inclined to think that its formation is due to the partial production of a mono-additive product which reacts with water in the manner just indicated. There is at present no direct evidence for this, but it is rendered probable, because if the time during which the action of concentrated sulphuric acid is continued is less than that mentioned above, a larger amount of the amide is formed. It is reasonable to suppose that the formation of a mono-additive product in every case precedes the formation of the di-additive product.

When the concentrated sulphuric acid solution of the imino-nitrile is poured into well-cooled absolute alcohol, the product is the same as with water, ethyl hydrogen sulphate being produced in accordance with the scheme :

No trace of the ethyl salt of the carboxylic acid is formed in this reaction, and in order to produce this substance the ethyl-alcoholic solution containing ethyl hydrogen sulphate must be heated for some considerable time on the water-bath.

As already mentioned, 2-aminoindene-3-carboxylic acid passes into β -hydrindone on distilling a solution of it in dilute sulphuric acid with steam :

The hydrolysis of the nitrogen group takes place as soon as and not until carbon dioxide is eliminated, and it is therefore probable that β -iminohydrindene (XIX) is a true imino-compound. Unfortunately, we have been unable to isolate this substance, for when the reactions which should give it, such as the elimination of carbon dioxide from the carboxylic acid by heat, are tried, only compounds formed by intramolecular condensation are produced. But that it is a true imino-compound readily hydrolysable by acids can be inferred by the production of β -hydrindone from β -nitroindene, which, as Wallach has shown (*Annalen*, 1904, **336**, 1), can be effected by reduction and hydrolysis.

β -Hydrindone has been prepared by Schad (*Ber.*, 1893, **26**, 222) and Benedikt (*Annalen*, 1893, **275**, 353) by the distillation of the calcium salt of *o*-phenylenediacetic acid; by Heusler and Schieffer (*Ber.*, 1899, **32**, 30) from the indene of coal-tar, and more recently by Wallach in the manner mentioned above. It is described as a white, crystalline substance which rapidly changes on exposure to the air to a brown resin. β -Hydrindone prepared by our method exhibits no tendency to decompose, and has been kept for many months without showing any signs of change. It is probable, therefore, that by our method of preparation some impurity has been removed which always accompanied β -hydrindone when prepared by the methods quoted.

All the derivatives of β -hydrindone and its imide described in this paper possess one characteristic reaction in common. When a trace is added to concentrated sulphuric acid a brilliant blue solution is produced. This colour is discharged on adding a further quantity of the hydrindene derivative, but on adding the colourless solution thus formed to a further quantity of sulphuric acid, the blue colour is again produced.

It was ultimately found that when the concentrated sulphuric acid had been carefully purified no colour was produced, but that immediately a trace of an oxidising agent such as nitric acid was added it was at once formed. It is very difficult to obtain sulphuric acid which does not give this reaction, the pure commercial acid giving it to a very marked degree. When very pure sulphuric acid which has been found not to give the colour is mixed with a trace of selenic acid, the blue colour formed is very intense.

Neither the α - nor β -hydrindone has, so far as we are aware, been observed to oxidise to the double molecule analogous to the formation of indigo from indoxyl, and it is therefore of interest to note that β -imino- α -cyanohydrindene readily undergoes this transformation. When a solution of this substance in alcoholic potash is shaken in the air, it rapidly becomes intensely purple, ammonia at the same time being eliminated. On standing, the solution deposits crystals of a potassium salt of the formula:

which dissolve in hot water, forming an intensely bluish-purple solution from which wool can be dyed a rich shade of purple. On treating the aqueous solution of the potassium salt with acids, the free hydroxyl compound is produced as a red amorphous precipitate. It is, however, insoluble in all solvents, and has not been obtained in a crystalline state.

EXPERIMENTAL.

o-Phenylenediacetonitrile, $C_6H_4(CH_2 \cdot CN)_2$.

The preparation of $\omega\omega'$ -dibromo-*o*-xylene was effected in the manner described in a previous paper (Trans., 1907, **91**, 1695), and it was converted into the dinitrile by the aid of potassium cyanide in dilute alcoholic solution. The method adopted was as follows, the operation being conducted in the open air, since $\omega\omega'$ -dibromo-*o*-xylene has a most painful effect on the eyes. About 10 per cent. more than the theoretical quantity of potassium cyanide was dissolved in as little water as possible, and then mixed with three times its volume of ethyl alcohol. After the mixture had been raised to the boiling point, the finely-ground bromo-compound was added in small portions at a time in such a manner that the heat of the reaction kept the liquid at the boiling point. When all had been added, the mixture was allowed to stand for half an hour, when it was diluted with water, and the oil which was then precipitated extracted with ether. After drying, the ethereal extract was evaporated to a small bulk and allowed to stand, when crystals of the dinitrile slowly separated. These were collected and recrystallised from alcohol, the dark-coloured oil which was obtained on evaporating the ethereal mother-liquor yielding a further quantity of crystals on being mixed with an equal volume of alcohol. Pure *o*-phenylenediacetonitrile melts at 60°.

When *o*-phenylenediacetonitrile is recrystallised from either methyl or ethyl alcohol, but best from the former, it can be obtained in two forms, one of which separates at temperatures below 18°, the other at temperatures above this point. The modification separating at the lower temperature which consists of needles is unstable, and almost immediately passes into the stable or prismatic form. At the same time there is evidently a considerable change in volume, since each needle on passing into the prismatic form breaks up with a loud report, which, if the needles have grown to any size, is almost explosive. This property is best shown by melting about a gram of the dinitrile under light petroleum (b. p. 80—90°), in which it is almost insoluble, and then rapidly cooling below 10°. On touching, the oil will solidify in the labile form, which will almost immediately pass into the stable variety, the change being accompanied by a loud explosion, which, in one or two experiments, shattered the test tube.

Formation of o-phenylenediacetamide and *o*-phenylenediacetic acid from *o*-phenylenediacetonitrile.

The transformation of *o*-phenylenediacetonitrile into *o*-phenylene-diacetamide may be readily effected by the aid of concentrated

sulphuric acid, the following conditions being found most suitable. The dinitrile was slowly added to five times its weight of concentrated sulphuric acid, and the solution, which became warm, allowed to stand at the ordinary temperature until a test portion, on being diluted with water, showed no deposition of oil. The whole was then poured into water, and the clear solution made alkaline with ammonia, when the formation of ammonium sulphate in the solution caused the diamide to be completely precipitated. It was collected by filtration and crystallised from water, from which solvent it separated in long, silky needles, resembling asbestos, melting at 198° :

0.1532 gave 0.3501 CO_2 and 0.0889 H_2O . $\text{C} = 62.30$; $\text{H} = 6.44$.

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$ requires $\text{C} = 62.5$; $\text{H} = 6.2$ per cent.

o-Phenylenediacetamide is very sparingly soluble in alcohol, and is readily hydrolysed by aqueous solutions of caustic alkalis. It was completely converted into *o*-phenylenediacetic acid by boiling with excess of caustic potash solution until the evolution of ammonia had ceased, and then acidifying the solution with hydrochloric acid. The acid was extracted by ether, the ethereal extract dried and evaporated, the residue, which solidified on cooling, being crystallised from water. *o*-Phenylenediacetic acid prepared in this way showed the correct melting point, namely, 150° :

0.2012 gave 0.4553 CO_2 and 0.0905 H_2O . $\text{C} = 61.70$; $\text{H} = 4.99$.

$\text{C}_{10}\text{H}_{10}\text{O}_4$ requires $\text{C} = 61.8$; $\text{H} = 5.1$ per cent.

The yield of the acid from *o*-phenylenediacetonitrile by this process is 90 per cent. of the theory.

In order to prepare this substance, 10 grams of *o*-phenylenediacetonitrile were dissolved in 40 c.c. of ethyl alcohol and introduced into a flask fitted with a reflux condenser, the apparatus being so devised that a current of dry hydrogen could be driven through the flask throughout the operation. The alcoholic solution was then heated to boiling on the water-bath, and 1 c.c. of a solution of one gram of sodium dissolved in 10 c.c. of alcohol added through the condenser. On adding the sodium ethoxide the solution became at once yellow, the yellow colour increasing in intensity as the reaction progressed. After one hour of gentle boiling, the contents of the flask were allowed to cool, when yellow prisms separated which were collected, washed and dried. The compound prepared in this way was almost pure, the yield being practically quantitative. It was purified for analysis by recrystallisation from hot alcohol, from which solvent it separated in prisms, usually slightly yellow, which melted at 193° :

0.1548 gave 0.4381 CO₂ and 0.0718 H₂O. C = 77.18; H = 5.15.

0.2072 „ 31.8 c.c. of nitrogen at 18° and 757 mm. N = 17.67.

C₁₀H₈N₂ requires C = 76.9; H = 5.1; N = 17.9 per cent.

The yellow colour of *β-imino-α-cyanohydrindene* is evidently due to the presence of traces of impurity, since on repeated crystallisation it can be obtained almost colourless. The imino-nitrile sublimes when heated, and does not form a sodium compound with sodium ethoxide. It is readily soluble in hot alcohol, sparingly so in cold alcohol or benzene, and practically insoluble in water. Its alcoholic solution gives no colour with ferric chloride, but when a small quantity of the solid is dissolved in concentrated sulphuric acid containing a trace of an oxidising agent, a fine blue coloration is produced. This reaction is best seen with sulphuric acid containing a trace of selenic acid. Indeed, it is a matter of some difficulty to obtain sulphuric acid which does not give this reaction. Ordinary sulphuric acid gives it at once, and even after careful distillation a faint colour is produced.

The *phenylhydrazone*.—*β*-Imino-*α*-cyanohydrindene reacts slowly when boiled in acetic acid solution with phenylhydrazine acetate, and, on cooling, yellow crystals are deposited which when crystallised from alcohol yield pale yellow plates which melt and decompose at 187°:

0.1643 gave 24.2 c.c. of nitrogen at 16° and 762 mm. N = 17.21.

C₁₆H₁₃N₃ requires N = 17.0 per cent.

This compound is evidently the same as that produced by the action of phenylhydrazine on *α*-cyano-*β*-hydrindone (see later).

Conversion of β-imino-α-cyanohydrindene into 3-cyano-2-ethoxyindene.

This conversion was effected by dissolving the imino-compound in ethyl alcohol, adding one-third of the volume of concentrated sulphuric acid, and, after boiling the solution on the water-bath for twenty minutes, allowing it to stand for twelve hours. At the end of this time the product was poured into water, the solid then formed filtered and crystallised from alcohol. In this way, colourless needles were obtained melting at 84°:

0.2636 gave 0.7516 CO₂ and 0.1450 H₂O. C = 77.76; H = 6.1.

0.2090 „ 14.3 c.c. of nitrogen at 14° and 746 mm. N = 7.9.

C₁₂H₁₁ON requires C = 77.8; H = 5.9; N = 7.6 per cent.

This compound is evidently the same as that produced by the ethylation of *α*-cyano-*β*-hydrindone (see later).

Bis-1-cyano-2-hydroxyindene.

The oxidation of β -imino- α -cyanohydrindene to the potassium salt of the above substance was effected in the following way: Five grams of the imino-compound were dissolved in alcohol containing rather more than one equivalent of potash. After the solution had been warmed to 50° , air was drawn through it until a test portion, on dilution with water, gave no precipitate of unchanged imino-compound. The deep purple solution was allowed to stand, when crystals of the *potassium* salt slowly separated. These were collected, washed with cold water and dried, yielding slender, deep blue needles with faint copper reflex:

0.2471 gave 0.1112 K_2SO_4 . $\text{K} = 20.12$.

$\text{C}_{20}\text{H}_8\text{O}_2\text{N}_2\text{K}_2$ requires $\text{K} = 20.20$ per cent.

The potassium salt is insoluble in cold water, but readily dissolves on boiling. The deep purple solution thus obtained deposits the crystalline salt completely on cooling, but in hot solution can be used for the purpose of dyeing wool. The *ammonium* and *sodium* salts show a greater degree of solubility in water.

The free *acid* is deposited as a red, amorphous precipitate on adding hydrochloric acid to a solution of the above potassium salt. It is insoluble in all the usual solvents, and therefore for the purposes of analysis the precipitated acid was washed and dried:

0.2317 gave 0.6560 CO_2 and 0.0690 H_2O . $\text{C} = 77.22$; $\text{H} = 3.31$.

$\text{C}_{20}\text{H}_{10}\text{O}_2\text{N}_2$ requires $\text{C} = 77.4$; $\text{H} = 3.2$ per cent.

When heated the compound partly sublimes, but for the most part chars without melting. It is readily soluble in alkali carbonates and caustic alkalis, forming the highly coloured alkali salts just described.

This substance was prepared in the following way: Ten grams of β -imino- α -cyanohydrindene were mixed with 200 c.c. of water to which 50 c.c. of concentrated hydrochloric acid had been added, and the mixture boiled until a test portion was completely soluble in dilute sodium carbonate solution, an operation which usually required from ten to fifteen minutes. The mixture was then cooled and extracted three times with ether, the yellow ethereal solution being subsequently thoroughly shaken with dilute aqueous sodium carbonate, whereby the colourless ketone was completely extracted, leaving the yellow impurities dissolved in the ether. The ketone was precipitated on

adding acid to the sodium carbonate solution, and was purified by recrystallisation from dilute alcohol, when it was obtained in colourless plates melting at 172° with decomposition. The compound also crystallises well from glacial acetic acid :

0.3704 gave 1.0316 CO_2 and 0.1509 H_2O . $\text{C} = 75.95$; $\text{H} = 4.49$.

0.1990 gave 15.6 c.c. of nitrogen at 19° and 772 mm. $\text{N} = 9.2$.

$\text{C}_{10}\text{H}_7\text{ON}$ requires $\text{C} = 76.4$; $\text{H} = 4.5$; $\text{N} = 8.9$ per cent.

α -Cyano- β -hydrindone is readily soluble in alkali carbonates. When a small quantity is added to concentrated sulphuric acid containing a trace of an oxidising agent, a deep blue solution is produced similar to that formed with the imino-compound. The ketone gives a green colour with ferric chloride, but its solution in alcoholic potash does not oxidise in the air.

The *phenylhydrazone*, $\text{C}_{16}\text{H}_{13}\text{N}_3$, is formed as a yellow, crystalline precipitate on adding a solution of phenylhydrazine acetate to a solution of the ketone in glacial acetic acid and boiling. It crystallises from absolute alcohol in small needles melting at 187° with decomposition :

0.2464 gave 36.0 c.c. of nitrogen at 13° and 752 mm. $\text{N} = 17.1$.

$\text{C}_{16}\text{H}_{13}\text{N}_3$ requires $\text{N} = 17.0$ per cent.

The *potassium salt*, $\text{C}_{10}\text{H}_6\text{ONK}$, is formed as a white, crystalline precipitate on adding a slight excess of alcoholic potash to a solution of the ketone in alcohol. It can be recrystallised from alcohol, from which solvent it separates in colourless plates :

0.4375 gave 0.1925 K_2SO_4 . $\text{K} = 19.72$.

$\text{C}_{10}\text{H}_6\text{ONK}$ requires $\text{K} = 20.0$ per cent.

The potassium salt is readily soluble in alcohol, whereas the *sodium salt* is very sparingly soluble. The sodium salt is, moreover, much less soluble in water than the potassium salt, and is completely precipitated from its aqueous solution by excess of sodium hydroxide.

The *silver salt*, $\text{C}_{10}\text{H}_6\text{ONAg}$, is precipitated on adding the calculated quantity of silver nitrate solution to an aqueous solution of the potassium salt. It is a white powder which becomes slowly coloured on exposure to light :

0.2731 gave 0.1119 Ag . $\text{Ag} = 40.97$.

$\text{C}_{10}\text{H}_6\text{ONAg}$ requires $\text{Ag} = 41.0$ per cent.

The *O-benzoyl derivative*, $\text{C}_6\text{H}_4\text{C}(\text{CN})\text{CH}_2\text{COBz}$, can be prepared by dissolving the ketone in excess of potassium hydroxide solution, adding excess of benzoyl chloride and shaking until all the chloride has dissolved. The insoluble precipitate which remains, on being filtered

and recrystallised from alcohol, can be obtained in slender, colourless needles melting at 123° :

0.1774 gave 0.5073 CO_2 and 0.0654 H_2O . $\text{C} = 77.99$; $\text{H} = 4.09$.

$\text{C}_{17}\text{H}_{11}\text{O}_2\text{N}$ requires $\text{C} = 78.1$; $\text{H} = 4.2$ per cent.

An intensely green compound is formed in this reaction, but since it is readily soluble in cold alcohol, the benzoyl derivative can be easily freed from it. The benzoyl derivative is quickly hydrolysed with dilute alcoholic potash, yielding α -cyano- β -hydrindone and benzoic acid.

Formation of o-phenylenediacetic acid from α -cyano- β -hydrindone.

On boiling α -cyano- β -hydrindone with excess of aqueous potassium hydroxide, ammonia was slowly evolved, and after heating for twelve hours the evolution had ceased. The solution was then acidified and extracted with ether, the ethereal extract evaporated and the residue crystallised from water, when the long, characteristic needles of o-phenylenediacetic acid, melting at 150° , separated :

0.2236 gave 0.5056 CO_2 and 0.1007 H_2O . $\text{C} = 61.66$; $\text{H} = 5.00$.

$\text{C}_{10}\text{H}_{10}\text{O}_4$ requires $\text{C} = 61.8$; $\text{H} = 5.1$ per cent.

Alkylation of α -cyano- β -hydrindone by etherifying agents.

In order to prepare this compound, 3 grams of the ketone were dissolved in 10 times its weight of methyl alcohol and the solution mixed with 5 grams of methyl sulphate. After being boiled for a few minutes, the solution was treated with excess of potassium hydroxide and vigorously shaken until all the excess of methyl sulphate had been destroyed, when the insoluble residue was filtered and recrystallised from methyl alcohol. The compound may also be prepared from methyl alcohol and sulphuric acid by dissolving 3 grams of the ketone in 10 times its weight of methyl alcohol, adding one-third of the volume of concentrated sulphuric acid and, after boiling, allowing to stand some hours. The methoxy-derivative then separates completely from the solution and can be collected at once by filtration. When recrystallised from methyl alcohol, 3-cyano-2-methoxyindene forms long, colourless needles melting at 88° and boiling at 195° (25 mm.) :

0.2139 gave 0.6043 CO_2 and 0.1045 H_2O . $\text{C} = 77.05$; $\text{H} = 5.42$.

$\text{C}_{11}\text{H}_9\text{ON}$ requires $\text{C} = 77.2$; $\text{H} = 5.3$ per cent.

The compound also crystallises well from light petroleum (b. p. $80\text{--}90^{\circ}$). When boiled for a few minutes with dilute hydrochloric acid,

3-cyano-2-methoxyindene slowly passes into solution, and on cooling the solution crystals of α -cyano- β -hydrindone melting and decomposing at 172° separate. It is evident, therefore, that the compound is the *O*-methyl derivative.

The ethoxy-derivative was prepared by the action of ethyl alcohol and sulphuric acid on α -cyano- β -hydrindone. Three grams were dissolved in 30 grams of ethyl alcohol and the solution mixed with one-third of its volume of concentrated sulphuric acid. After having been raised to the boiling point, the solution was allowed to stand, when crystals of the ethoxy-derivative slowly separated. These were collected and recrystallised from ethyl alcohol, when they were obtained in slender, colourless needles melting at 84° and boiling at 212° (25 mm.):

0.2451 gave 0.6990 CO_2 and 0.1349 H_2O . $\text{C} = 77.78$; $\text{H} = 6.11$.

$\text{C}_{12}\text{H}_{11}\text{ON}$ requires $\text{C} = 77.8$; $\text{H} = 5.9$ per cent.

When boiled with dilute hydrochloric acid, 3-cyano-2-ethoxyindene passes slowly into solution, and if the solution is cooled crystals of α -cyano- β -hydrindone melting and decomposing at 172° separate. Both the methoxy- and ethoxy-derivatives give the characteristic blue colour of derivatives of β -hydrindone and β -iminohydrindone with concentrated sulphuric acid containing a trace of an oxidising agent. The vapours of both compounds possess a peculiar garlic-like odour.

Alkylation of α -Cyano- β -hydrindone through the Alkali Salts with an Alkyl Iodide.

It has already been mentioned that the sodium salt of α -cyano- β -hydrindone is sparingly soluble in hot alcohol, whereas the potassium salt readily dissolves. For reasons given in the introduction, it was therefore necessary to investigate the action of methyl iodide on both the sodium and potassium salts, but since the reactions were carried out in the same way, and the products in each case were found to be identical, it is only necessary to describe one of them in detail: 3.6 grams of pure potassium hydroxide were dissolved in 100 c.c. of methyl alcohol, and the solution mixed with 10 grams of α -cyano- β -hydrindone. The clear yellow solution was then transferred to a Geissler flask, mixed with 20 grams of methyl iodide and heated on the water-bath for two hours. At the end of this time the excess of methyl iodide was removed by distillation, water added to the residue,

and the oil which separated extracted by ether. The ethereal solution was then washed with water to remove alcohol, and finally with dilute aqueous sodium carbonate to remove any unchanged ketone, dried and evaporated. The oil which remained boiled at 187° (25 mm.), passing over as a viscous, colourless liquid, which could not, however, be induced to solidify:

0.2201 gave 0.6211 CO_2 and 0.1071 H_2O . $\text{C} = 76.96$; $\text{H} = 5.40$.

$\text{C}_{11}\text{H}_9\text{ON}$ requires $\text{C} = 77.2$; $\text{H} = 5.3$ per cent.

The *phenylhydrazone*, $\text{C}_{17}\text{H}_{15}\text{N}_3$, was prepared by dissolving the ketone in glacial acetic acid, adding a solution of phenylhydrazine acetate in glacial acetic acid, and boiling for a few minutes. On cooling, yellow crystals of the salt separated, which were obtained in yellow prisms, melting at 169° by recrystallisation from alcohol:

0.2179 gave 30.7 c.c. of nitrogen at 17° and 756 mm.; $\text{N} = 16.26$.

$\text{C}_{17}\text{H}_{15}\text{N}_3$ requires $\text{N} = 16.1$ per cent.

The constitution of α -cyano- α -methyl- β -hydrindone was proved by the formation of the above acid on hydrolysis. The ketone was boiled in a Geissler flask with a solution of one and a half times the calculated quantity of potash dissolved in methyl alcohol until a test portion on dilution with water showed no separation of oil. Water was then added, and the solution freed from methyl alcohol by evaporation. The clear aqueous solution was then acidified and extracted with ether, the ethereal extract being free from the acid by extracting it with a little aqueous sodium carbonate. On acidifying the sodium carbonate extract, the acid was precipitated and was purified by recrystallisation from hot water, being obtained in small, colourless needles melting at 152° :

0.2011 gave 0.4665 CO_2 and 0.1067 H_2O . $\text{C} = 63.27$; $\text{H} = 5.90$.

$\text{C}_{11}\text{H}_{12}\text{O}_4$ requires $\text{C} = 63.5$; $\text{H} = 5.8$ per cent.

The acid is much less soluble in ether than *o*-phenylenediacetic acid.

3-Cyano-2-ethoxyindene.

The action of ethyl iodide on either the sodium or potassium salts of α -cyano- β -hydrindone in ethyl-alcoholic solution leads to the formation of the above *O*-ethyl derivative, although the experimental conditions were precisely the same as those which in the case of methyl iodide led to the production of the *C*-methyl derivative. Ten grams of the ketone were added to a solution of 3.6 grams of potassium hydroxide in 100 c.c. of ethyl alcohol, excess of ethyl

iodide was then added and the solution heated on the water-bath for two hours. At the end of this time the excess of ethyl iodide was removed by evaporation, water added, and the resulting oil, which rapidly solidified, was extracted by ether. The ethereal extract, after being washed with water, was shaken with dilute sodium carbonate solution to remove any unchanged ketone, dried and evaporated.

The oily residue quickly became solid, and after being recrystallised from ethyl alcohol was obtained in slender, colourless needles melting at 84° :

0.2094 gave 0.5980 CO_2 and 0.1155 H_2O . $\text{C} = 77.8$; $\text{H} = 6.1$.

$\text{C}_{12}\text{H}_{11}\text{ON}$ requires $\text{C} = 77.8$; $\text{H} = 5.9$ per cent.

When the compound was mixed with a specimen of 3-cyano-2-ethoxyindene prepared by the etherification of α -cyano- β -hydrindone (see page 181), no alteration in the melting point was produced, and when it was boiled for a few minutes with dilute hydrochloric acid it was completely hydrolysed to α -cyano- β -hydrindone. There could be no doubt, therefore, that it was the *O*-ethyl derivative.

Action of Concentrated Sulphuric Acid on β -Imino α -cyanohydrindene.

The formation of 2-aminoindene-3-carboxylic acid from the imino-nitrile can be readily effected by the action of concentrated sulphuric acid. Twenty grams of β -imino- α -cyanohydrindene were added gradually to 200 c.c. of concentrated sulphuric acid, with constant stirring, whereby the temperature rose to 30° . On adding the first portion of the imino-nitrile, the deep blue solution to which reference has already been made was formed. This colour disappeared on adding more of the imino-nitrile, and when all had dissolved, the solution, which was pale yellow, was left at the ordinary temperature for one hour. The strongly acid solution was then poured in a thin stream on ice, when the clear solution which was first formed gradually deposited a heavy white precipitate. The decomposition of the sulphuric acid addition product takes place, however, only slowly at 0° , and the above solution must be left for at least an hour before the decomposition is complete.

After the ice had all melted, the solution was filtered, and the insoluble residue treated with dilute sodium hydroxide solution and filtered, the insoluble portion being subsequently washed with dilute alkali in order to remove the last traces of acid. The alkaline solution, on being acidified with hydrochloric acid, gave a precipitate of the free acid which was collected and recrystallised from alcohol,

when it was obtained in pale yellow needles melting and decomposing at 171° :

0.2632 gave 0.6622 CO_2 and 0.1270 H_2O . $\text{C} = 68.6$; $\text{H} = 5.3$.

$\text{C}_{10}\text{H}_9\text{O}_2\text{N}$ requires $\text{C} = 68.6$; $\text{H} = 5.1$ per cent.

The acid is soluble in hot water and can be recrystallised from this solvent, but it is advisable to use alcohol for this purpose, since at the higher temperature some carbon dioxide is always eliminated.

The compound is both an acid and a base. Thus it is readily soluble in alkali carbonates and dissolves in dilute ammonia, but the salts formed are evidently unstable, since, for example, on boiling a solution of the ammonium salt containing excess of ammonia, the free acid separates on cooling even though the solution is still alkaline to litmus.

The *hydrochloride*, $\text{C}_{10}\text{H}_9\text{O}_2\text{N} \cdot \text{HCl}$, can be prepared by cautiously dissolving the carboxylic acid in concentrated hydrochloric acid, filtering and allowing to stand, when slender, colourless needles of the salt separate. It is at once dissociated by water:

0.2318 gave 0.1564 AgCl . $\text{Cl} = 16.69$.

$\text{C}_{10}\text{H}_9\text{O}_2\text{N} \cdot \text{HCl}$ requires $\text{Cl} = 16.8$ per cent.

2-Aminoindene-3-carboxylic acid gives a blue colour with concentrated sulphuric acid containing a trace of an oxidising agent.

The portion of the product which remained undissolved after extracting 2-aminoindene-3-carboxylic acid in the above experiment with aqueous potash, was recrystallised from alcohol and obtained in pale yellow plates melting with decomposition at 202° :

0.2099 gave 0.5275 CO_2 and 0.1108 H_2O . $\text{C} = 68.54$; $\text{H} = 5.86$.

$\text{C}_{10}\text{H}_{10}\text{ON}_2$ requires $\text{C} = 68.9$; $\text{H} = 5.7$ per cent.

The amide forms salts with acids which are unstable in aqueous solution. The *hydrochloride*, $\text{C}_{10}\text{H}_{10}\text{ON}_2 \cdot \text{HCl}$, is prepared by dissolving the amide in concentrated hydrochloric acid and allowing the solution to stand. It forms colourless plates:

0.2158 gave 0.1462 AgCl . $\text{Cl} = 16.76$.

$\text{C}_{10}\text{H}_{10}\text{ON}_2 \cdot \text{HCl}$ requires $\text{Cl} = 16.9$ per cent.

When the amide is warmed with dilute aqueous potash, ammonia is evolved, and if, when the evolution is complete, the solution is acidified, 2-aminoindene-3-carboxylic acid separates from the solution.

Ethyl 2-aminoindene-3-carboxylate, $C_6H_4 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ C(CO_2Et) \end{array} \gg C \cdot NH_2$.

This substance can be prepared by the etherification, by alcohol and sulphuric acid, of the corresponding carboxylic acid. It was, however, conveniently prepared directly from β -imino- α -cyanohydrindene by the following process. Twenty grams of the imino-nitrile were dissolved in 200 c.c. of concentrated sulphuric acid in the manner already described, and after the solution had stood for one hour it was poured into three times its volume of absolute alcohol, and then heated on the water-bath for three hours. At the end of this time, the product was poured into water and the aqueous solution extracted with ether. The ethyl salt being very insoluble in ether remained for the most part suspended in the solvent, but the aqueous solution was clear and could be separated. The ethereal solution containing the ethyl salt in suspension was then shaken with dilute sodium carbonate solution to remove any unchanged acid, and then filtered. The solid thus obtained, on being recrystallised from alcohol, yielded flat, glistening, pale yellow needles melting at 206° :

0.3062 gave 0.7960 CO_2 and 0.1770 H_2O . $C = 70.9$; $H = 6.4$.

$C_{12}H_{13}O_2N$ requires $C = 70.9$; $H = 6.4$ per cent.

The ethyl salt is readily hydrolysed by dilute hydrochloric acid to 2-aminoindene-3-carboxylic acid.

The *hydrochloride*, $C_{12}H_{13}O_2N \cdot HCl$.—The ethyl salt quickly dissolves in concentrated hydrochloric acid, and the solution on standing deposits the hydrochloride in colourless needles which are at once dissociated by water:

0.2297 gave 0.1363 $AgCl$. $Cl = 14.68$.

$C_{12}H_{13}O_2N \cdot HCl$ requires $Cl = 14.8$ per cent.

Both the ethyl salt and the carboxylic acid give the characteristic blue colour with concentrated sulphuric acid containing a trace of an oxidising agent.

Elimination of Nitrogen from 2-Aminoindene-3-carboxylic Acid and from Ethyl 2-Aminoindene-3-carboxylate by means of Nitrous Acid.

2-Aminoindene-3-carboxylic Acid.—The experiment was carried out in such a manner that the nitrogen evolved by the action of nitrous acid could be measured. A weighed quantity of the acid was introduced into a small flask, in which it was brought into solution by means of a little sodium hydroxide. Excess of sodium nitrite solution was then added, and the flask connected on the one hand with a nitrometer filled with potassium hydroxide solution, and on the other with a

carbon dioxide generating apparatus. At the same time, a dropping funnel was inserted in the neck of the flask. After all the air had been expelled by carbon dioxide, the solution in the flask was warmed to 80° and excess of hydrochloric acid run in slowly through the dropping funnel. When the evolution of nitrogen had ceased, the gas left in the flask was swept out by carbon dioxide and the amount of nitrogen measured :

0.2219 gave 23.5 c.c. of nitrogen at 18° and 756 mm.

$C_{10}H_9O_2N + HNO_2$ requires 23.8 c.c.

No trace of 2-hydroxyindene-3-carboxylic acid could be isolated from the products of this reaction, the chief compound formed being a yellow, amorphous substance which has not as yet been identified.

Ethyl 2-aminoindene-3-carboxylate.—The apparatus employed in this experiment was the same as that used above, only the weighed quantity of the ethyl salt, after being introduced into the flask, was dissolved in concentrated hydrochloric acid, and, after the air in the flask had been replaced by carbon dioxide, an excess of sodium nitrite solution was run in from the dropping funnel :

0.2138 gave 24.9 c.c. of nitrogen at 17° and 766 mm.

$C_{12}H_{13}O_2N + HNO_2$ requires 25.2 c.c.

In this case also no ethyl 2-hydroxyindene-3-carboxylate was formed in the reaction, the product consisting of an ill-defined resinous substance, evidently of high molecular weight.

This substance was best produced from 2-aminoindene-3-carboxylic acid in the following way. Thirty grams of the acid were mixed with a solution of 80 grams of concentrated sulphuric acid in 240 of water, which was quickly raised to boiling and a rapid current of steam passed into it, when the hydrindone passed over as a colourless oil which solidified in the receiver. It was collected and recrystallised from alcohol, being obtained in large, colourless needles melting at 58° . These crystals showed no tendency to alter on exposure to the air.

The substance was further characterised by the formation of its phenylhydrazone, melting at 120° , and its oxime, melting at 152° . In preparing the phenylhydrazone, however, care must be taken not to boil the acetic acid solution of the reacting substances ; otherwise a compound melting at 210° separates out which contains 6.8 per cent. of nitrogen. It is probably the phenylhydrazone of a condensation product. β -Hydrindone gives a deep blue colour with concentrated sulphuric acid containing a trace of an oxidising agent ; an examination

of the properties of this substance and of those of its derivatives is in progress.

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