IV.—*The Oxime of Mesoxamide and some Allied Compounds. Part II. Disubstituted Derivatives.*

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THE investigation which forms the subject of this paper is a continuation of the work on the oximes of mesoxamide and its dimethyl derivative (Whiteley, Trans., 1900, '77, 1040): compounds characterised by their bright yellow alkali and rich violet ferrous salts. From the constitution of the original compound, it is clear that the acidic hydrogen is furnished either by one of the $-\text{CO}\cdot\text{NH}_2$ groups reacting in the tautomeric form $-\text{C}(\text{OH})\cdot\text{NH}$, or by the oximino-group itself.

The possibility of the acidic hydrogen being derived from one of the $-\text{CO}\cdot\text{NH}_2$ groups was first of all examined, as this explanation had suggested itself at the time the previous communication was published (*loc. cit.*, p. 1045). A series of compounds was therefore prepared in which alkyl or aryl radicles replace partially or wholly the hydrogen atoms of the original amido-groups.

A list of the compounds examined, their colours, and the colours of the alkali and ferrous salts obtained from them is given in the following table:

	Colour of		
	Oxime.	Alkali salt.	Ferrous salt.
$(\text{CO}\cdot\text{NH}_2)_2\text{C}\cdot\text{N}\cdot\text{OH}$ <i>iso</i> Nitrosomalonamide.	$\left\{ \begin{array}{l} \alpha \text{ Colourless} \\ \beta \text{ Yellow} \end{array} \right\}$	Yellow	Violet.*
$(\text{CO}\cdot\text{NHMe})_2\text{C}\cdot\text{N}\cdot\text{OH}$ <i>iso</i> Nitrosomalondimethylamide.	Colourless	Yellow	Violet
$(\text{CO}\cdot\text{NHPh})_2\text{C}\cdot\text{N}\cdot\text{OH}$ <i>iso</i> Nitrosomalonanilide.	$\left\{ \begin{array}{l} \alpha \text{ Colourless} \\ \beta \text{ Yellow} \end{array} \right\}$	Yellow	Blue
$\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{C}(\text{CO}\cdot\text{NH}_2)_2\cdot\text{N}\cdot\text{OH}$ <i>iso</i> Nitrosomalonmono- <i>p</i> -tolylamide.	Yellow	Yellow	Purple
$(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2\text{C}\cdot\text{N}\cdot\text{OH}$ <i>iso</i> Nitrosomalondi- <i>p</i> -tolylamide.	$\left\{ \begin{array}{l} \alpha \text{ Colourless} \\ \beta \text{ Yellow} \end{array} \right\}$	Yellow	Blue
$(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2\text{C}\cdot\text{N}\cdot\text{OH}$ <i>iso</i> Nitrosomalondi- <i>o</i> -tolylamide.	$\left\{ \begin{array}{l} \alpha \text{ Colourless} \\ \beta \text{ Yellow} \end{array} \right\}$	Yellow	Blue
$\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{C}(\text{CO}_2\text{Et})_2\cdot\text{N}\cdot\text{OH}$ Ethyl <i>iso</i> nitrosomalon- <i>o</i> -tolylamate.	Yellow	Yellow	Purple

* Ferrous potassium salt.

	Colour of		
	Oxime.	Alkali salt.	Ferrous salt.
$(\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7)_2\text{C}\cdot\text{N}\cdot\text{OH}$ <i>iso</i> Nitrosomalondi- α -naphthylamide.	Orange	Yellow	Blue
$(\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7)_2\text{C}\cdot\text{N}\cdot\text{OH}$ <i>iso</i> Nitrosomalondi- β -naphthylamide.	Yellow	Yellow	Blue
$(\text{CO}\cdot\text{NMePh})_2\text{C}\cdot\text{N}\cdot\text{OH}$ <i>iso</i> Nitrosomalondimethylanilide.	$\left\{ \begin{array}{l} \alpha \text{ Colourless} \\ \beta \text{ Yellow} \end{array} \right.$	Yellow Colourless	Purple —*

From these results, it follows that the replacement of one or both aminic hydrogen atoms of the $-\text{CO}\cdot\text{NH}_2$ groups does not interfere in any way with the production of yellow alkali salts and violet or blue ferrous salts. The acidic hydrogen, therefore, of the oxime of mesoxamide and its derivatives is *not* furnished by either of the $-\text{CO}\cdot\text{NH}_2$ groups. Further evidence in favour of this view is afforded by the alkyl-substituted violuric acids, monomethylvioluric acid (Andreasch, *Monatsh.*, 1900, 21, 281), dimethylvioluric acid (Andreasch, *Monatsh.*, 1895, 16, 17), and diethylvioluric acid (Sembritzki, *Ber.*, 1898, 30, 1814), all of which give the red alkali salts and deep blue ferrous salts characteristic of the group, whilst neither of the last two compounds contains a $-\text{CO}\cdot\text{NH}-$, complex as the formulæ show

Dimethylvioluric acid.

Diethylvioluric acid.

Dismissing, therefore, the view that the $-\text{CO}\cdot\text{NH}_2$ group furnishes the acidic hydrogen, attention was then concentrated on the oximino-group, and a number of substances were examined with the object of ascertaining the conditions under which compounds containing this group yield coloured salts. The formation of yellow alkali salts is characteristic of α -oximinoketones, to which class the oximes under discussion belong. Schramm (*Ber.*, 1883, 16, 183) first drew attention to this influence of a neighbouring radicle on the acid character of the oximino-group, and, later, Guinchard (*Ber.*, 1900, 32, 1723) pointed out the difference in colour of the alkali salts of this class according as they are open chain or ring compounds, the former yielding yellow the latter red to violet salts. The purple or blue ferrous salts are, however much more strikingly characteristic of the oximes under discussion than the yellow alkali salts, and yet with the exception of violuric acid and its mono- and di-substituted alkyl derivatives no reference to the production of coloured ferrous salts by oximes of this class

* No ferrous salt. Crimson ferric salt.

has been met with in the literature. In view of this seeming omission, a number of α -oximinoketones were prepared and examined with respect to their behaviour with ferrous sulphate and an alkali; the results are recorded in the following table:

	Colour of	
	Alkali salt.	Ferrous salt.
$\text{CH}_3 \cdot \text{CO} \cdot \text{CH} \cdot \text{N} \cdot \text{OH}$ <i>iso</i> Nitrosoacetone.	Yellow	Blue
$\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CO}_2\text{Et}$ Ethyl <i>isonitroso</i> acetoacetate.	Yellow	Blue
$\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CO}_2\text{Et}$ Ethyl <i>isonitroso</i> benzoylacetate.	Yellow	Blue
$\text{CH}_3 \cdot \text{CO} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CO} \cdot \text{CH}_3$ <i>iso</i> Nitrosoacetylacetone.	Yellow	Blue
$\text{C}_2\text{H}_5 \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CO} \cdot \text{CH}_3$ γ - <i>iso</i> Nitroso- β -ketopentane.	Yellow	Blue
$\text{CH}_3 \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{CO} \cdot \text{NH}_2$ Oxime of pyruvamide.	Yellow	Reddish-brown
$\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{CO} \\ \diagdown \end{array} \text{C} \cdot \text{N} \cdot \text{OH}$ <i>iso</i> Nitrosocamphor.	Yellow	Blue
$\text{Ph} \cdot \underset{\text{N} \cdot \text{OH}}{\underset{ }{\text{C}}} \cdot \text{CO} \cdot \text{Ph}$ α -Benzilmonoxime.	Yellow	Blue
$\text{Ph} \cdot \underset{\text{HO} \cdot \text{N}}{\underset{ }{\text{C}}} \cdot \text{CO} \cdot \text{Ph}$ β -Benzilmonoxime.	Yellow	No ferrous salt
$\text{N} \begin{array}{c} \diagup \text{CPh} \\ \diagdown \end{array} \text{O} \cdot \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{OH}$ <i>iso</i> Nitrosophenylisoxazolone.	Red	Greenish-blue
$\text{N} \begin{array}{c} \diagup \text{CMe} \\ \diagdown \end{array} \text{O} \cdot \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{OH}$ <i>iso</i> Nitrosomethylisoxazolone.	Red	Chocolate-brown

Of the compounds tabulated, two only, the monoximes of benzil, exhibit isomerism, and one of these affords the only exception to the formation of a ferrous salt of characteristic colour by the α -oximinoketones which have been examined. Attention was therefore directed to the stereoisomeric oximes, and the dioximes of benzil, the series most readily prepared, were investigated, with the result that, whilst these compounds gave a pale yellow colour with alkalis, they showed a

difference of behaviour on the further addition of ferrous sulphate; α -benzildioxime gave a rich, purple colour; β -benzildioxime gave no trace of a coloration, and γ -benzildioxime gave a reddish-purple colour changing rapidly to the dark brown of ferric hydroxide. Representing these substances by the constitutional formulæ assigned to them by Beckmann and Köster (*Annalen*, 1893, 274, 32), it will be seen that the *syn*-isomeride forms a stable purple ferrous salt, the *amphi*-isomeride an unstable purple ferrous salt, whilst the *anti*-isomeride is destitute of colour-giving properties:

These compounds present a further point of interest in that they are diketoximes, and the fact of all three yielding yellow alkali salts, and one of them a purple ferrous salt, indicates that the radicle $\text{=C:N} \cdot \text{OH}$, like carbonyl itself, can sometimes influence the acidic nature of a contiguous oximino-group. This conclusion is opposed to that drawn by Schramm (*Ber.*, 1883, 16, 183), who attributed the non-formation of coloured alkali salts from methylglyoxime to the inoperative character of two oximino-groups as compared with the colour-giving property of the carbonyl-oximino-group in *isonitrosoacetone* (methylglyoxaldoxime).

In the literature of the dioximes, only two cases could be found in which mention is made of the production of a coloured ferrous salt by compounds of this class; these are the two dioximes of dihydroxytartaric acid (Söderbaum, *Ber.*, 1892, 24, 1215) and the two dioximinopropionic acids (Söderbaum, *Ber.*, 1893, 25, 905). The formulæ ascribed to them are as follows:

Dioximes of dihydroxytartaric acid.

Violet-red coloration with ferrous sulphate and an alkali.

Dioximinopropionic acids.

Fleeting dark violet coloration with ferrous sulphate and caustic alkali.

The fact that each of the isomeric forms of these two compounds gives the colour reaction is not surprising, since in addition to being a dioxime each contains the grouping $\begin{array}{c} -\text{CO}\cdot\text{C}- \\ | \\ \text{HO}\cdot\text{N} \end{array}$, which is present in α -benzilmonoxime.

In each case, Söderbaum succeeded in obtaining two isomeric forms of his dioximes out of the three and four theoretically possible; this is of especial interest, because isomerism in oximes of the aliphatic series is of rare occurrence. A few dioximes of this series in which no isomeric forms could be obtained were prepared, and each was found to give a characteristic coloration with ferrous sulphate and an alkali:

	Colour of	
	Alkali salt.	Ferrous salt.
$\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{CO}_2\text{Et}$ Oxime of ethyl isonitrosoacetoacetate.	Colourless	Violet
$\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}_2\text{H}_5$ Methylethylglyoxime.	Yellow	Dark brown
$\text{CH}_3\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{C}(\text{N}\cdot\text{OH})\cdot\text{OH}$ Methylhydroxyglyoxime.	Yellow	Reddish-brown

Among the trioximino-compounds, oximinomesoxaldoxime,

is described by Pechmann and Wehsarg (*Ber.*, 1889, 21, 2989) as giving a wine-red colour with ferrous sulphate and a violet precipitate on the addition of aqueous soda to the solution.

A consideration of the facts so far presented makes it clear that the production of coloured alkali salts by α -oximinoketones, and, probably, by dioximes, and the production of coloured ferrous salts by these compounds are two distinct phenomena, the former being a general characteristic, whilst the latter is influenced by the isomerism of the oximino-group. These two phenomena must therefore receive separate consideration.

The question of the production of coloured alkali salts by colourless

compounds containing the $\begin{array}{c} \text{CO} \\ | \\ \text{C}:\text{N}\cdot\text{OH} \\ | \end{array}$ complex has received much

attention from Hantzsch and his pupils (*Ber.*, 1899, 32, 593; Hantzsch and Farmer, *ibid.*, 3101; Guinchard, *ibid.*, 1723). According to Hantzsch, the salts of all α -oximinoketones have a constitution different from that of the original or pseudo-acid, and they are formed from the latter by an alteration in the relative position of the atoms during the dissociation into ions. Thus in the case of violuric acid:

Pseudo-acid.

Salt.

In the previous communication (*loc. cit.*, p. 1044), it was pointed out that the formation of coloured salts by the colourless oxime of mesoxamide might be explained by assuming a similar tautomeric change to take place, that is to say, the colourless oxime and its yellow alkali salt may be differently constituted thus :

Oxime.

Salt.

The present investigation, however, shows that another interpretation can be given in which no such far-reaching structural modification is involved. If reference be made to page 24, it will be seen that the oxime of mesoxamide itself, and three out of the eight mono- and di-substituted derivatives of it, exist in two forms, one colourless and the other having the yellow colour of the alkali salt. Of the remaining five, one has so far been obtained only in the colourless form, and the other four are yellow.

The isomerism observed in this series of compounds is similar to the "tautomerism" discovered by Wislicenus (*Annalen*, 1896, 291, 147) in α - and β -ethyl phenylformylacetate, and to the "dynamic isomerism" observed by Lowry (*Trans.*, 1899, 75, 211) in nitrocamphor and π -bromonitrocamphor, in so far as the two forms are mutually convertible (1) by the action of solvents, (2) by fusion, and (3) by the action of acids on solutions of the alkali salts. Thus in the case of *isonitrosomalonanilide*, in which the isomerism is most clearly defined, the white isomeride crystallises in brilliant scales with a pearly lustre from a solution of ethyl or methyl alcohol, ethyl acetate, acetone, ether, or acetic acid, whilst from a solution in benzene or chloroform the other isomeride is obtained in the form of bright yellow, prismatic crystals. The white isomeride melts at 141°, the yellow has no apparent melting point, but softens and turns white at 120–122°, and melts at 141°. There is a third form melting at 124°, which appears to be the equilibrium mixture of the other two (compare Lowry, *loc. cit.*, p. 224): it is obtained in tufts of needles of a pale yellow colour by the rapid cooling of hot concentrated solutions of the yellow or white isomeride in any solvent (except methyl or ethyl alcohol), or by rapidly cooling the yellow liquid obtained by the fusion of the white variety. By long

contact with the solvent, this form is converted into the white or yellow isomeride according to the nature of the solvent.

This tautomerism, which occurs in some of the oximes under discussion, has an important bearing on the question of the colour of the alkali salts, for it is not unreasonable to suppose that the difference in structure between the colourless and yellow forms of these oximes is the same as that which obtains between the colourless oximes and their yellow alkali salts. According to Hantzsch's hypothesis, this difference is due to a structural change in which, not only the oximino-, but also the neighbouring carbonyl groups take part; a far simpler explanation, however, is afforded if it is assumed that the structural change affects the oximino-group alone, the colourless isomeride having the *isooximino*-structure, and the coloured form and the alkali salts that of the true oxime (compare Dunstan and Goulding, *Trans.*, 1901, 79, 628) thus:

{ } This explanation of the difference in structure between the coloured and colourless isomerides receives considerable support from the fact that the constitution suggested for the former contains the complex $\text{--}\underset{|}{\text{C}}\text{--}\underset{|}{\text{C}}\text{--}\underset{|}{\text{C}}\text{--}$, which is present in the coloured triketones and their coloured derivatives, and thus belongs to that group which Armstrong, in his classification of coloured organic compounds, calls "pseudo-quinonoid" (*Encyclopædia Britannica*, vol. 26, *Art. Chemistry*, p. 746).

The complex $\text{--}\underset{|}{\text{C}}\text{--}\underset{|}{\text{C}}\text{--}\underset{|}{\text{C}}\text{--}$, on the other hand, which occurs in the colourless oxime is characteristic of the colourless derivatives of triketones, such as diphenyltriketone (Pechmann and de Naufville, *Ber.*, 1890, 23, 3379), triketopentane (Sachs and Barschall, *Ber.*, 1901, 34, 3047), and phenyltriketobutane (Sachs and Röhmer, *Ber.*, 1902, 35, 3307).

Finally, this explanation of the formation of coloured alkali salts by α -oximinoketones can be extended to the cases of the yellow alkali salts of nitrosoguanidine and nitrosocarbamide (p. 31), to which Hantzsch's hypothesis cannot be applied.

Passing now to a consideration of the formation of ferrous salts of characteristic colour by α -oximinoketones and dioximes, no satisfactory explanation of this colour reaction presents itself. With the exception of the soluble ferrous potassium salt of the oxime of mesoxamide, the

coloured compounds are insoluble simple ferrous salts, and do not in any respect, save that of colour, correspond with that curious complex iron compound of carboxime or fulminic acid discovered by Nef (*Annalen*, 1894, 280, 335), which appears to be a salt bearing the same relation to fulminic acid that Prussian blue does to hydrogen cyanide.

Among the fairly large and representative number of α -oximino-ketones which have been examined in respect of their behaviour with ferrous sulphate and an alkali, one only, β -benzilmonoxime, has failed to give the colour reaction, whilst among the oximes, isomerism again seems to play an important part in this connection. The extension of the investigation to a large number of isomeric mono- and di-oximes may possibly throw some light on this subject, and show how far ferrous sulphate and an alkali is a reagent capable of discriminating between the isomerides.

In conclusion, reference must be made to a few compounds not belonging to the oximinoketones or to the dioximes, which give a purple or blue coloration with ferrous sulphate and an alkali. These include alloxan and its mono- and di-alkyl derivatives, which give a blue colour with the reagents. Ethylnitrolic acid, which forms red alkali salts (Meyer and Constam, *Annalen*, 1882, 214, 329), was found to give a characteristic chocolate-brown coloration on the addition of ferrous sulphate to the alkaline solution. Nitrosoguanidine and nitrosocarbamide* each give a yellow alkali salt and a purple-red colour with ferrous sulphate and an alkali (Thiele, *Annalen*, 1893, 273, 133 ; 1895, 288, 303).

EXPERIMENTAL.

I. *Yellow Variety of the Oxime of Mesoxamide.*

In the original preparation of the oxime of mesoxamide (Trans., 1900, 77, 1040), gaseous nitrosyl chloride was passed into

* From the constitution ascribed to these compounds by Thiele, the acidic hydrogen is iminic, and the salts of a totally different constitution from those of the large class of oximes considered in this paper, with which they are so closely allied in colour. If, however, the salts of these compounds were derived from tautomeric forms of the original substances,

in which the grouping $\text{:N}\cdot\text{OH}$ is present, they would come into line with those described in this paper, and it is worthy of note in this connection that Hantzsch (*Ber.*, 1899, 32, 592) classes nitrosourethane with the *antidiazohydroxides*, $\text{R}_1\cdot\text{N:N}\cdot\text{OH}$, because of its acidic nature.

finely powdered malonamide suspended in chloroform or ether; the yield of the oxime was so poor, owing to the fact that neither the malonamide nor the oxime was appreciably soluble in the medium, that the use of nitrosyl chloride was abandoned in favour of the nitrous gases evolved by the action of nitric acid (sp. gr. 1.3) on arsenious oxide, which, acting on malonamide in concentrated aqueous solution, gave the oxime, the yield being 40 per cent. of the theoretical.

Later work on the substituted malonamides having shown that a quantitative yield of the oxime could be readily obtained by the action of nitrosyl chloride in a medium in which either the amide or the oxime, or both, were soluble, the action of nitrosyl chloride on malonamide in various organic solvents was examined. In acetic acid, ethyl acetate, methyl alcohol, or ethyl alcohol, in which the amide is sparingly, and the oxime readily, soluble, the reaction proceeded far more readily than had been observed in the case when chloroform was the medium employed. A remarkable difference, however, was observed in the products obtained under these new conditions, for whereas the oxime obtained from the ethyl acetate and methyl alcoholic solutions was colourless and coincided in properties with that previously obtained, the product of the action of nitrosyl chloride on malonamide in alcoholic solution, although agreeing in chemical properties with the original oxime, differed from it in possessing a *bright yellow colour*.

The yellow isomeride is readily soluble in water, forming a yellow solution, which gives, with potash and ferrous sulphate, the rich violet coloration characteristic of the oxime of mesoxamide. It is sparingly soluble in alcohol or ethyl acetate, more readily so in acetone or glacial acetic acid, and crystallises from each solvent in bright yellow, prismatic crystals. After recrystallising once from absolute alcohol and twice from slightly moist alcohol, it was obtained in bright yellow, prismatic crystals, melting with decomposition at 187—188°:

0.1162 gave 31.95 c.c. moist nitrogen at 17° and 763 mm. $N = 32.06$.

$C_3H_5O_3N_3$ requires $N = 32.11$ per cent.

The two forms of the oxime appear to yield identical salts, and from the potassium salt of the yellow variety the colourless oxime is formed by the action of dilute acids.

The *ethyl ether* was prepared from the silver salt of the yellow form by the action of ethyl iodide; it is identical with the corresponding derivatives of the white oxime, is colourless, melts at 150°, and does not depress the melting point of the original ether.

The *silver salt*, $(CO \cdot NH_2)_2C:N \cdot OAg, 2NH_3$, is precipitated by the addition of silver nitrate to an aqueous solution of the yellow or white variety of the oxime containing a little ammonia; the precipitate

dissolves readily in excess of ammonia, and from the solution by slow evaporation the salt is obtained in well formed, deep yellow, prismatic crystals, containing two mols. of ammonia, which it loses partially in a desiccator over sulphuric acid, and completely when heated at 100° :

I. 0.4529, dried in air, gave 0.1800 Ag. Ag = 39.76 per cent.

$C_3H_4O_3N_3Ag \cdot 2NH_3$ requires Ag = 39.65 per cent.

II. Specimen kept in desiccator for three days:

0.5004 lost 0.0587 at 100° , and gave 0.2002 Ag. $NH_3 = 11.72$; Ag = 45.32.

$C_3H_4O_3N_3Ag \cdot 2NH_3$ requires $NH_3 = 12.55$ per cent.

$C_3H_4O_3N_3Ag$ requires Ag = 45.32 per cent.

II. *Malondimethylamide.*

Malondimethylamide was prepared by Freund's method (*Ber.*, 1884, 17, 134) from ethyl malonate and a solution of methylamine ($33\frac{1}{2}$ per cent.). On mixing the two liquids, there was a development of heat and the ethyl malonate readily passed into solution. The mixture was shaken for six hours and then evaporated on the water-bath to a small bulk; on cooling, malondimethylamide crystallised out, and from the mother liquor by further evaporation a second crop of crystals was obtained. The product was pure (m. p. 135° ; Freund gives 128°), and the yield 78 per cent. of the theoretical. Malondimethylamide is very readily soluble in acetone, acetic acid, ethyl or methyl alcohol, or chloroform, but less so in ethyl acetate, sparingly so in benzene, and insoluble in carbon tetrachloride, ether, or light petroleum; it can be most readily crystallised from ethyl acetate or acetone.

isoNitrosomalondimethylamide, $(CO \cdot NH \cdot CH_3)_2C : N \cdot OH$.—Malondimethylamide in solution is very readily converted into the *isonitroso*-derivative by the action of gaseous nitrosyl chloride at 0° . Chloroform is the most convenient solvent in which to effect the reaction; the product is pure *isonitrosomalondimethylamide* melting at 157° , and the yield is theoretical.

The *isonitrosomalondimethylamide* thus prepared is identical with the compound obtained by the decomposition of dimethylvioluric acid with barium hydroxide; it crystallises in the characteristic monosymmetric prisms, and gives the yellow alkali and the purple ferrous salt (see this vol., page 22).

III. *Malonanilide*.

Malonanilide was prepared by Freund (*Ber.*, 1884, 17, 134) by the condensation of aniline and ethyl malonate. By a slight modification of the method, a yield of 81 per cent. of the theoretical was obtained and the product was pure (m. p. 225° ; Freund gives 223°). The aniline and ethyl malonate were heated to gentle boiling in a reflux apparatus for 5 hours; on cooling, a large quantity of malonanilide separated in long, silky needles; these were collected, the mother liquor and alcohol washings concentrated to remove the alcohol, and boiled until, on cooling, the contents of the flask became solid; the solid cake was then broken up, ground with alcohol, filtered, washed, dried, and used in the preparation of the *isonitroso*-derivative.

isoNitrosomalonanilide, $(\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5)_2\text{C}:\text{N}\cdot\text{OH}$.—All attempts to prepare *isonitrosomalonanilide* by the action of nitrous acid on malonanilide were fruitless. Owing to its insolubility in water, acids, or alkali, malonanilide is not acted on by potassium nitrite and sulphuric acid, and it is unchanged when suspended in water and submitted to the action of a stream of nitrous gases from arsenious oxide and nitric acid. When sealed in a tube with the liquefied gases, no *isonitroso*-compound could be separated from the mixture. Amyl nitrite or ethyl nitrite has no action on the compound.

isoNitrosomalonanilide was, however, readily prepared from malonanilide by the action of nitrosyl chloride. The malonanilide was suspended in chloroform, in which it is insoluble, and a stream of nitrosyl chloride passed through the mixture until all the solid had passed into solution and the liquid was saturated at 0° with the gas. By spontaneous evaporation, *isonitrosomalonanilide* was obtained as a yellow, crystalline solid melting at 124° ; the product was pure and the yield quantitative. The substance is very readily soluble in benzene, chloroform, acetone, ethyl acetate, or methyl alcohol, but less so in alcohol, acetic acid, or carbon tetrachloride, and dissolves only sparingly in ether, light petroleum, or water. It crystallises from a hot concentrated alcoholic solution in the form of pure white, crystalline scales with a pearly lustre; chloroform solutions on complete evaporation deposit bright yellow, prismatic needles; from a concentrated benzene solution, pale yellow needles separate, which, when left in contact with the solvent for several days, slowly change into well formed, thick, flat prisms of a bright yellow colour. From ethyl acetate, methyl alcohol, ether, or acetic acid, on slow evaporation, the white, pearly scales are deposited, and the crust on the walls of the vessel is a mixture of yellow and white crystalline matter.

Effect of Fusion.—When the white isomeride of *isonitrosomalon-*

anilide is heated in a capillary tube, it softens and becomes yellow at 138—140°, and melts to a yellow liquid at 141°; on cooling gradually, the yellow liquid solidifies to a mixture of white and yellow crystalline matter. When the mixture is reheated, the yellow portion melts at 124° and the white remains floating in the yellow liquid until the temperature reaches 141°, when it also melts. If the yellow liquid formed by the melting of the white isomeride at 141° is rapidly cooled, the solid product appears to be uniformly yellow, and on rapidly heating melts completely at 124°. The flat, yellow prisms formed by the prolonged action of benzene on the yellow needles also become white at 120—122° and melt at 141°.

It is evident from these facts that *isonitrosomalonanilide* exists in tautomeric forms, one yellow and one white, differing in solubility and melting point. The yellow needles melting at 124° appear to be the equilibrium mixture of the two isomerides.

The specimen used for analysis was white and melted at 141°:

0.2324 gave 30.8 c.c. moist nitrogen at 24° and 766 mm. $N = 14.98$.

$C_{15}H_{13}O_3N_3$ requires $N = 14.86$ per cent.

The *potassium* salt, $(CO \cdot NH \cdot C_6H_5)_2C : N \cdot OK$, crystallises in long, thin, silky needles of a bright yellow colour, and is readily soluble in hot alcohol or water:

0.2434, dried at 100°, gave 0.0650 K_2SO_4 . $K = 11.98$.

$C_{15}H_{12}O_3N_3K$ requires $K = 12.17$ per cent.

Regeneration of the isoNitroso-derivative from the Potassium Salt.—

Carbon dioxide was passed through an aqueous solution of the potassium salt until no further precipitate was produced. The precipitate, which was white in colour, was filtered off, washed, and dried; it melted at 140° to a yellow liquid, which solidified to a yellow solid and then melted at 124°. Sulphuric acid or acetic acid also precipitated the white isomeride from solutions of the alkali salt.

The *ferrous* salt, $[(CO \cdot NH \cdot C_6H_5)_2C : NO]_2Fe$, was precipitated in the form of a dark blue solid, not unlike Prussian blue, when ferrous sulphate solution was added to an aqueous solution of the potassium salt; it was not possible to recrystallise it owing to its insoluble nature, so for the purpose of analysis it was well washed, dried in a vacuum over sulphuric acid, and finally at 100°:

0.2404 gave 0.0319 Fe_2O_3 . $Fe = 9.29$.

$C_{20}H_{24}O_6N_6Fe$ requires $Fe = 9.03$ per cent.

Acid Silver Salt, $(CO \cdot NH \cdot C_6H_5)_2C : N \cdot OAg, (CO \cdot NH \cdot C_6H_5)_2C : N \cdot OH$.

—By the action of aqueous silver nitrate on an alcoholic solution of *isonitrosomalonanilide*, a yellow silver salt was obtained as a flocculent

precipitate. Before analysis, it was extracted two or three times with boiling alcohol to remove traces of unchanged *isonitrosomal*-anilide:

0.2559 gave 0.0413 Ag. $\text{Ag} = 16.15$.

$\text{C}_{30}\text{H}_{25}\text{O}_6\text{N}_6\text{Ag}$ requires $\text{Ag} = 16.03$ per cent.

IV. *Malondi-p-tolylamide*, $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2$.

This compound was prepared by Guthzeit and Laska (*J. pr. Chem.*, 1898, [ii], 58, 414) by the action of *p*-toluidine on the triethyl ester of isaconitic acid, $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, and is described as crystallising well from alcohol in silky needles and melting at 248° .

For the purpose of this investigation, it was more readily prepared by the condensation of ethyl malonate and *p*-toluidine, the operation being conducted as in the case of the anilide derivative. The *p*-toluidine dissolved readily in the ethyl malonate, much heat being absorbed. The product was pure, melting at 250° , and the yield 53 per cent. of the theoretical. *Malondi-p-tolylamide* is sparingly soluble in alcohol or ethyl acetate, but readily so in acetic acid; it was therefore recrystallised from a mixture of ethyl acetate and acetic acid, and obtained in the form of brilliant scales with a pearly lustre.

Ethyl Malon-p-tolylamate, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5$.—The residual alcoholic mother liquor from the preparation of malon-*p*-tolylamide deposited on evaporation large, prismatic crystals, which, after recrystallisation from alcohol and water, melted at 86° . By its solubility and appearance, the substance was identified with the malon-*p*-tolylamate prepared by Rügheimer and Hoffmann (*Ber.*, 1885, 18, 2975) from malon-*p*-tolylamic acid, but they do not give the melting point.

isoNitrosomalondi-p-tolylamide, $(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2\cdot\text{C}\cdot\text{N}\cdot\text{OH}$. — The malondi-*p*-tolylamide was suspended in chloroform, in which it was insoluble, and saturated at 0° with nitrosyl chloride; the solid dissolved completely, and the resulting yellow solution yielded on spontaneous evaporation the *isonitroso*-derivative in the form of a crystalline, pale yellow solid melting at 170 — 171° . It is readily soluble in methyl alcohol, ethyl acetate, acetone, acetic acid, benzene, chloroform, or carbon tetrachloride, but less so in ethyl alcohol or toluene, and only sparingly so in ether or light petroleum. The recrystallised product consists usually of yellow scales or flattened needles melting at 170 — 171° ; from a methyl alcohol solution, however, the product separates almost entirely in pure white needles, which, on being heated, change to a yellow colour at about 150° and melt at 170 — 171° . Traces of the white isomeride are also formed on complete evaporation

of solutions in ethyl alcohol, ethyl acetate, acetone, or carbon tetrachloride :

0.1994 gave 23.9 c.c. moist nitrogen at 23.5° and 765 mm. $N = 13.57$.

$C_{17}H_{17}O_3N_3$ requires $N = 13.52$ per cent.

The *potassium salt*, $(CO \cdot NH \cdot C_7H_7)_2C:N \cdot OK$, is a pale yellow, crystalline solid, deposited in the form of clusters of fine needles from a concentrated hot alcoholic solution :

0.3073 gave 0.0766 K_2SO_4 . $K = 11.19$.

$C_{17}H_{16}O_3N_3K$ requires $K = 11.19$ per cent.

Regeneration of the isoNitroso-derivative from the Potassium Salt.—From aqueous solutions of the potassium salt, carbon dioxide precipitated the white isomeride, whilst dilute sulphuric or acetic acid precipitated the yellow.

The *ferrous salt* is thrown down as a dark blue precipitate, indistinguishable in appearance from the corresponding compound of *isonitrosomalonanilide*, when ferrous sulphate is added to an aqueous solution of the potassium salt.

Acid Silver Salt, $(CO \cdot NH \cdot C_7H_7)_2C:N \cdot OAg, (CO \cdot NH \cdot C_7H_7)_2C:N \cdot OH$.—This is obtained as a pale yellow, flocculent precipitate when silver nitrate solution is added to an alcoholic solution of the *isonitroso*-compound :

0.2750 gave 0.0414 Ag. $Ag = 15.06$.

$C_{34}H_{33}O_6N_6Ag$ requires $Ag = 14.79$ per cent.

V. *Malonmono-p-tolylamide*, $C_7H_7 \cdot NH \cdot CO \cdot CH_2 \cdot CO \cdot NH_2$.

Thirty grams of ethyl malonate ($1\frac{1}{4}$ mols.) and 15 grams of *p*-toluidine (1 mol.) were heated to gentle ebullition in a reflux apparatus for 12 hours, 100 c.c. of ammonia solution (sp. gr. 0.88) added to the cooled product, the flask corked, and the contents repeatedly shaken during two days. The semi-solid mass, when allowed to evaporate spontaneously, yielded 40 grams of a crystalline solid consisting of a mixture of 17 grams of malonamide, 1.5 grams of *p*-toluidine, 14 grams of malonmono-*p*-tolylamide, and 4.5 grams of malondi-*p*-tolylamide. These were readily separated by taking advantage of their difference in solubility.

The malonmono-*p*-tolylamide consisted of white, crystalline scales with a pearly lustre, readily soluble in alcohol and the ordinary organic solvents, and crystallising well from a mixture of water and alcohol (about 6 : 1). It melted at 144° with slight decomposition.

The substance contains half a molecular proportion of water of crystallisation, which it loses when dried at 100° , the crystals becoming dull and opaque :

0.4723 lost 0.0214 H_2O at 100° . $\text{H}_2\text{O} = 4.53$.

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 4.47$ per cent.

The hydrated compound becomes strongly electrified by pressure or friction; the dehydrated compound has not this characteristic.

The anhydrous form of malonmono-*p*-tolylamide melts at 163 — 164° with slight decomposition :

0.1935 gave 23.9 c.c. moist nitrogen at 16.5° and 765 mm. $\text{N} = 14.46$.

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2$ requires $\text{N} = 14.61$ per cent.

isoNitrosomalonmono-p-tolylamide, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{C}(\text{CO}\cdot\text{NH}_2)\cdot\text{N}\cdot\text{OH}$ —A quantitative yield of the *isonitroso*-derivative was obtained from the amide by suspending it in chloroform and saturating it at 0° with nitrosyl chloride; the solid did not appreciably pass into solution, but changed in appearance from white to yellow. On spontaneous evaporation of the chloroform, a pale yellow, crystalline residue was obtained, which was the *isonitroso*-derivative. It dissolves readily in alcohol or ethyl acetate, crystallising from a hot solution of the latter in the form of brilliant, prismatic, lemon-yellow crystals melting at 183° with slight decomposition. The white isomeride of this compound has not yet been isolated; from solutions in any of the ordinary organic solvents only the yellow form is obtained :

0.1694 gave 28 c.c. moist nitrogen at 18.5° and 758 mm. $\text{N} = 19.00$.

$\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}_3$ requires $\text{N} = 19.03$ per cent.

The *isonitroso*-derivative is soluble in alkali containing a little alcohol, the alkali salt separating on evaporation in the form of needle-shaped crystals of a deeper yellow colour than the *isonitroso*-compound.

Regeneration of the isoNitroso-derivative from the Potassium Salt.—The potassium salt of *isonitrosomalonmono-p-tolylamide* is very readily soluble in water, forming a solution of a deep yellow colour. When this solution is treated with carbon dioxide or sulphuric or acetic acid, it becomes perfectly colourless, and from the clear, colourless liquid the *isonitroso*-derivative slowly separates in the form of the characteristic yellow prisms. This result is of especial interest as serving to show that although the white isomeride of this compound cannot be separated in the solid form it does exist in acidified aqueous solutions.

Ferrous Salt.—A solution of the alkali salt gives, with ferrous sulphate, an intense bluish-purple coloration and precipitate. The shade of colour of the ferrous salt is interesting, being intermediate between the deep blue of the *isonitrosomalondi-p-tolylamide* compound, and the violet colour of the *isonitrosomalonamide* salt, and shows that the colour is influenced by the nature of the radicles replacing the hydrogen of the amido-groups.

VI. *Malondi-o-tolylamide*, $\text{CH}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2$.

Malondi-o-tolylamide was made by the same method as that used in obtaining the *p*-tolylamide, *o*-toluidine being substituted for *p*-toluidine. The condensation was effected much more quickly and completely than in the case of the *para*-compound. The product was a white, crystalline solid melting at 193° , and the yield 71 per cent. of the theoretical. It was sparingly soluble in alcohol or ethyl acetate, but readily so in glacial acetic acid. When recrystallised from a mixture of ethyl acetate and glacial acetic acid, it was obtained in the form of long, silky needles with a pearly lustre and melted at 193° :

0.2303 gave 19.4 c.c. moist nitrogen at 19° and 780 mm. $\text{N} = 9.94$.
 $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_2$ requires $\text{N} = 9.94$ per cent.

isoNitrosomalondi-o-tolylamide, $(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2\text{C}\cdot\text{N}\cdot\text{OH}$.—The conversion of the amide into the *isonitroso*-derivative is effected readily and quantitatively by the method employed in the case of the anilide and *p*-tolylamide compounds, namely, by saturating finely-powdered *malondi-o-tolylamide* suspended in chloroform with nitrosyl chloride at 0° . *isoNitrosomalondi-o-tolylamide* is very readily soluble in all the ordinary organic solvents, and crystallises well from ethyl alcohol or light petroleum in the form of fine, bright yellow needles. The yellow variety is obtained from solutions of other solvents with the exception of methyl alcohol, which yields also the white variety in the form of tufts of white needles. The yellow isomeride melts at 111° , the white changes to the yellow at about 75° and melts at 111° :

0.2150 gave 24.7 c.c. moist nitrogen at 20.5° and 779.5 mm. $\text{N} = 13.46$.
 $\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}_3$ requires $\text{N} = 13.52$ per cent.

The *potassium* salt, $(\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7)_2\text{C}\cdot\text{N}\cdot\text{OK}$, is soluble in water and slightly so in alcohol, crystallising from a mixture of water and alcohol (2:1) in the form of thin needles of a rich yellow colour:

0.2645, dried at 110° , gave 0.0640 K_2SO_4 . $\text{K} = 10.86$.
 $\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_3\text{K}$ requires $\text{K} = 11.19$ per cent.

Regeneration of the isoNitroso-derivative from the Potassium Salt.—Carbon dioxide or dilute sulphuric or acetic acid precipitates the yellow isomeride from aqueous solutions of the potassium salt.

The *ferrous* salt is thrown down as a precipitate of a rich dark blue colour when ferrous sulphate is added to a solution of the potassium salt.

Ethyl Malon-o-tolylamate, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{C}_2\text{H}_5$.—The final alcoholic mother liquor from which the *malondi-o-tolylamide* had been

separated yielded on evaporation well-formed, prismatic crystals in stellate clusters. When recrystallised from alcohol and water, these melted at 78° , and were identified as ethyl malon-*o*-tolylamate originally prepared by Rügheimer and Hoffmann (*Ber.*, 1885, 18, 2975) from malon-*o*-tolylamic acid, who give $73\text{--}74^{\circ}$ as the melting point. The substance was prepared in larger quantity by heating a mixture of ethyl malonate and *o*-toluidine in molecular proportion. A mixture of 5 grams of malondi-*o*-tolylamide and 16 grams of ethyl malon-*o*-tolylamate was obtained from 16 grams of ethyl malonate. The two were readily separated by extraction with boiling ether, in which the ethyl malon-*o*-tolylamate is soluble.

*Ethyl isonitrosomalon-*o*-tolylamate*, $C_7H_7 \cdot NH \cdot CO \cdot C(CO_2C_2H_5) : N \cdot OH$.—By the action of nitrosyl chloride on ethyl malon-*o*-tolylamate in chloroform solution at 0° , a quantitative yield of the *isonitroso*-derivative is obtained in the form of tufts of yellow needles. The compound is very readily soluble in all the ordinary organic solvents, and does not crystallise well from any of them. It separates, however, from a mixture of alcohol and water in tufts of beautiful, long, pale yellow needles melting at $140\text{--}141^{\circ}$:

0.2448 gave 23.1 c.c. moist nitrogen at 16.5° and 778 mm. $N = 11.23$.

$C_{12}H_{14}O_4N_2$ requires $N = 11.22$ per cent.

The compound is soluble in aqueous potash, forming a bright yellow solution, the colour changing to a rich bluish-purple on the addition of ferrous sulphate.

VII. *Malondi- α -naphthylamide*, $CH_2(CO \cdot NH \cdot C_{10}H_7)_2$.

Seventeen grams of α -naphthylamine (2 mols.) and 10 grams of ethyl malonate (1 mol.) were heated to gentle ebullition in a reflux apparatus for 5 or 6 hours; on cooling, the contents of the flask became solid. After grinding the product with alcohol, filtering, and washing, 16.5 grams of the amide were obtained, or 75 per cent. of the theoretical.

Malondi- α -naphthylamide is very sparingly soluble in alcohol, chloroform, ethyl acetate, or benzene, but fairly so in toluene and in glacial acetic acid. It crystallises from acetic acid in tufts of pale red needles melting at 225° :

0.3216 gave 21.8 c.c. moist nitrogen at 18° and 763 mm. $N = 7.86$.

$C_{23}H_{18}O_2N_2$ requires $N = 7.92$ per cent.

isoNitrosomalondi- α -naphthylamide, $(CO \cdot NH \cdot C_{10}H_7)_2C : N \cdot OH$.—Malondi- α -naphthylamide is completely converted into the *isonitroso*-derivative when suspended in ethyl acetate, xylene, or toluene, and saturated with nitrosyl chloride at the temperature of melting ice. After evaporating the product to dryness and washing with alcohol, the

isonitroso-derivative is obtained as a dark orange, crystalline solid, sparingly soluble in ethyl acetate or glacial acetic acid, but more soluble in alcohol, and readily so in benzene, toluene, or xylene; it crystallises from toluene in bright orange prisms and melts at 184° :

0.2513 gave 23.5 c.c. moist nitrogen at 18.7° and 752 mm. $N = 10.68$.

$C_{23}H_{17}O_3N_3$ requires $N = 10.98$ per cent.

The *potassium* salt, $(CO \cdot NH \cdot C_{10}H_7)_2C:N \cdot OK$, crystallises in thin orange-yellow needles, and is sparingly soluble in water, but dissolves readily in alcohol or ethyl acetate. For analysis, it was crystallised from alcohol:

0.3128, dried at 120° , gave 0.0637 K_2SO_4 . $K = 9.14$.

$C_{23}H_{16}O_3N_3K$ requires $K = 9.28$ per cent.

VIII. *Malondi-β-naphthylamide*, $CH_2(CO \cdot NH \cdot C_{10}H_7)_2$.

The condensation of ethyl malonate and β -naphthylamine is readily effected by heating the substances in the requisite proportion in a reflux apparatus; the solid product separates from the boiling mixture as a crust, and the yield is 95 per cent. of the theoretical.

After washing with alcohol, the product is a white, crystalline powder which can be used in the preparation of the *isonitroso-derivative* without recrystallisation.

Malondi-β-naphthylamide is sparingly soluble in alcohol, acetone, ethyl acetate, light petroleum, benzene, toluene, or xylene, crystallising from each of these solvents in long needles; it is more readily soluble in glacial acetic acid, crystallising from a boiling solution in white scales with a brilliant, pearly lustre. It melts at 235° to a yellow liquid and immediately solidifies to a yellow, crystalline solid which does not melt at 300° , but chars at the edges:

0.3198 gave 21.9 c.c. moist nitrogen at 19° and 766 mm. $N = 7.93$.

$C_{23}H_{18}O_2N_2$ requires $N = 7.92$ per cent.

isoNitrosomalondi-β-naphthylamide, $(CO \cdot NH \cdot C_{10}H_7)_2C:N \cdot OH$.—The insoluble nature of *malondi-β-naphthylamide* made it difficult to find a medium in which the *isonitroso-derivative* could be produced by the action of nitrosyl chloride. Preliminary experiments with most of the organic solvents showed that in ethyl acetate or toluene the reaction was more complete than in any other solvent; the products obtained in the two cases were different, and in neither case was a good yield obtained. The product obtained by the use of toluene was a pale yellow, crystalline solid melting with slight decomposition at 219° . It was sparingly soluble in alcohol, ethyl acetate, or chloroform, but more readily so in benzene, toluene, or acetic acid. For analysis,

it was recrystallised from acetic acid, from which it separated in pale yellow, shining plates melting at 221° :

0.2380 gave 21.8 c.c. moist nitrogen at 17.2° and 765 mm. $N = 10.69$.

$C_{23}H_{17}O_3N_3$ requires $N = 10.98$ per cent.

The *potassium* salt is slightly soluble in water and readily so in alcohol, crystallising from moist alcohol in the form of wart-like tufts of very pale yellow, slender needles.

The *ferrous* salt is a dark blue solid precipitated by ferrous sulphate from a solution of the potassium salt.

The *acetyl* derivative, $(CO \cdot NH \cdot C_{10}H_7)_2C:N \cdot O \cdot CO \cdot CH_3$, crystallises from alcohol or ethyl acetate in thin, pale green, silky needles, melting with decomposition at 179° . The colour appears to be due to the trace of an impurity, for it becomes less intense with each recrystallisation:

0.2422 gave 20 c.c. moist nitrogen at 16° and 744 mm. $N = 9.42$.

$C_{25}H_{19}O_4N_3$ requires $N = 9.90$ per cent.

Chlorinated isoNitrosomalondi- β -naphthylamide, $C_{23}H_{16}O_3N_3Cl$.—When nitrosyl chloride acts on malondi- β -naphthylamide suspended in ethyl acetate, the product is a pale yellow, crystalline powder from which boiling ethyl acetate extracts a bright yellow solid crystallising in shining plates and melting at 202° . The melting point is not changed by recrystallising the substance from (1) a mixture of ethyl acetate and acetic acid, or (2) toluene. When heated on oxidised copper wire, the compound imparts a green colour to the flame, and therefore contains chlorine. Analyses of two different specimens of the substance showed it to be a chlorinated *isonitrosomalondi- β -naphthylamide*:

I. 0.2130 gave 19.3 c.c. moist nitrogen at 20.5° and 748 mm. $N = 10.17$.

II. 0.2446 „ 21.5 c.c. „ „ 17° „ 757 mm. $N = 10.16$.

$C_{23}H_{16}O_3N_3Cl$ requires $N = 10.09$ per cent.

The position of the chlorine atom in this compound was not investigated. The potassium salt is yellow, and yields a dark blue, insoluble ferrous salt when mixed in solution with ferrous sulphate.

IX. *isoNitrosomalondimethylanilide*, $[CO \cdot N(CH_3) \cdot C_6H_5]_2C:N \cdot OH$.

isoNitrosomalondimethylanilide is prepared by the action of nitrosyl chloride on malondimethylanilide; it crystallises with one molecular proportion of methyl alcohol, melts at 109° , and gives the yellow coloration with alkalis, and the deep purple colour with ferrous sulphate, which is characteristic of this group of oximes. The acetyl

derivative melts at 130° , the benzoyl derivative at 157 — 158° , and the ethyl ether at 138° .

In addition to the normal reaction between malondimethylanilide and nitrosyl chloride, there is a further reaction whereby an isomeride of *isonitrosomalondimethylanilide* is obtained together with the corresponding ketonic compound. Up to the present, the conditions under which the reaction proceeds thus abnormally have not been determined and a full account of this part of the work is reserved for a later paper dealing with the tetra-substituted derivatives of the oxime of mesoxamide. It may, however, be stated that the ketone corresponding with *isonitrosomalondimethylanilide*, or mesoxdimethylanilide,

crystallises in well-developed, prismatic crystals of a deep orange colour and melts at 172° ; it yields the normal *isonitroso*-derivative melting at 109° by the action of hydroxylamine both in acid and alkaline solution. The isomeric *isonitrosomalondimethylanilide*, ($\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}_3$), crystallises in tufts of thin, flattened needles of a pale yellow colour melting at 192° ; the ethyl ether melts at 168° , and the acetyl derivative at 223° . It forms colourless, crystalline alkali salts which are very soluble in water, the solutions give a rich purple-crimson colour with *ferric* chloride. From aqueous solutions of the alkali salts, mineral acids precipitate a well-defined colourless, crystalline, compound which melts at 256° and has not yet been identified; on treatment with sodium ethoxide, it regenerates the original sodium salt, from which, through the silver salt, the ethyl ether melting at 168° is obtained.

X. Behaviour of α -Oximinoketones with Ferrous Sulphate and Alkali.

(1) *isoNitrosoacetone* forms a bright yellow alkali solution (Meyer and Züblin, *Ber.*, 1878, 11, 695); the addition of ferrous sulphate produces an intense blue coloration.

(2) *Ethyl isonitrosoacetoacetate* gives a yellow colour with soda (Jovitschitsch, *Ber.*, 1895, 28, 2683); on the further addition of ferrous sulphate, a deep blue coloration is produced.

(3) *Ethyl isonitrosobenzoylacetate* dissolves readily in alkalis with a yellow colour (Perkin, *Trans.*, 1885, 47, 244); on the addition of ferrous sulphate, a deep indigo-blue precipitate is thrown down.

(4) *isoNitrosoacetylacetone* is readily soluble in alkalis giving a bright yellow colour (Zanetti, *Ber.*, 1893, 26, Ref. 598); the addition of a drop of ferrous sulphate produces an intense blue coloration.

(5) γ -*isoNitroso- β -ketopentane* melts at 53 — 55° and is soluble in alkalis with a yellow colour (Meyer and Züblin, *Ber.*, 1878, 11, 323). The

melting point was found to be 58—59°, and the addition of ferrous sulphate to the yellow alkaline solution produced a deep blue coloration.

(6) iso*Nitrosocamphor* is soluble in alkalis with a yellow colour (Claisen and Manasse, *Annalen*, 1893, 274, 77); the addition of ferrous sulphate develops a deep blue coloration.

(7 and 8) α -*Benzilmonoxime* and β -*benzilmonoxime* dissolved readily in alkalis giving deep yellow solutions (Auwers and Meyer, *Ber.*, 1889, 22, 540). On the further addition of ferrous sulphate, the solution of the α -oxime gave a Prussian blue precipitate, which, when dried, dissolved readily in benzene forming a deep blue solution. The alkali solution of the β -oxime, on the other hand, gave only the green precipitate of ferrous hydroxide.

(9) iso*Nitrosophenylisoxazolone* dissolves in alkalis with a rose-red colour (Claisen and Zedel, *Ber.*, 1891, 24, 140); the addition of ferrous sulphate throws down a dark greenish-blue precipitate.

(10) iso*Nitrosomethylisoxazolone* dissolves in alkalis with a red colour (Nussberger, *Ber.*, 1892, 25, 2157); the colour changes to a deep chocolate-brown on the addition of ferrous sulphate.

XI. Behaviour of Dioximes with Ferrous Sulphate and Alkali

(1) α -*Benzildioxime* (Auwers and Meyer, *Ber.*, 1888, 21 793) is sparingly soluble in alkalis yielding solutions of a faint yellow colour, which changes to a rich purple on the addition of ferrous sulphate. Attempts to prepare the potassium salt were unsuccessful, as it is rapidly hydrolysed by hot water or by methyl or ethyl alcohol.

The *ferrous* salt was obtained in the form of a finely-divided precipitate by adding freshly prepared ferrous sulphate solution to a solution of the oxime in aqueous potash; it was filtered, washed with water until the washings were no longer alkaline, and dried in the desiccator. The dry mass was almost black and had a peculiar shining appearance, not unlike that of coal. For the purpose of analysis, it was finely powdered and dried at 100° until the weight was constant:

0.4574 gave 0.1211 Fe_2O_3 and 0.0107 K_2SO_4 . Fe = 18.53; K = 1.05.

0.5410 „ 0.1460 Fe_2O_3 „ 0.0132 K_2SO_4 . Fe = 18.89; K = 1.09.

$\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2\text{Fe}$ requires Fe = 19.04; K = 0 per cent.

Before the second analysis was made, the salt was extracted several times with boiling water and then with alcohol, but although the results serve to show that the purple colour obtained by the interaction of α -benzildioxime with ferrous sulphate and an alkali is due to the formation of a coloured ferrous salt, the latter was not isolated in a pure form.

(2) *β-Benzildioxime* (Auwers and Meyer, *Ber.*, 1888, 21, 794) dissolves in alkalis with a pale yellow colour; the solution gives with ferrous sulphate only a ferrous hydroxide precipitate.

(3) *γ-Benzildioxime* (Beckmann and Köster, *Annalen*, 1893, 274, 19). The pale yellow sodium salt dissolves readily in water, and on adding ferrous sulphate solution a precipitate is formed of a dull purple colour, changing rapidly to brown.

(4) Syn-oxime of *ethyl isonitrosoacetoacetate* dissolves in alkalis forming a colourless solution (Ceresole and Köckert, *Ber.*, 1884, 17, 821); on the further addition of ferrous sulphate, a deep purple coloration is developed.

(5) *Methylethylglyoxime* (Schramm, *Ber.*, 1883, 16, 180) is sparingly soluble in alkalis giving a pale yellow solution which changes to a deep reddish-brown on the addition of ferrous sulphate.

Ethylnitrolic acid gives an orange-yellow colour with alkalis (Meyer and Constam, *Annalen*, 1882, 214, 329); the colour changes to a deep chocolate brown on the addition of ferrous sulphate.

The colour reactions with ferrous sulphate described in this and in the preceding section form very delicate tests for the respective oximes.

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