54. *The Metallic Derivatives of Hydrazones and of the Oxime-Hydrazones of Benzil.*

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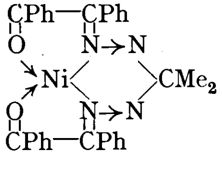
This paper describes experiments on the formation of metallic complexes, containing metals such as iron and nickel, by organic compounds which contain the hydrazone group, $=C:N\cdot NH_2$. Several such complexes are described, and it is shown that stereochemical configuration plays a part in complex formation in the hydrazones just as it does in the oximes. The hydrazone complexes are, however, profoundly different from the oxime complexes and are much more difficult to purify; consequently, it is impossible to argue on any analogy to the oxime complexes, and the stereochemical deductions which it was hoped to make concerning the configurations of the hydrazones are of little value.

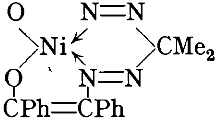
THE chance observation that benzilmonohydrazone, $COPh\cdot CPh:N\cdot NH_2$, reacts in alcoholic solution with nickel acetate to give a dark reddish, insoluble complex containing nickel has led to experiments undertaken in the hope that metallic-complex formation would throw light on the stereochemical configurations of the hydrazones. For few types of hydrazones are methods known whereby configurations can be assigned with any certainty (see, *e.g.*, Busch, Friedenberger, and Tischbein, *Ber.*, 1924, **57**, 1785; Hieber and Sonnenkalb, *Annalen*, 1927, **456**, 86). The stereochemical configurations of certain classes of oxime have been found to be connected with their ability to form co-ordination complexes (for references see Taylor and Baker, " The Organic Chemistry of Nitrogen," 1937, pp. 193 *et seq.*) and it was thought that, with this knowledge, the behaviour of the hydrazone complexes might lead to the information desired. This hope has been frustrated by the fact that most of the hydrazone complexes obtained are considerably less stable than the oxime complexes and that no satisfactory method for their purification could be devised; they separate as intractable, fine precipitates, and only one complex could be obtained crystalline.

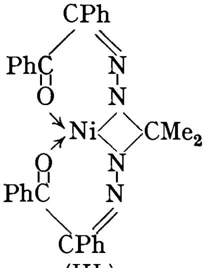
The Benzilmonohydrazone Complex.—Benzilmonohydrazone reacts with nickel acetate in a variety of solvents to give a red *complex* which separates slowly; the yield is higher if ammonia is added or if pyridine is used as solvent, and this, coupled with the fact that no complex is obtained when nickel chloride is used instead of the acetate unless ammonia is also added, indicates that replacement of a hydrogen atom is involved in complex formation. This view is strengthened by indications that a complex is formed with benzilmonophenylhydrazone, although it could not be isolated, but there are no such indications with benzilmonophenylmethylhydrazone (COPh·CPh:N·NMePh), in which both hydrogen atoms are replaced by hydrocarbon radicals. The colour change when sodium ethoxide is added to an alcoholic solution of the monohydrazone also indicates that the hydrazone can behave as a weak acid, since it is very much like the colour change caused by adding alkali to α-benzilmonoxime.

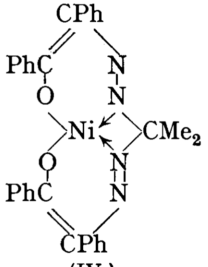
The monohydrazone complex is slightly soluble in benzene to give a dark red-brown solution. Hence it is almost certainly not a salt and does not contain the metal as a complex ion. It is probable that the nickel atom is held by two covalencies and two co-ordinate links, as in the majority of its metallic complexes. The nickel content of this complex varied between 10·34% and 15·10% without any marked difference in the appearance or properties of the samples. Those of lower nickel content almost correspond in composition to a complex R_2Ni ($R = COPh\cdot CPh{:}N\cdot NH-$), but the analyses of the majority of the preparations approximate fairly closely to the unexpected formula R_3Ni_2, and the composition scarcely changes when they are rapidly precipitated from benzene solution or are washed with solvents. This complex is only slowly attacked by hydrogen sulphide and not at all by potassium cyanide, but it is decomposed by nitric acid to give either benzil or benzoylphenylketazine (COPh·CPh:N·N:CPh·COPh) according to the conditions; both of these compounds are formed from the original hydrazone by the action of mineral acids. The benzene solution of the hydrazone complex decomposes slowly, particularly in air, and the product has a higher nickel content.

The "Azine Complex."—A peculiar reaction takes place when the nickel complex of benzilmonohydrazone is prepared in boiling acetone solution. If the insoluble precipitate is removed, a small quantity of a new complex (here called the "azine complex") separates in red needles on cooling. This is a stable and definite *substance.* Its composition and molecular weight are in agreement with the formula $C_{31}H_{26}O_2N_4Ni$, which may be built up from $2COPh\cdot CPh{:}N\cdot NH_2 + (CH_3)_2CO + Ni - H_2O - 2H$. The same complex may also be prepared in small yield from nickel acetate, benzilmonohydrazone, and *benzil acetone azine* ($COPh\cdot CPh{:}N\cdot N{:}CMe_2$), although the last compound forms no complexes under any conditions. A further important point is that the azine complex does not react further with acetone even on prolonged treatment. These facts shed some light on the constitution of the azine complex and afford a possible explanation of the behaviour of the hydrazone complex. The acetone has clearly reacted with the imino (or amino)-groups of the hydrazone, but one acetone molecule is sufficient for two hydrazone residues present in the azine complex, and after this there is no further reaction. Hence the acetone residue must form a kind of bridge between the two hydrazone residues and the formula of the azine could be of the type (I), which can also be written as (II). This formula implies one of the two possible configurations of the hydrazone group. Similar formulæ but with four-atom rings (III, IV) are possible with the other configuration.


(I.)

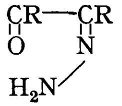

(II.)

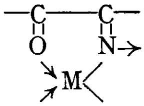

(III.)


(IV.)

Hence the formation of the azine complex does not settle the stereochemical problem except in so far as formula (I) or (II) is preferable on general grounds to (III) or (IV). The reaction with acetone shows that the hydrazone complex must contain reactive imino-groups, and its instability and indeterminate nature may thus be explained.

Reactions of Other Compounds containing the $-CO\cdot CR{:}N\cdot NH_2$ *Group.*—Other compounds containing the group $\cdot CO\cdot CR{:}N\cdot NH_2$ form nickel complexes with properties similar to those of benzilmonohydrazone, but they are even less stable. tert.-*Butylglyoxal* can be prepared by the oxidation of pinacolone with selenium dioxide. Its *monohydrazone* forms a complex of composition approximating to R_3Ni_2, but this is decomposed by water with separation of nickelous hydroxide. The behaviour of the two geometrically isomeric monohydrazones of camphorquinone showed that stereochemical configuration is of importance for complex formation; the α-monohydrazone (m. p. 206°) gives no sign of complex formation under any conditions, but the β-compound (m. p. 102°) gives a red colour with nickel acetate when ammonia is added, although no solid complex could be isolated. Hence it would seem that the stereochemical configurations of benzilmonohydrazone and of *tert.*-butylglyoxalhydrazone are the same as those of the β-hydrazone of camphorquinone. According to Forster and Zimmerli (J., 1910, **97**, 2156), the configuration of the latter is (V), and if this is true, complex formation in these hydrazones must involve the formation of a six-membered ring, the nickel atom being presumably attached to the oxygen atom by a co-ordinate link and to the nitrogen by a covalent link, replacing hydrogen. This is the opposite to what

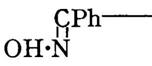

(V.)

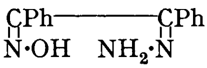

(VI.)

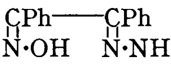
would be expected, since no complexes are formed by β-benzilmonoxime, which is known, from the work of Meisenheimer (*Ber.*, 1921, **54**, 3206), and of Pfeiffer and Richarz (*Ber.*, 1928, **61**, 103), to have a configuration corresponding to (V), and all complexes of the monoximes are undoubtedly of the type (VI). It would also imply the unstable four-membered ring structure (III) for the azine complex.

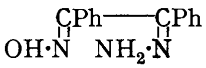
Because of the intractable nature of the complexes so far described, the observations have been extended to other compounds containing the hydrazone group. Since replacement of one hydrogen atom of the hydrazone group seems to be necessary for formation of the hydrazone complexes, and this may be the reason for their instability, it seemed that a compound which contained, in addition to the hydrazone group, another acidic group in a suitable spatial position might form stable complexes, and that evidence might be forthcoming of the stereochemical configuration of the hydrazone group. Salicylaldoxime, which exists in only one form, is known to form stable complexes with certain metals (Ephraim, *Ber.*, 1930, **63**, 1928; 1931, **64**, 1215; Brady, J., 1931, 105), the structure of which is known both from chemical evidence (Feigl and Bondi, *Ber.*, 1931, **64**, 2819) and from *X*-ray investigation of the crystal (Cox, Pinkard, Wardlaw, and Webster, J., 1935, 459; Cox and Webster, *ibid.*, p. 731). Salicylaldehydehydrazone, of which, again, only one form is known, also affords complexes with copper, nickel, cobalt, and ferric iron. They are, however, much less stable than the corresponding oxime complexes and are as difficult to separate and purify as the benzilhydrazone derivatives. They present no true analogies with the complexes of salicylaldoxime, and no trustworthy deduction as to the configuration of the hydrazone can be made from their behaviour. It is possible that the differences are due, not to a difference in stereochemical configuration, but to the presence in the hydrazone molecule of two nitrogen atoms, each of which is capable of uniting with a metal atom by a co-ordinate link, so that the complex formed is of the chain type, with many molecules linked together through metallic atoms.

The oxime-hydrazones of benzil gave more definite results, leading to useful deductions about the configurations. There should be four geometrical isomerides, but only one

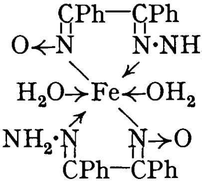

$$\begin{array}{cc}\mathrm{CPh}\text{——}&\mathrm{CPh}\\ \| & \|\\ \mathrm{OH\cdot N} & \mathrm{N\cdot NH_2}\end{array}$$
(VII.)


$$\begin{array}{cc}\mathrm{CPh}\text{————}&\mathrm{CPh}\\ \| & \|\\ \mathrm{N\cdot OH} & \mathrm{NH_2\cdot N}\end{array}$$
(VIII.)


$$\begin{array}{cc}\mathrm{CPh}\text{——}&\mathrm{CPh}\\ \| & \|\\ \mathrm{N\cdot OH} & \mathrm{N\cdot NH_2}\end{array}$$
(IX.)


$$\begin{array}{cc}\mathrm{CPh}\text{——}&\mathrm{CPh}\\ \| & \|\\ \mathrm{OH\cdot N} & \mathrm{NH_2\cdot N}\end{array}$$
(X.)

has been described, *viz.*, that obtained by Forster and Dey (J., 1912, **101**, 2234) and by Darapsky and Spannaegel (*J. pr. Chem.*, 1915, **92**, 289) from β-benzilmonoxime. If the configuration of the oxime group has not changed, the configuration of this oxime-hydrazone, which we call the β-compound, must be (VIII) or (IX). Contrary to Forster and Dey, we find that α-benzilmonoxime forms a new and less soluble oxime-hydrazone, which we call the *α-oxime-hydrazone*. No other oxime-hydrazones could be prepared. There is an obvious analogy between the oxime-hydrazones and the dioximes of benzil; in the latter class the *amphi*-compound is the least stable, so that the two missing oxime-hydrazones are very probably the *amphi*-compounds (IX) and (X), and on this view the two known compounds, α and β, have the configurations (VII) and (VIII), respectively. The physical properties of the two oxime-hydrazones support this conclusion because they differ just as do the α- and β-dioximes. Now, the last two compounds differ sharply in their behaviour towards the salts of the transitional metals; the β-dioxime forms no complexes, but the α-dioxime forms very stable complexes with nickel and palladium (Tschugaev, *Z. anorg. Chem.*, 1905, **46**, 144). The same difference exists between the two oxime-hydrazones, the β-compound giving no indication of complex formation and the α- combining with several metals to give complexes of which the most characteristic is the magenta *ferrous* compound, $R_2Fe,2H_2O$, the structure of which is very probably (XI).



(XI.)

This contrast between the α- and β-benziloxime-hydrazones can be taken, on the analogy of the dioximes, to be further evidence that the α-oxime-hydrazone has configuration (VII) and the β-compound (VIII), although (IX) is not excluded for the latter.

The corresponding cobalt complex, which is much less soluble in organic solvents and behaves more like a compound of high molecular weight, may have a similar structure without the water molecules, its complexity being due to co-ordination of the free amino-groups to other cobalt atoms. It seems to be a cobaltous compound and not cobaltic, because it is formed rapidly from cobalt acetate and only slowly from chloropentammino-cobaltic chloride.

Certain additional observations are given in the next section.

EXPERIMENTAL.

The *nickel* complex of benzilmonohydrazone can be obtained most conveniently by dissolving 4·5 g. of the hydrazone (Curtius and Thun, *J. pr. Chem.*, 1891, **44**, 176) in hot alcohol and adding an alcoholic solution of nickel acetate (5 g.); the colour changes to dark red, and the complex begins to separate immediately. When the cooled solution is filtered, a dark red solid is obtained, which can be freed from excess of hydrazone by extraction with hot alcohol; yield, 5 g. If a little acetic acid is present, there is no colour change and no complex is formed; the presence of a little ammonia makes no difference to the yield, but with large excess (alcohol and an equal volume of ammonia, *d* 0·880) very little complex is obtained and benzoylphenylketazine, COPh·CPh:N·N:CPh·COPh, m. p. 202°, separates. The same complex is formed when acetone replaces alcohol, but with pyridine as solvent the yield is small. With nickel chloride there is no colour change; subsequent addition of ammonia precipitates the red complex.

The complex is insoluble in water, alcohol, acetone, acetic acid, and light petroleum, but dissolves to some extent in benzene, chloroform, carbon tetrachloride, nitrobenzene, tetralin, pyridine, and quinoline; the solutions are dark red, except that in quinoline, which is purple. The complex can be precipitated from benzene solution with light petroleum or alcohol, but always with much loss; it is difficult to wash with most solvents and tends to become pasty; it decomposes indefinitely in the range 200—230°. It is fairly stable in the solid state, but decomposes slowly in solution, the colour changing to brown-yellow; the solid recovered from these yellow solutions was gummy (Ni, 24·5%). Extraction with benzene of samples of the red solid which had been kept some time left an insoluble yellow residue (Ni, 26·5%). The red complex was analysed for nickel by decomposition with concentrated nitric acid; the diluted solution was filtered from the benzil formed, and the nickel estimated with dimethylglyoxime. The results of the many analyses may be summarised as follows: if the precipitation from benzene solution had taken much time through slowness in filtering, etc., the nickel content was above 18% and usually 20—21%; with the most rapid precipitation and washing possible, the values were 10·56, 10·34, 11·13% [$(C_{14}H_{11}ON_2)_2Ni$ requires Ni, 11·6%], but a large number of samples contained Ni, 14—15%. Molecular-weight determinations gave inconsistent results. Prof. S. Sugden kindly measured the magnetic moment of the complex and found it to be paramagnetic ($\chi = 9{\cdot}6 \times 10^{-6}$); it thus resembles the nickel complexes of acetylacetone and of oximinoketones (Cambi, *R. Inst. Lombardo Sci. Lettre Rend.*, 1933, **66**, 1091; Cambi and Szegö, *Ber.*, 1931, **64**, 2391).

Benzilmonohydrazone forms a palladium complex which is yellow but otherwise resembles the nickel complex in most of its properties; its composition is again indefinite and varies between the values expected for R_2Pd and RPd. With copper salts there is no complex formation, but only reduction by the hydrazone group to metallic copper, and there is no sign of complex formation with cobaltous or cobaltic compounds.

Behaviour of Other Hydrazones towards Nickel Acetate, etc.—Benzilmonophenylhydrazone (Bülow, *Annalen*, 1886, **236**, 197) in pyridine with nickel acetate gives a dark red colour similar to that with the monohydrazone, but the colour is destroyed by adding water and is not observed in alcoholic solution. Benzilmonophenylmethylhydrazone (Kohlrausch, *Annalen*, 1889, **253**, 16) does not give a red colour in either solvent; the same is true for benzilsemicarbazone (Biltz and Arnd, *Ber.*, 1902, **35**, 344), which is surprising in view of the properties of the semicarbazone group. There is no sign of complex formation with deoxybenzoinhydrazone (Curtius and Blumer, *J. pr. Chem.*, 1895, **52**, 136) or with benzoinhydrazone (*ibid.*, p. 124); the latter compound only reacts with copper salts to reduce them to metal, and the results with it stand in marked contrast to the ready formation of metallic complexes by benzoinoxime (" cuproin "). Benzildihydrazone gives a yellow-green complex when treated with nickel acetate in alcohol; this is insoluble in all organic solvents except pyridine, and is decomposed to the dihydrazone when washed with water; a sample washed with alcohol contained Ni, 19·3%.

β-Camphorquinonehydrazone gives an immediate deep red colour with nickel acetate in alcohol, intensified by adding aqueous ammonia, but no solid complex could be isolated; the α-compound does not show this reaction.

tert.-*Butylglyoxal*, $CMe_3{\cdot}CO{\cdot}CHO$.—Pinacolone (93 g.) was refluxed with purified selenium dioxide (68 g.) in an oil-bath at 110—120° for 20 hours. The resulting dark yellow liquid was decanted into an equal bulk of water, and the mixture distilled with a 50-cm. column; at 81—95° a mixture of pinacolone and water came over, and at 95—98° a homogeneous yellow distillate. The latter was repeatedly extracted with ether, the united extracts dried over calcium chloride, and the ether removed; the residue, a yellow oil, boiled at 115°. On standing overnight it was converted into a colourless crystalline mass, which was recrystallised from light petroleum (b. p. 60—80°); m. p. 85°; yield, 20 g. (27% on the selenium dioxide used). As with methylglyoxal, this is a *hemihydrate* (Found: C, 58·6; H, 8·9. $C_6H_{10}O_2,\frac{1}{2}H_2O$ requires C, 58·5; H, 8·9%). It is soluble in water, and the solution reduces ammoniacal silver nitrate, but not Fehling's solution, and gives white flocks of a glyoxaline with ammonia.

tert.-*Butylglyoxalmonohydrazone*, $CMe_3{\cdot}CO{\cdot}CH{:}N{\cdot}NH_2$.—The preceding compound was warmed with hydrazine hydrate (1 mol.) in aqueous-alcoholic or alcoholic solution for 5—30 minutes; extraction with ether, drying the extract with magnesium sulphate, and removal of the ether gave a colourless solid; recrystallised from light petroleum, this had m. p. 81°. The *compound* is volatile in steam; as it readily reacts with copper oxide, the analyses for nitrogen were unsatisfactory (Found: C, 56·5; H, 9·2. $C_6H_{12}ON_2$ requires C, 56·3; H, 9·4%).

With nickel acetate in alcohol and a few drops of aqueous ammonia, a cherry-red colour appears, and after boiling, a dark red solid separates [Found: Ni, 21·5. Calc. for $C_6H_{10}ON_2Ni$: Ni, 31·6%. Calc. for $(C_6H_{11}ON_2)_2Ni$: Ni, 18·7%]. This complex is soluble in benzene to give a rich red solution, but is not precipitated by adding light petroleum or alcohol; it is decomposed by water, nickelous hydroxide being formed.

Benzil Acetone Azine, $COPh{\cdot}CPh{:}N{\cdot}N{:}CMe_2$.—This *compound* is not formed by boiling benzilmonohydrazone with acetone for long periods. When, however, benzil is heated in alcohol with acetonehydrazone (Staudinger and Gaule, *Ber.*, 1916, **49**, 1905) for 6 hours, it crystallises from the solution on cooling together with unchanged benzil; the two were separated by repeated recystallisation from alcohol. It forms thick yellow needles, m. p. 86° (Found: N, 10·8. $C_{17}H_{16}ON_2$ requires N, 10·6%). The same compound is also formed by refluxing benzilmonohydrazone in acetone with a little nickel acetate. After cooling, the nickel complex of the hydrazone and the azine complex (see below) are filtered off, and the bulk of the acetone distilled from the filtrate; the residue deposits the azine together with the azine complex, and these are separated by recrystallisation from warm (not boiling) alcohol, in which the latter is sparingly soluble. No indications of complex formation were observed when this azine was treated with derivatives of iron, nickel, and cobalt under a variety of conditions.

The " Azine Complex."—The above azine (1 mol.) was heated in alcohol with nickel acetate (1 mol.), and an alcoholic solution of benzilmonohydrazone (1 mol.) added slowly with shaking. After 6 hours' boiling under reflux, the hydrazone complex which had formed was separated from the hot solution, and on cooling, a small quantity of the azine complex separated in bright red needles; more was obtained from the mother-liquor. The same compound is more readily obtained by adding nickel acetate (1 mol.) in alcoholic solution to benzilmonohydrazone (2 mols.) in acetone and boiling under reflux for 6 hours; the azine complex is worked up as before. The yield is about 5%. In this case the mother-liquor also contains the azine described above. The *azine nickel complex* can be recrystallised from alcohol; it then has m. p. 239—240°. It is sparingly soluble in cold alcohol and light petroleum, and more soluble in benzene, acetone, and carbon disulphide. It is unaffected by dilute mineral acids and by hydrogen sulphide and sodium sulphide in aqueous alcohol, but is decomposed by nitric acid and hot concentrated hydrochloric acid to give benzil and the salt of nickel; this method of decomposition was used in the analyses for nickel [Found: C (micro), 68·0; H (micro), 4·8; N, 10·3; Ni, 10·6. $C_{31}H_{26}O_2N_4Ni$ requires C, 68·3; H, 4·8; N, 10·3; Ni, 10·8%]. The solubility in benzene is not large enough for good molecular-weight determinations, but 0·1294 g. in 20·14 g. of benzene gave $\Delta = 0{\cdot}067°$, whence $M = 502$ (Calc.: 545).

Attempts to obtain a similar compound with palladium in place of nickel failed; the yellow hydrazone complex of palladium was formed, but boiling in acetone led to reduction to metallic palladium.

Benzil benzaldehyde azine, COPh·CPh:N·N:CHPh, was obtained by heating benzilmonohydrazone with the equivalent of purified benzaldehyde in alcohol until the smell of benzaldehyde disappeared (¾ hour). When a little water was added to the cooled solution, the *azine* separated. It crystallised in yellow needles, m. p. 151°, from alcohol; yield 66% (Found: N, 9·1. $C_{21}H_{16}ON_2$ requires N, 9·0%). All attempts to obtain a nickel complex of this azine and benzilmonohydrazone, analogous to the azine complex described above, failed.

The Metallic Derivatives of Salicylaldehydehydrazone.—When salicylaldehydehydrazone (Cajar, *Ber.*, 1898, **31**, 2803) is treated with nickel acetate or copper acetate in alcohol, finely divided precipitates are formed; the former is yellow and the latter ochre-coloured. Both are insoluble in water and all organic solvents, and tend to become colloidal when washed with hot benzene; they are attacked by dilute mineral acids, acetic acid, and ammonia, giving salicylaldehydeazine, m. p. 216°, and are partly decomposed by boiling with water. The copper complex detonates with warm nitric acid, and, unlike the nickel complex, is stable to aqueous sodium hydroxide. Samples of both complexes, analysed for carbon, hydrogen, nitrogen, and the metal, gave figures in rough agreement with the formulæ R_2Ni and R_2Cu.

The Oxime-hydrazones of Benzil.—The action of hydrazine hydrate on β-benzilmonoxime (Taylor and Marks, J., 1930, 2305) was repeated as described by Forster and Dey (J., 1912, **101**, 2234); the m. p. of the β-oxime-hydrazone was 171°. No indication of complex formation between this compound and iron, nickel, cobalt, or palladium was observed.

α-Benziloxime-hydrazone.—α-Benzilmonoxime (23 g.) in alcohol was refluxed with hydrazine hydrate (5·5 g.); after 1 hour white crystals began to separate, and after 6 hours these were collected, washed with alcohol, and recrystallised from pyridine–alcohol; m. p. 216°, yield 6·6 g. (Found: N, 17·7. $C_{14}H_{13}ON_3$ requires N, 17·6%). The filtrate on standing deposited 1 g. of benzilmonohydrazone, and 13 g. of α-benzilmonoxime were also recovered. *α-Benziloxime-hydrazone* is insoluble in alcohol, benzene, xylene, and chloroform, and dissolves in pyridine, dioxan, and aqueous sodium hydroxide. It forms complexes with metallic salts in pyridine or dioxan; with nickel salts there is a red colour similar to that given by benzilmonohydrazone, with copper salts a yellow colour, with ferrous salts an intense rose-red colour, and with cobalt salts a very dark brown colour.

Ferrous Complex of α-Benziloxime-hydrazone.—To a hot pyridine solution of the oxime-hydrazone (2 mols.) an aqueous solution of ferrous sulphate (1 mol.) was added; an intense rose-red colour appeared immediately. After the solution had been heated for 2 minutes and cooled, 20% aqueous sodium hydroxide was added to precipitate unchanged iron. The pyridine layer was separated and filtered, and pyridine distilled off from the moist solution under reduced pressure at or below 40°. The deep purple residue was dissolved in the minimum of chloroform (in which the α-oxime-hydrazone is insoluble), the solution filtered, and the complex precipitated by addition of an equal volume of light petroleum (b. p. 60—80°). The mixture was cooled to − 20°, and the complex collected and washed with light petroleum; 2·4 g. of the oxime-hydrazone gave 1·5 g. of the ferrous complex. The substance could not be obtained crystalline: removal of the solvent from its solution leaves a hard red varnish. It is somewhat soluble in alcohol, acetone, benzene, and ethyl acetate, and very soluble in pyridine, chloroform, dioxan, and tetrachloroethane. It is not completely decomposed by mineral acids in the cold, and only slowly on heating, but its pyridine solution is immediately decolorised by mineral acids.

Analysis of a sample washed with much light petroleum indicates that the compound is a *dihydrate*, and this recalls the hygroscopic nature of the ferrous complexes of certain oximino-ketones (Taylor and Ewbank, J., 1926, 2818) (Found: C, 60·2; H, 5·2; N, 14·9; Fe, 9·6. $C_{28}H_{24}O_2N_6Fe,2H_2O$ requires C, 59·2; H, 4·9; N, 14·8; Fe, 9·8%).

The cobalt complex of this oxime-hydrazone forms a dark brown, non-crystalline powder, m. p. 119°, which can be obtained, probably somewhat impure, by the interaction of the compound in pyridine with cobalt acetate, followed by precipitation with a limited amount of water. The same complex is formed slowly if chloropentamminocobaltic chloride replaces the cobalt acetate. It is fairly soluble in alcohol and very soluble in chloroform, pyridine, dioxan, and benzene, and can be precipitated from benzene solution with light petroleum. Its brown colour and solubilities are reminiscent of the cobaltous complexes of certain oximino-ketones described by Ponzio (*Gazzetta*, 1922, **52**, i, 285) and by Taylor (J., 1931, 2025).

It is curious that the metallic derivatives of hydrazones which have been investigated are amorphous and (except the azine complex described above) cannot be obtained crystalline, whereas the metallic derivatives of oximes usually crystallise well and are easy to purify.

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