

CCCLXXV.—*The Metallic Compounds of Certain Monoximes and the Structure of the Oximes.*

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THAT certain oximes will form stable compounds with metals has long been known and indications exist that the power of forming such compounds is determined by the constitution and configuration of the oxime; for example, Tschugaev (*Z. anorg. Chem.*, 1905, **46**, 148) has shown that α -benzildioxime will form complexes with heavy metals, whereas the β -dioxime will not. The question of configuration and constitution necessary in an oxime for metallic complex formation has also been partly investigated by Whiteley (*J.*, 1903, **83**, 24) and Ponzio (*Gazzetta*, 1922, **52**, i, 285), but no generalisation has been put forward which attempts to explain the experimental results.

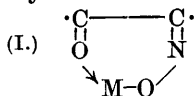
The interest attaching to the oximes led us to investigate eleven monoximes of different types and the possibility of obtaining from them complexes with iron, nickel, cobalt, or copper. The results are in Table I; the following points will be noticed.

(i) The oximes investigated fall into two classes, those forming metallic complexes and giving a characteristic blue colour with alkaline solutions of ferrous salts, and those that do not; the only doubtful case is methyl α -oximinoethyl ketone, which gives no complexes but shows the characteristic blue colour.

(ii) Of the metals used, cobalt forms complexes with greater facility than the others.

(iii) Nickel complexes could be obtained from oximinoacetylacetone and ethyl oximinoacetoacetate only in the presence of ammonia, and ammonia residues are contained in the resulting complex.

The structure of the metallic complexes formed by oximino-ketones, -esters or -amides, to which classes the oximes investigated belong, is almost certainly



where the arrow represents a co-ordinate link formed by two electrons from the oxygen atom; this structure explains the non-salt-like properties of the complexes, and also their actual formulæ, as, for example, Tschugaev's compound of cobalt and α -benzilmonoxime, $\text{Co}(\text{Ph}\cdot\text{CO}\cdot\text{CPh}\cdot\text{NO})_3$, where the typical co-ordination number of cobalt, six, can be recognised.

TABLE I.

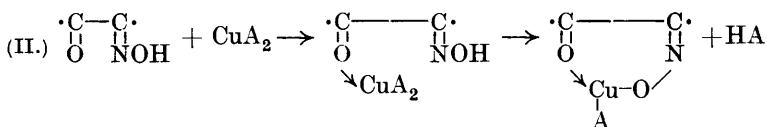
In cols. 2, 3, 4, and 5 are the formulæ of the metallic complexes obtained; R represents a molecule of the oxime minus a hydrogen atom. Compounds marked with a query are those which it was difficult to obtain analytically pure or those whose formula is doubtful for some other reason (see experimental section).

Oxime.	Fe.	Co.	Ni.	Cu.
Me·CO·CH:NOH.	Blue col. Sol. in benzene.	?R ₂ Co. ?R ₂ Ni.		Indeterminate.
Me·CO·C(:NOH)·C(OMe).	"	R ₃ Co.	[Me·C(:NH)·C(:N·O)·C(OMe) ₂]Ni.	?R·Cu·O·CO·CH ₃ , H ₂ O.
Ph·CO·C(:NOH)·C(OMe).	"	R ₃ Co.	Nil.	R·CuOH.
Me·CO·C(:NOH)·CO ₂ Et.	"	R ₃ Co.	[Me·C(:NH)·C(:N·O)·CO ₂ Et] ₂ Ni.	R·CuOH, H ₂ O and R·CuOH.
Ph·CO·CH:NOH.	R ₂ Fe.	R ₃ Co.	Indeterminate.	Nil.
OH·N:C(CO·NHPh) ₂ .	R ₂ Fe. ^o	?R ₂ Co.	R ₂ Ni.	R ₂ Cu.
Ph·CO·CPh:NOH(α).	Blue col. Sol. in benzene.	R ₃ Co.†	Indeterminate.	R·CuOH.
Me·CO·CMe:NOH.	"	Nil.	Nil.	Nil.
Ph·CO·C(:NOH)·CO ₂ Et.	No blue col.	"	"	"
OH·N:C(CO ₂ Et) ₂ .	"	"	"	"
Ph·CO·CPh:NOH(β).	"	"	"	"

^o Whiteley, *loc. cit.*

† Tschugaev, *J. pr. Chem.*, 1907, **76**, 88.

The view that leads to the most consistent explanation of the results in Table I is that, in oximes of the classes investigated, formation of metallic complexes is determined by the presence of a reactive carbonyl group: oximinoacetylacetone forms complexes, but ethyl oximinomalonate does not; α-benzilmonoxime, which forms complexes, contains a reactive carbonyl group, whereas that in the β-oxime, which forms no complexes, is less reactive. That the presence of such a group should be the determining factor is easily comprehensible if it is assumed that the mechanism of metallic complex formation is not formation of the true metallic salt of the oxime followed by closure of the co-ordinated ring, but an initial formation of a co-ordinate link between the reactive carbonyl group and the metallic ion or salt followed by ring closure through elimination of a hydrogen ion or a molecule of the acid originally united with the metal—a scheme shown in (II).



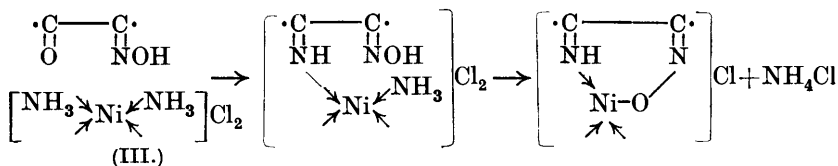
In a complex such as R₃Co the process occurs three times, and if no sufficiently reactive carbonyl group is present the initial step cannot take place and no complex can result.

The view receives some support from the work of Feigl and Rubinstein (*Annalen*, 1923, **433**, 183), who isolated and analysed a co-ordination compound [Co(DH₂)₂]Cl₂ (DH₂ = dimethylglyoxime formed from dimethylglyoxime and cobaltous chloride; this is

evidence that union can take place between an analogous compound and a cobalt salt without preliminary elimination of the anion united with the cobalt.

It may be objected to this view that the work of Hieber (*Ber.*, 1921, **54**, 902) shows that, in a keto-enol tautomeride, the enol alone forms complexes, at least with copper, and that the enolic form of a compound such as ethyl acetoacetate contains no reactive carbonyl group. It is highly probable, however, that the two reactions are dissimilar: ethyl acetoacetate forms with cobalt and nickel under the conditions which are sufficient for the oximes, not simple complexes but compounds of unknown constitution, $\text{Ni}_2\text{C}_{20}\text{H}_{32}\text{O}_{11}$ and $\text{Co}_2\text{C}_{20}\text{H}_{30}\text{O}_{11}$ (Wislicenus and Stoeber, *Ber.*, 1902, **35**, 546); and its copper compound has no analogy with those of the oximes investigated, with the exception of oximinomalonanilide, which stands apart from the other oximes in possessing a mobile hydrogen atom and is in this comparable with ethyl acetoacetate.

In the nickel complexes which require ammonia for their formation and contain ammonia residues it is probable that the primary step is reaction between the carbonyl group and the ammonia-nickel complex present in the ammoniacal solution. As can be seen in Table I, nickel-oxime complexes are rare; this suggests that a carbonyl group is incapable of forming a stable co-ordinate link with nickel, but that in some cases it can react with the nickel ammine complex to give the necessary first step and thus the ammonia-containing complex (III).



No explanation is offered for the failure of ethyl oximinobenzoylacetate to form complexes, although the corresponding acetyl compound does so. Whatever view is taken, the sharp distinction between the two is difficult to explain if it is assumed that they possess similar constitutions.

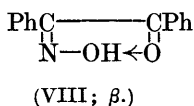
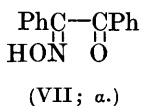
The difference in reactivity of the carbonyl groups in α - and β -benzilmonoximes already referred to may possibly arise from purely steric causes, the proximity of the hydroxyl group affecting the reactivity of the carbonyl group in the β -oxime but not that in the α -oxime. A much more probable explanation is, however, that in α -oximino-ketones and similarly constituted compounds the stereoisomeride which contains the less reactive carbonyl group itself possesses a six-membered co-ordinated ring structure.

Sidgwick (J., 1925, **127**, 907) has pointed out that the physical properties of the enolic form of a β -diketone or ketonic ester can be accounted for only by assigning to the enol the structure (IV).



Further strong evidence for his view is afforded by the chemical properties of ethyl *cyclobutenolone*carboxylate (V) (Schroeter, *Ber.*, 1916, **49**, 2714; see also Dieckmann and Wittmann, *Ber.*, 1922, **55**, 3331), which, although in many ways constituted identically with the enolic form of a β -ketonic ester, differs from such enols in being an acid strong enough to decompose carbonates. Co-ordination between the enolic hydrogen atom and a carbonyl group is obviously not present in this compound, and this can be ascribed to the presence of the four-membered ring; for co-ordination would mean the formation of the ring system (VI), a system which is very rare, if, indeed, it occurs at all.

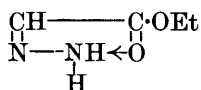
In the α -oximino-ketones similar six-membered co-ordinated rings can occur, and the properties of the benzilmonoximes [α -benzilmonoxime, m. p. 137.8° , is sparingly soluble in benzene or carbon disulphide and reacts with aniline in the cold in 8 days and with phenylhydrazine at $30-40^\circ$ (von Auwers and V. Meyer, *Ber.*, 1889, **22**, 540); β -benzilmonoxime, m. p. $113-114^\circ$, is easily soluble in all organic solvents and does not react with aniline and phenylhydrazine under the conditions stated (von Auwers and Siegfeld, *Ber.*, 1893, **26**, 794)] indicate that these have the structures (VII) and (VIII).



This view not only accounts satisfactorily for the chemical reactivity of these oximes but implies a stereochemical configuration, for it implies that the configuration about the $>\text{C}:\text{N}$ group is favourable in the β -oxime and unfavourable in the α -oxime to the formation of the co-ordinated ring. The configurations so arrived at are those deduced by Meisenheimer from the oxidation product of triphenylisooxazole (*Ber.*, 1921, **54**, 3208).

This view of the difference in reactivity between the benzilmonoximes and the deduction of stereochemical configurations from it receive support from the recorded properties of the stereoisomeric hydrazones of camphorquinone (Forster and Zimmerli, J., 1910, **97**, 2156) and of glyoxylic ester (Staudinger, Hammet, and Siegwart, *Helv. Chim. Acta*, 1921, **4**, 228), where the striking difference

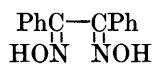
in reactivity of the isomerides clearly points to the presence of a co-ordinated ring in one isomeride and its absence in the other. In the latter case, one isomeride, the liquid, is more volatile and less soluble in water than the other, and reacts only slowly with phenylcarbimide and not at all with diphenylketen; its molecular weight in benzene is normal: the other, the solid, is associated in solution and reacts readily with both reagents. Here the structures must be those shown in (IX) and (X), and the stereochemical configurations follow.



(IX; liquid form.)



(X; solid form.)



(XI.)

The benzildioximes deserve some mention: the α -dioxime forms a nickel complex, R_2Ni , and the β -dioxime forms no metallic complexes (Tschugaev, *loc. cit.*). If the initial step in complex formation is co-ordination of the metal with one of the tervalent nitrogen atoms, the α -dioxime should have a configuration such that there is less possibility of the dioxime itself possessing a co-ordinated structure; it should be represented by (XI), which is the configuration assigned to it by Meisenheimer (*loc. cit.*). The γ -dioxime forms a nickel complex (Atack, J., 1913, **103**, 1317), but it is of quite different constitution from that of the α -dioxime and cannot be formed by a reaction of mechanism similar to that outlined above.

EXPERIMENTAL.

The blue colour produced in the presence of ferrous iron (Table I) was observed on shaking the oxime with aqueous ferrous sulphate and adding dilute caustic soda solution. In all cases, on shaking with benzene, the colour passed into the benzene; all the colorations were destroyed on heating, except that given by oximinoacetylacetone.

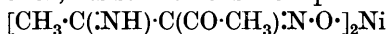
Iron was estimated as ferric oxide, and cobalt as the sulphate. The nickel compounds were very explosive if heated in a crucible with nitric acid; they were decomposed by heating in a glass tube in a stream of oxygen; the residue of nickel oxide and some metallic nickel, probably produced by the decomposition of nickel carbonyl, was treated with nitric acid and weighed as nickel oxide. Copper was estimated iodometrically after the complex had been treated with nitric and sulphuric acids.

Oximinoacetone was prepared from ethyl acetoacetate by Ceresole's modification of Meyer and Zublin's method (Charrier, *Centr.*, 1907, II, 1231). No compounds were obtained on treatment with a

solution of cobalt or nickel acetate or on the further addition of ammonia. Ill-defined compounds were obtained, if caustic soda was present, after 1 hour's heating or a fortnight's keeping (Found : Ni, 26.4. R_2Ni requires Ni, 25.4%. Found : Co, 26.1, 24.6, 26.2. R_2Co requires Co, 25.5%). No conclusive results were obtained with copper acetate, although there were indications of the formation of an unstable complex.

Oximinoacetylacetone (Wolff, *Annalen*, 1902, **325**, 139) (1.3 to 3 mols.) in warm aqueous solution was mixed with aqueous cobalt acetate (1 mol.). The reddish-orange precipitate was washed with water and cold alcohol (Found : Co, 13.2, 13.3; *M*, in benzene, 406. R_3Co requires Co, 13.3%; *M*, 443). The complex is readily soluble in benzene and soluble in alcohol. Ponzio (*loc. cit.*) obtained a compound R_2Co by this method.

An alcoholic solution of the oxime, on mixing with an aqueous ammoniacal solution of nickel acetate, gave a green precipitate, rapidly changing to reddish-brown. This was digested with hot water and alcohol; its structure is most probably



(Found : C, 38.3; H, 4.5; N, 17.5; Ni, 19.0; *M*, in naphthalene, 305. Calc. : C, 38.4; H, 4.5; N, 17.9; Ni, 18.8%; *M*, 310). The initial green precipitate contains 23.0% of Ni and is probably $CH_3 \cdot C(NH) \cdot C(CO \cdot CH_3) \cdot N \cdot O \cdot Ni \cdot O \cdot CO \cdot CH_3$ (Calc. : Ni, 23.1%).

The oxime and copper acetate (1 or 0.5 mol.) in aqueous solution gave a green compound (Found : Cu, 24.0, 24.3%), probably



(Calc. : Cu, 23.7%); it decomposed on heating. Ponzio's olive-green compound R_2Cu could not be prepared by the above procedure.

Oximinobenzoylacetone (Wolff, *loc. cit.*). Addition of aqueous cobalt acetate (1 mol.) to an alcoholic solution of the oxime (2 or 3 mols.) gave in the presence of a little ammonia a yellow compound, which was digested with hot water and alcohol (Found : C, 57.0; H, 4.1; N, 6.8; Co, 9.4, 9.35; *M*, in benzene, 540. R_3Co requires C, 57.2; H, 3.8; N, 6.7; Co, 9.4%; *M*, 629). Here again Ponzio describes a cobaltous compound. No complex could be obtained containing nickel, but with an aqueous solution of copper acetate the oxime gave a green precipitate, which was digested with hot alcohol (Found : Cu, 23.2, 23.4. $R \cdot CuOH$ requires Cu, 23.5%).

Ethyl oximinoacetoacetate (Boullanger, *Bull. Soc. chim.*, 1905, **33**, 560), dissolved in dilute ammonia and mixed with aqueous cobalt acetate, gave a rather unstable, red compound, which was washed with cold water (it is decomposed by hot water) (Found : Co, 11.8, 11.6; *M*, in benzene, 530, 553. R_3Co requires Co, 11.1%; *M*, 533).

With nickel acetate in aqueous solution the oxime gave on addition of ammonia, followed by boiling, a yellow complex containing ammonia. The yield corresponded to one-fifth of the oxime taken, the remainder being recovered unchanged. The complex is probably similar in structure to that obtained from oximinoacetylacetone (Found: C, 38.5; H, 4.7; N, 14.7; Ni, 15.9; *M*, in nitrobenzene, 386. Calc.: C, 38.65; H, 4.8; N, 15.0; Ni, 15.7%; *M*, 373). It is decomposed by dilute sulphuric acid and is somewhat soluble in alcohol and in aqueous ammonia.

An alcoholic solution of the oxime gave with aqueous copper acetate a green precipitate, which was washed with hot water and alcohol (Found: Cu, 24.7, 24.5, 24.4; H₂O, 7.1. R·Cu·OH, H₂O requires Cu, 24.7; H₂O, 7.0%). On drying at 85–90° or in a desiccator the anhydrous compound, which is hygroscopic, was obtained (Found: Cu, 26.8, 26.1. Calc.: Cu, 26.5%). The compound explodes at 100–110° and is insoluble in naphthalene, benzene, and tetrahydronaphthalene.

Oximinoacetophenone (Claisen, *Ber.*, 1887, 20, 2194). In aqueous solution with ferrous sulphate and ammonium acetate a stable, blue precipitate was formed which was purified as before and dried at 60° (Found: C, 54.2; H, 3.6; N, 7.6; Fe, 16.15, 15.9. R₂Fe requires C, 54.6; H, 3.5; N, 8.0; Fe, 15.9%). The compound is hygroscopic and is insoluble in benzene; it appears to decompose when dissolved in molten naphthalene.

The oxime (3 mols.) and cobalt acetate (1 mol.) in aqueous solution gave a third of the theoretical yield of a brownish-yellow precipitate, which, after washing, was dried at 100° (Found: C, 57.6; H, 3.8; N, 8.0, 7.8; Co, 11.85, 11.4; *M*, in nitrobenzene, 534. R₃Co requires C, 57.25; H, 3.6; N, 8.35; Co, 11.7%; *M*, 503). If the proportion of oxime to salt is 2:1, indeterminate compounds containing a higher percentage of cobalt are obtained.

With aqueous solutions of nickel acetate, indeterminate, dull green compounds were obtained, very soluble in alcohol and only slightly soluble in benzene. They are much more explosive than any of the other nickel compounds and are best decomposed by heating them in a stream of air. They char below 100° and possibly have the constitution R·Ni·O·CO·CH₃.

Oximinomalonanilide (Whiteley, *loc. cit.*). The compound R₂Fe (Whiteley, *loc. cit.*) was prepared (Found: C, 57.6; H, 3.9; N, 13.4; Fe, 9.2, 9.05. Calc.: C, 58.1; H, 3.9; N, 13.55; Fe, 9.0%). The complex is insoluble in benzene.

Compounds with cobalt (i; R₂Co, buff), nickel (ii; R₂Ni, buff), and copper (iii; R₂Cu, green) were obtained from the corresponding acetates and washed with hot water and alcohol [Found (i): C,

57.8; H, 4.1; N, 13.4; Co, 9.55, 9.5. Calc.: C, 57.8; H, 3.85; N, 13.5; Co, 9.5%. Found (ii): C, 57.4; H, 4.0; N, 12.9; Ni, 9.5, 9.15. Calc.: C, 57.8; H, 3.8; N, 13.5; Ni, 9.4%. Found (iii): C, 57.1; H, 3.95; N, 13.1; Cu, 10.0, 10.2. Calc.: C, 57.4; H, 3.8; N, 13.4; Cu, 10.1%. Molecular-weight determinations were untrustworthy because of the small solubility of the compounds in suitable solvents; in naphthalene, in which they dissolve slowly at 150—200°, the cobalt compound showed a molecular weight roughly double that required for R_2Co , and the nickel compound one of 589 (calc. for R_2Ni , 620).

α-Benzilmonoxime (von Auwers and Siegfeld, *Ber.*, 1893, **26**, 791). The cobalt compound has been described by Tschugaev (*loc. cit.*) and Ponzio; it can be obtained in better yield by adding a little ammonia to the solution. Its molecular weight in nitrobenzene is 690 (calc., 731). With nickel acetate in the presence of excess caustic potash, indefinite, green compounds were obtained containing from 14.2 to 16.6% of the metal; they were soluble in pyridine, benzene and tetrahydronaphthalene, but not in alcohol. The oxime in alcohol gave with aqueous copper acetate a green precipitate containing 21.2% of Cu (calc. for $R \cdot CuOH$, 20.9%).

Methyl α-oximinoethyl ketone (Diels and Jost, *Ber.*, 1902, **35**, 3292). No definite compounds with the metals investigated could be obtained, although there were indications of complex formation with copper.

Ethyloximinobenzoylacetate (Wolff, *Ber.*, 1903, **36**, 3614). No blue colour with alkaline ferrous solution was observed—a result in disagreement with that of Whiteley (*loc. cit.*), but it is possible that her sample was contaminated with oximinoacetophenone, since it was prepared by Perkin's method (J., 1885, **47**, 244).

Ethyloximinomalonate was prepared by Bouveault and Wahl's method (*Bull. Soc. chim.*, 1903, **29**, 961).

β-Benzilmonoxime was prepared by the method of von Auwers and Siegfeld (*loc. cit.*). No indications could be found of metallic complex formation with any of the last three oximes.

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