CCCLXXXV.—*The Configurations of the Aldoximes.*

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At the present time configurations are allotted to a pair of geometrically isomeric aldoximes on the following basis :—an oxime whose acetyl derivative on alkaline hydrolysis regenerates the original oxime is said to have the configuration (I), while if the product of the action of alkali is the nitrile $R \cdot CN$ or the acid $R \cdot CO_2H$, the configuration is said to be (II). These on the convention of Brady and Bishop (J., 1925, **127**, 1357) are respectively the α- and β-configurations.

$$\text{(I.)} \quad \underset{\text{NOH}}{R \cdot \overset{\textstyle |}{\underset{\textstyle |}{C}} H} \qquad\qquad \underset{\text{HON}}{R \cdot \overset{\textstyle |}{\underset{\textstyle |}{C}} H} \quad \text{(II.)}$$

The evidence upon which this view is based is not extensive and the configurations of the aldoximes are known with less certainty than are those of the ketoximes. The more important points of the evidence are the study of the optical properties by von Auwers and Ottens (*Ber.*, 1924, **57**, 446), the investigation of the action of alkalis on the isomeric 2-chloro-5-nitrobenzaldoximes by Brady and Bishop (*loc. cit.*), and the properties of salicylaldoximes (Brady, this vol., p. 105). None of these is conclusive if taken alone; the deduction from the optical properties depends upon the assumption that in geometrical isomerism arising from the arrangement of the groups attached to the system $>C:N-$ the optical properties of the isomerides will differ in the same direction as do those of compounds where the isomerism arises from the arrangement about the group $>C:C<$ or about a saturated carbon ring. The second piece of evidence is perhaps stronger, but is somewhat invalidated by the fact that in the splitting off of hydrogen chloride from one of the isomeric oximes the product was not an *iso*oxazole but a hydroxy-nitrile, and there is no proof that a ring has been formed as a stage of the reaction ; if this stage does not exist, the argument loses much of its force. Taken together the three pieces of evidence are more convincing, but it seemed desirable to seek in a new direction for fresh evidence.

The configurations of two isomeric oximino-ketones, such as the benzilmonoximes, are known with a reasonable degree of certainty (see, *inter alia*, Taylor, this vol., p. 2018).   One marked distinction between such isomerides is that the α-form (III) readily gives a series of co-ordination complexes with metals, whereas the β-form (IV) gives none, or else gives them much less readily and in doing so is converted into the α-form.   This distinction appears to be general for all oximes of the type, and the compositions and characteristics of the complexes obtained from such α-oximes are, in general, the same whatever the nature of the groups R_1 and R_2.

$$R_1 \cdot C \!\!-\!\! C \cdot R_2 \qquad\qquad R_1 \cdot C \!\!-\!\!\!-\!\! C \cdot R_2$$
$$\text{(III.)} \quad\ \ O \quad \text{NOH} \qquad\qquad\quad O \quad\ \ \text{HON} \quad \text{(IV.)}$$

If it were possible to obtain the two isomeric forms of an aldoxime in which an atom capable of forming a co-ordinate link with a metal was situated with respect to the oxime group in exactly the same way as the oxygen atom of the carbonyl group is situated with respect to the oxime group in the benzilmonoximes, the formation of metallic complexes by one oxime and the failure to obtain them from the other would justify the conclusion that the former oxime has a stereochemical configuration similar to that of α-benzilmonoxime and the latter has one similar to that of β-benzilmonoxime.   A study of the behaviour of their acetyl derivatives towards alkalis would then provide fresh evidence as to the *syn-* or *anti-*elimination of acetic acid in the case of the nitrile-forming (β) aldoxime, and the con-figuration of all aldoximes would be known with greater certainty.

No oxime having the suitable structure and occurring in two geometrically isomeric forms is known.   Some preliminary experi-ments were made with the two furfuraldoximes; one of these was found to give metallic complexes and the other not, but it soon became clear that the complexes formed were in no way similar in structure to those given by α-benzilmonoxime.   One marked characteristic of oximes of type (III) is that they form with ferrous iron a blue compound soluble in benzene, but form no ferric complex (Whiteley, J., 1903, **83**, 24; Taylor and Ewbank, J., 1926, 2818). The complex-forming furfuraldoxime (β, m. p. 91°), however, forms no ferrous complex, but gives a deep red coloration with ferric solutions; further its cobalt complex is entirely unlike that of α-benzilmonoxime.   The complexes obtained resemble much more closely those formed by β-benzaldoxime which have been described by Hieber and Leutert (*Ber.*, 1927, **60**, 2296), and it was clear that the oxygen atom of the furan ring was not entering into the complex formation.   This is not surprising in view of such facts as the extremely feeble basicity of the nitrogen atom in the pyrrole system.

The desired oximes could be found in the oximes of quinoline-2-aldehyde (V and VI), since the work of Tschugaev (*Ber.*, 1906, **39**, 3382) and of Emmert and Diehl (*Ber.*, 1929, **62**, 1738) shows clearly that the nitrogen atom is capable of forming co-ordinate links with metals. Unfortunately all attempts to obtain the two geometrically isomeric forms of this oxime have been unsuccessful; only one form seems to exist.

This oxime, however, forms a series of metallic complexes which are analogous with those of α-benzilmonoxime : there is the very characteristic blue ferrous compound; there is no ferric compound; it gives a typical grass-green copper complex and a cobalt complex, R_3Co, whose physical properties closely resemble those of the complexes from the benzilmonoxime. Hence there is little doubt that the configuration of this oxime is similar to that of α-benzilmonoxime and that it is (V) and not (VI). Now alkaline hydrolysis of the acetyl derivative of this oxime has been found to regenerate the oxime unchanged; on the convention of Brady and Bishop it is an α-oxime. These facts provide strong evidence to support the view that the original assumption of Hantzsch, that an acetylaldoxime loses acetic acid under the action of alkalis if the hydrogen atom and the acetoxy-group are in the *syn*-position to one another, is erroneous, a deduction which is in agreement with that made from the three pieces of evidence already in existence which have been discussed above.

The failure to obtain the second stereoisomeric quinoline-2-aldoxime hardly weakens the force of the argument used here unless the assumption is made that in solution the oxime is a mixture of the two forms and that the metallic complexes are derived from one of these, while the acetyl compound is derived from the other. Since there was no sign of a second form under any conditions, such an assumption seems extremely improbable. The only other possibility would be that the oxime is really a β-oxime, but on acetylation gives the α-acetyloxime; this would seem to be excluded by the fact that hydrolysis by sodium carbonate regenerates the same and not a different oxime.

EXPERIMENTAL.

The methods of analysis for the metallic complexes were those described by Taylor and Ewbank (J., 1926, 2818). All temperatures are corrected for the error of the emergent stem.

(1) *The Furfuraldoximes.*—The α- and β-oximes were prepared as

described by Brady and Goldstein (J., 1927, 1961). No indications of metallic complex formation with cobalt, nickel, copper, ferrous or ferric iron could be obtained from the α-oxime.

The β-oxime in alcoholic solution with ferric chloride gives a red coloration which fades on standing, but no coloration with ferrous sulphate and sodium hydroxide solutions. If aqueous copper acetate is added to the alcoholic solution of the oxime, a dark green copper complex is precipitated; for analysis it was well washed with alcohol and hot water (Found : Cu, 21·9, 22·3; N, 6·5%). These figures correspond to no simple derivative, but resemble those obtained by Hieber and Leutert (*loc. cit.*) for the copper derivative of β-benzaldoxime.

No nickel complex could be obtained, but cobalt acetate gave a snuff-coloured complex which explodes above 200°. It is soluble in alcohol, chloroform, benzene, acetone and pyridine, but could not be recrystallised. Unlike the cobalt complex of α-benzilmonoxime it is decomposed by hot dilute mineral acids; it is stable to alkalis. It was very difficult to purify the complex; its analysis seems to indicate the formula R_2Co (Found : Co, 20·6; N, 9·7. Calc. : Co, 21·1; N, 10·0%).

(2) *Quinoline-2-aldoxime.*—o-Aminobenzaldehyde (Muller, D.R.-P. 418497) and oximinoacetone (Charrier, *Gazzetta*, 1907, **37**, 145) were condensed together according to the method of Pfitzinger (*J. pr. Chem.*, 1902, **66**, 263). The product was recrystallised twice from alcohol and once from benzene, m. p. 188°.

An acetyl derivative has been described by Pfitzinger; his observations could not be repeated and from the melting point that he records there is little doubt that his conditions of treatment were too vigorous and that his acetyl compound is the dehydration product, quinaldinonitrile. The oxime can be acetylated by gently warming it with excess of acetic anhydride and then diluting the solution with aqueous sodium carbonate, or more conveniently by the action of acetyl chloride in benzene solution in the presence of a little pyridine. *Acetylquinoline-2-aldoxime* forms colourless needles, m. p. 128—130° (decomp.), from benzene–ligroin (Found : C, 67·0; H, 4·7. $C_{12}H_{10}O_2N_2$ requires C, 67·3; H, 4·7%). When it was boiled for 3 hours with dilute sodium carbonate solution, a crude product resulted, m. p. 184—185°, which after recrystallisation from alcohol was identified by m. p. and mixed m. p. as the original oxime.

The oxime gives with aqueous ferrous sulphate and sodium hydroxide a blue precipitate which is rapidly oxidised in the air with separation of ferric hydroxide; if the oxime is dissolved in aqueous-alcoholic sodium hydroxide, addition of benzene, followed

by that of ferrous sulphate, gives a blue coloration in the benzene layer which fades on standing.

The *cobalt* complex separated slowly as dark red crystals from an aqueous-alcoholic solution containing the oxime, and cobalt and ammonium acetates; it is sparingly soluble in benzene (Found : Co, 10·0. R_3Co requires Co, 10·3%).   With cupric solutions in the presence of ammonium acetate, the alcoholic solution of the oximes gives a grass-green precipitate of the copper complex similar in appearance and properties to that of α-benzilmonoxime.

Repeated attempts were made to convert the oxime into its stereoisomeric form by means of the ordinary hydrogen chloride method, the action of sulphuric acid (Brady and Whitehead, J., 1927, 2933), and the action of ultra-violet light on the alcoholic solution contained in a quartz vessel (Stoermer, *Ber.*, 1911, **44**, 667; Brady and McHugh, J., 1924, **125**, 547).   In every case the oxime recovered was identical with that described above, and there was no sign that any conversion had taken place.

The So-called Metallic Derivatives of β-*Benzilmonoxime* (Note by T. W. J. T.).—Pfeiffer and Richarz (*Ber.*, 1928, **61**, 106) obtained a cobalt complex by allowing β-benzilmonoxime to stand for a long time with a solution of cobalt acetate; this they describe as a complex of the β-oxime (compare Gmelin's " Handbuch," 8th edn, Kobalt B 309).   As has already been pointed out, the stability of these complexes is so great that it is impossible to regenerate the oxime from them and determine its configuration.   Experiments with the copper derivative, which is easily decomposed, indicate, however, that during the formation of metallic complexes by the β-oxime the configuration is changed and the complexes are really those of the α-oxime.   β-Benzilmonoxime in alcoholic solution with copper acetate gives very slowly a green precipitate, the formation of which is accelerated by the presence of ammonia.   From this complex by the action of dilute mineral acids the α-oxime is obtained.   Now, since the β-oxime is the more stable of the two, and is never converted into the α-form by any direct method, this result must mean that the conversion has taken place during the formation of the metallic complex and that the complex is derived from the α-form.   This view is confirmed by the fact that the formation of the cobalt complex from the β-form, which is very slow, is accelerated by illumination with ultra-violet light, a procedure which is known to convert the more stable form of a ketoxime into the less stable form (Stoermer, *loc. cit.*).

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Summary.

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Quinoline-2-aldoxime forms a series of metallic derivatives which are of the same type as those given by α-benzilmonoxime.   It is thus

highly probable that the configuration of the oxime group with respect to the co-ordinating atom (nitrogen in the one case and oxygen in the other) is the same in the two compounds.   Since the configuration of α-benzilmonoxime is known with reasonable certainty, that of the aldoxime can be taken as established.   The configuration so reached indicates that the elimination of acetic acid from an acetylaldoxime with nitrile formation is a reaction involving groups in the *anti*-position to one another, and supports the views as to the configurations of aldoximes which have recently been put forward.

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