CCLXVIII.—*The Isomerism of the Oximes. Part VI.*
p-Dimethylaminobenzaldoxime.

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ALTHOUGH *p*-dimethylaminobenzaldoxime, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}:\text{NOH}$, has been described (Knofler and Boessneck, *Ber.*, 1887, **20**, 3195) it has not been studied from the point of view of the Hantzsch-Werner hypothesis.

As this compound contains no possibly labile hydrogen atom in the para-substituting group it would be expected to exist in the two isomeric forms, *anti* and *syn* (compare Brady and Dunn, this vol., p. 824); indeed, as the basicity of the substituting group seems to influence the stability of the two isomerides, it seemed possible that the oxime prepared from *p*-dimethylaminobenzaldehyde by the usual methods would be a *syn*-derivative, or, if not, the *syn*-isomeride would be readily obtained from it, and would be more stable than is usually the case with these compounds. Additional interest is added by the fact that no benzaldoxime containing a basic group as a substituent has been obtained in two isomeric forms; indeed, compounds of this class have been little studied.

As regards the preparation of a *syn*-derivative of this compound the authors' expectations have not been fulfilled, and *p*-dimethyl-

aminobenzaldoxime must be added to the considerable number of aromatic aldoximes that appear to exist only in one form.

The oxime as ordinarily prepared by the action of hydroxylamine hydrochloride on the aldehyde in the presence of sodium carbonate has undoubtedly the *anti*-configuration, since it yields an acetyl derivative and not a nitrile on treatment with acetic anhydride and sodium carbonate solution. This acetyl derivative yields the original oxime on hydrolysis with alkalis. Dry hydrogen chloride, when passed into a dry ether or chloroform solution of the oxime, precipitates a hydrochloride which regenerates the original oxime on treatment with sodium carbonate solution. Under the above conditions the oxime unites with only one molecule of hydrogen chloride, and it was possible that the acid was attached to the dimethylamino- and not to the oximino-group, a fact which would account for the failure to obtain a *syn*-oxime. Support is lent to this contingency by the behaviour of the *O*-methyl ether of *p*-dimethylaminobenzaldoxime, which readily yields a hydrochloride under similar conditions, differing in this respect from the *O*-methyl ethers of oximes which contain no basic substituent in the benzene ring. On the other hand it is noteworthy that the hydrochloride of the *O*-methyl ether, in which the hydrogen chloride is undoubtedly attached to the dimethylamino-group, does not evolve hydrogen chloride at its melting point, whereas the hydrochloride obtained from *p*-dimethylaminobenzaldoxime resembles the hydrochlorides of other oximes and suffers decomposition at its melting point owing to loss of hydrogen chloride.

An attempt was made to overcome this difficulty by preparing the hydrochloride directly from the aldehyde and hydroxylamine hydrochloride in the absence of alkali (Beckmann, *Annalen*, 1909, 365, 201):

This method yielded, however, a hydrochloride melting at the same temperature as the hydrochloride obtained from the oxime, and this hydrochloride gave the *anti*-oxime on treatment with sodium carbonate solution. It is possible that by this method the hydrochloride, $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{NOH}, \text{HCl}$, is first formed which is then decomposed with the formation of the hydrochloride,

this seems, however, unlikely, although the basic nature of the oximino-group is much less marked than that of the dimethylamino-group.

Diphenylcarbamyl-p-dimethylaminobenzaldoxime has been prepared, and like other diphenylcarbamyl derivatives of the aromatic

aldoximes has the *syn*-configuration, yielding on hydrolysis diphenylamine and *p*-dimethylaminobenzonitrile (compare Brady and Dunn, T., 1913, 103, 1613):

Carbanilino-p-dimethylaminobenzaldoxime,

obtained by the action of phenylcarbimide on the oxime, is of especial interest as it resembles carbanilino-*m*-nitrobenzaldoxime in that the compound first obtained, on boiling with alcohol, changes to an isomeric compound of higher melting point, which seems still to be a carbanilino-oxime. Up to the present there has been no satisfactory explanation suggested for the existence of the three carbanilino-derivatives obtained from the *m*-nitrobenzaldoximes, two from the *anti*- and one from the *syn*-compound. The authors have been engaged for some time on this question, which will form the subject of their next communication; for the present it will be sufficient to state that the carbanilino-derivative of *p*-dimethylaminobenzaldoxime as prepared by the action of phenylcarbimide on the *anti*-oxime is the *syn*-derivative, and gives on hydrolysis *p*-dimethylaminobenzonitrile and aniline, whereas the product of higher melting point obtained by boiling this compound with alcohol is the *anti*-compound, and on hydrolysis gives aniline and *p*-dimethylaminobenzaldoxime as its main decomposition products:

EXPERIMENTAL.

The *p*-dimethylaminobenzaldoxime employed was prepared by Knofer and Boessneck's method (*loc. cit.*) by boiling a mixture of the aldehyde, hydroxylamine hydrochloride, and anhydrous sodium carbonate in equivalent proportions with alcohol under a reflux condenser for three hours, and pouring the product into water. As, however, in the authors' experiments the oxime separated as a

crystalline solid on stirring the aqueous emulsion, it was removed by filtration instead of extraction with ether. After recrystallisation from alcohol the oxime melted at 144° .

Acetyl-p-dimethylaminobenzantialdoxime.—The oxime was dissolved in acetic anhydride, warming very gently, and left for fifteen minutes. A bright green solution was thus obtained (it may be noted here that this colour is very generally met with in working with dimethylaminobenzaldoxime, and is probably due to a trace of some oxidation product). The excess of acetic anhydride was decomposed by shaking with sodium carbonate solution, when the acetyl derivative was obtained as a mass of pale green crystals, which separate from dilute alcohol in colourless needles melting at 108° :

0.1569 gave 18.2 c.c. N_2 at 11° and 746 mm. $N = 13.7$.

$C_{11}H_{14}O_2N_2$ requires $N = 13.6$ per cent.

This compound was boiled for ten minutes with 2*N*-sodium hydroxide when it passed completely into solution, the solution was acidified with dilute sulphuric acid, and made faintly alkaline with sodium carbonate; the solid separating proved to be *p*-dimethylaminobenzaldoxime, and acetic acid could be detected in the mother liquor. The formation of this acetyl derivative and its hydrolysis establish the *anti*-configuration of the oxime.

Action of Hydrogen Chloride on p-Dimethylaminobenzantialdoxime.

The oxime was dissolved in anhydrous ether, and dry hydrogen chloride passed into the solution; a yellow, pasty mass was first precipitated, which rapidly became white and crystalline. The hydrochloride obtained in this way melted and decomposed at 170° :

0.3078 required 15.2 c.c. $N/10\text{-AgNO}_3$. $Cl = 17.5$.

$C_9H_{12}ON_2 \cdot HCl$ requires $Cl = 17.7$ per cent.

When decomposed with sodium carbonate solution the original oxime was obtained, the crude product melting at 140° , and after recrystallisation from cold acetone and water at 144° , moreover, admixture with this substance did not depress the melting point of *p*-dimethylaminobenzantialdoxime.

The action of dry hydrogen chloride on a solution of the oxime in dry chloroform was also investigated, but a hydrochloride of the same melting point was obtained, and this also regenerated the original oxime on treatment with sodium carbonate solution. The hydrochloride was also prepared according to Beckmann's method (*loc. cit.*). Equivalent quantities of the aldehyde and hydroxylamine hydrochloride were heated in alcohol for three hours at

50—55°. A copious precipitate formed, which proved to be the same hydrochloride as previously obtained, melting at 170° and giving *p*-dimethylaminobenzantialdoxime on treatment with sodium carbonate solution.

O-Methyl Ether of p-Dimethylaminobenzantialdoxime.—This was prepared in the usual way by boiling on the water-bath for fifteen minutes an alcoholic solution of the oxime with an equimolecular amount of sodium ethoxide and a slight excess of methyl iodide. The green product was poured into water and extracted with ether, the ethereal solution being shaken with sodium hydroxide solution to remove unaltered oxime, washed with water, and evaporated. A pale amber-coloured oil was thus obtained, which when cooled in ice set to a greenish-white, crystalline mass. On recrystallisation from dilute alcohol the ether separates in colourless plates with a slight fragrant odour, and melting at 69°:

0.1638 gave 22.2 c.c. N_2 at 17° and 751 mm. $N=15.8$.

$C_{10}H_{14}ON_2$ requires $N=15.7$ per cent.

Hydrochloride of the O-Methyl Ether of p-Dimethylaminobenzantialdoxime.

The *O*-methyl ether was dissolved in dry ether, and dry hydrogen chloride was passed into the solution. A viscid substance was precipitated, which soon became crystalline. This hydrochloride melts at 118—122°, but, unlike the hydrochlorides of the oximes, does not evolve hydrogen chloride at its melting point:

0.2134 required 10.0 c.c. $N/10\text{-AgNO}_3$. $Cl=16.6$.

$C_{10}H_{14}ON_2 \cdot HCl$ requires $Cl=16.5$ per cent.

Decomposition of the hydrochloride with sodium carbonate solution regenerated the *O*-methyl ether.

Diphenylcarbamyl-p-dimethylaminobenzsynaldoxime.

This compound was prepared by dissolving the oxime in alcohol and adding one equivalent of sodium in alcohol and one equivalent of diphenylcarbamyl chloride. On adding the latter a voluminous, pasty mass was formed, which was well shaken, heated on the water-bath for ten minutes, cooled, filtered, and washed with water. This substance is almost insoluble in hot alcohol, but is readily soluble in chloroform, and may be recrystallised from a mixture of this solvent and light petroleum, when it separates in small, colourless needles, melting and decomposing at 171°:

0.2930 gave 29.0 c.c. N_2 at 16° and 751 mm. $N=11.5$.

$C_{22}H_{21}O_2N_3$ requires $N=11.7$ per cent.

Diphenylcarbamyl-*p*-dimethylaminobenzsynaldoxime was hydro-

lysed by boiling with alcoholic sodium hydroxide for two hours. The sodium carbonate which separated was filtered off, and the solution diluted considerably with water and filtered. The solid so obtained was washed repeatedly with very dilute hydrochloric acid, and the residue recrystallised from alcohol; this proved to be diphenylamine. The washings were extracted with ether to remove diphenylamine, then made alkaline, and again extracted with ether. After removal of the ether the residue was crystallised from alcohol, and found to be dimethylaminobenzonitrile. From the first filtrate above a small quantity of dimethylaminobenzaldoxime was obtained by extracting the alkaline solution with ether to remove diphenylamine, etc., acidifying, making faintly alkaline with sodium carbonate, and again extracting with ether. This ethereal solution yielded a small quantity of solid, which was recrystallised from alcohol and shown to be the oxime.

Carbanilino-p-dimethylaminobenzsynaldoxime.—A solution of *p*-dimethylaminobenzaldoxime in ether was treated with an equimolecular amount of phenylcarbimide. After a few moments pale brown, shining plates began to separate; the solution was left for twenty-four hours and then filtered. The solid was recrystallised from cold acetone and water, from which solution it separated in sulphur-yellow plates, melting and decomposing at 117°. A further recrystallisation from alcohol removed most of the colour, but did not raise the melting point:

0.2021 gave 25.2 c.c. N_2 at 16° and 761 mm. $N = 14.7$.

$C_{16}H_{17}O_2N_3$ requires $N = 14.8$ per cent.

This carbanilino-derivative was hydrolysed by boiling with 30 per cent. sodium hydroxide solution for five minutes. Aniline was easily recognised in the steam, whilst oily drops remained suspended in the liquid. These on cooling set to a solid, which was crystallised from dilute alcohol, and melted at 75°; a mixture with *p*-dimethylaminobenzaldehyde (m. p. 73°) melted at 55°, and with *p*-dimethylaminobenzonitrile (m. p. 75–76°) at 75°. The mother liquor from the hydrolysis was acidified, and then made faintly alkaline with sodium carbonate solution, when, after some time, a small quantity of substance crystallised out, which proved to be *p*-dimethylaminobenzaldoxime, formed probably by the conversion of a little of the *syn*- into the *anti*-carbanilino-compound during the warming and the subsequent hydrolysis of the latter.

A similar decomposition takes place if the carbanilino-derivative is boiled with alcohol alone for some time. Carbanilino-*p*-dimethylaminobenzsynaldoxime was boiled with alcohol under a reflux condenser for twenty-four hours; the solution so obtained was diluted with about half its volume of water and cooled. The crystalline

precipitate which formed proved to be diphenylcarbamide (m. p. 232°). The mother liquor was diluted, and the milky liquid acidified with dilute hydrochloric acid; silky needles which remained suspended in the solution were collected, and shown to be diphenylcarbamide. The filtrate was again made alkaline with sodium hydroxide, stirred, and set aside for some hours, when a quantity of dimethylaminobenzonitrile separated out. The mother liquor was acidified and made alkaline with sodium carbonate, and the solid separating was crystallised from alcohol, and proved to be dimethylaminobenzaldoxime.

In each of the above cases the primary products of the reaction may be regarded as *p*-dimethylaminobenzonitrile and the hypothetical phenylcarbamic acid; the latter in the presence of alkalis is decomposed into carbon dioxide and aniline, and in the absence of alkalis two molecules yield water, carbon dioxide, and diphenylcarbamide:

The much larger amount of oxime found as the result of prolonged boiling with alcohol is due to the conversion of most of the *syn*- into the *anti*-derivative, and the subsequent hydrolysis of that compound (see below).

Carbanilino-p-dimethylaminobenzaldoxime.—The freshly prepared *syn*-carbanilino-derivative described above was covered with alcohol and boiled under a reflux condenser for one hour. On cooling, carbanilino-*p*-dimethylaminobenzaldoxime crystallised in large, colourless plates, melting and decomposing at 152°:

0.2646 gave 32.4 c.c. N₂ at 13° and 768 mm. N = 14.9.

C₁₆H₁₇O₂N₃ requires N = 14.8 per cent.

This compound is also formed if the *syn*-carbanilino-derivative is kept for any length of time, there being formed simultaneously a small amount of aniline and dimethylaminobenzonitrile. Carbanilindimethylaminobenzaldoxime on boiling with 2*N*-sodium hydroxide passes almost completely into solution, no nitrile being formed; the solution on treatment in the usual way yields dimethylaminobenzaldoxime and aniline.

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