CLXXV.—*The Isomerism of the Oximes. Part I.
The Diphenylcarbamoyloximes.*

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THE action of phenylcarbimide on isomeric oximes has been studied by Goldschmidt and his collaborators (*Ber.*, 1889, **22**, 3112; 1890, **23**, 2136; 1891, **24**, 2546; 1893, **26**, 2087), by Beckmann (*Ber.*, 1890, **23**, 3321), and others.

In accordance with the Hantzsch-Werner hypothesis, the action has been represented as follows:

and

These compounds are readily decomposed by alkali hydroxides, the *anti*-compounds yielding aniline, carbon dioxide, and the *anti*-oxime, whilst the *syn*-compounds give aniline, carbon dioxide, a small quantity of diphenylcarbamide, the *syn*-oxime, and the nitrile.

In two cases three carbanilino-oximes, corresponding with one aldehyde, have been described, namely, two isomeric carbanilino-derivatives have been obtained from benzsynaldoxime and one from benzantialdoxime, whilst *m*-nitrobenzantialdoxime gives two carbanilino-oximes and *m*-nitrobenzsynaldoxime another.

There is at present no wholly satisfactory explanation of the existence of the third isomeride, and the authors hope in a subsequent communication to throw more light on this question. Conduché (*Ann. Chim. Phys.*, 1907, [viii], **12**, 533; 1908, [viii], **13**, 1), by the interaction of *isohydroxycarbamide* and aldehydes,

obtained the same compounds as by the action of *isocyanic acid* on the corresponding oximes.*.

Conduché represented the action thus :

He considered that his compounds were derivatives of the *syn*-oximes, as on treatment with hydrochloric acid the nitriles were obtained, although alkalis yielded the *anti*-oximes.

Beck and Hase (*Annalen*, 1907, **355**, 50) by the action of phenylhydroxycarbamide on *m*-nitrobenzaldehyde obtained the same compound as had been obtained previously by Goldschmidt (*loc. cit.*) by the action of phenylcarbimide on *m*-nitrobenzanti-aldoxime. As in this case the corresponding *syn*-derivative had been obtained, it was obvious that this compound could not have the *syn*-structure, so it was considered to have the constitution $\text{NO}_2 \cdot \text{C}_6\text{H}_5 \cdot \text{CH} \cdot \text{N} \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$.

It seemed unlikely that the unsubstituted hydroxycarbamide would behave differently as stated by Conduché, and it was with the object of elucidating this matter that the present investigation was undertaken.

When phenylcarbimide is condensed with the oximes, or the hydroxycarbamides with the aldehydes, there is a considerable rearrangement in the molecule, whilst by the action of diphenylcarbamyl chloride on the sodium salt of the oxime this could be avoided, and little doubt left as to the structure of the resulting diphenylcarbamyl derivative :

The authors have accordingly prepared by this method the diphenylcarbamyl derivatives of benzaldoxime and of the three nitrobenzaldoximes, and studied their properties.

It was found that identical products were obtained by the action of diphenylcarbamyl chloride on the sodium salts of both *anti*- and *syn*-oximes. In the case of the preparation from the *syn*-oximes, the reaction was carried out in the cold in dry non-aqueous solvents to avoid isomeric change as much as possible.

It has been shown (Goldschmidt, *Ber.*, 1895, **28**, 2013) that the formation of sodium salts from *syn*-oximes does not at once bring

* Conduché and Beck and Hase adopt Beckmann's *iso*-oxime formula, $\text{R} \cdot \text{CH} \cdot \text{NH}$,

for the *syn*-oximes. In this paper, to avoid confusion, the generally accepted terms *anti* and *syn* are used throughout, the *anti*- and *syn*-oximes corresponding with the α - and β -oximes of Beckmann and his followers.

about isomeric change into the *anti*-form, a result confirmed by the present authors in the case of *m*-nitrobenzsynaldoxime. The sodium salt from *o*-nitrobenzsynaldoxime mentioned in a previous communication (P., 1911, **27**, 239) as consisting mainly of "*anti*" salt had been obtained as an oil and left for several days to crystallise, during which time isomeric change had probably taken place. The subject of the salts of the oximes is, however, being further investigated.

The behaviour of the diphenylcarbamyI derivatives on treatment with alkalis pointed to their having the *syn*-configuration, and the authors have accordingly assigned to them the structural formula :

DiphenylcarbamyIbenzsynaldoxime, $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{N} \cdot \text{O} \cdot \text{CO} \cdot \text{N}(\text{C}_6\text{H}_5)_2$, on heating with alcoholic potassium hydroxide, is decomposed into diphenylamine, carbon dioxide, and benzonitrile.

In the case of the diphenylcarbamylnitrobenzsynaldoximes, it was found impossible to separate the nitrile from the other products of the reaction, but by heating for an hour with 2 per cent. alcoholic potassium hydroxide under reflux, these compounds were decomposed into carbon dioxide, diphenylamine, a small quantity of diphenylurethane, ammonia, and the corresponding acid, there being no evidence of the formation of oxime or aldehyde.

The production of diphenylurethane and the failure to obtain any trace of oxime lead the authors to consider that these compounds behave similarly to the acetyl derivatives of the *syn*-oximes, and that their decomposition may be represented thus :

It seems probable that the compounds obtained by Conduché from the aldehydes and hydroxycarbamide are not derivatives of the *syn*- but of the *anti*-oximes, especially in view of the production of *anti*-oxime and not of nitrile by the action of alkalis.

It is true that he obtained the nitriles on treatment of his compounds with hydrochloric acid, but the authors have been able to show that the carbanilino-derivatives of the *anti*-oximes where the isomeric *syn*-compounds are known yield with hydrochloric acid the corresponding benzoic acid, ammonium chloride, and

aniline hydrochloride, but no oxime, indicating the formation of nitrile and its subsequent hydrolysis.

The carbanilino-derivatives are more difficult to decompose than the unsubstituted carbamyl compounds, and the more vigorous treatment needed to decompose them with hydrochloric acid would account for the disappearance of the *syn*-oxime and nitrile obtained by Conduché from his compounds. It may be noted that the diphenylcarbamyloximes are still more difficult to decompose. The action of hydrochloric acid can be understood when it is realised that the *anti*-aldoximes are converted into the *syn*-aldoximes by excess of hydrochloric acid in aqueous solution (Dunstan and Thole, P., 1911, 27, 233), an observation repeated and confirmed by the authors in the case of benzaldoxime and *m*-nitrobenzaldoxime.

Conduché has prepared the same carbamyloxime from benzanti- and benzsyn-aldoxime, this being apparently the only case in which he investigated the action of isocyanic acid on both isomerides. He, however, treated the hydrochloride of the *syn*-oxime with an aqueous solution of potassium cyanate, under which conditions there are ample opportunities for isomeric change.*

In conclusion, the authors consider that their work, which is being continued, tends to confirm still further the Hantzsch-Werner hypothesis of the isomerism of the oximes.

EXPERIMENTAL.

Diphenylcarbamylobenzsynaldoxime.—Benzantialdoxime (5 grams) was treated with sufficient sodium (0.895 gram) dissolved in alcohol to form the sodium salt, and the alcohol evaporated. The sodium salt was suspended in dry chloroform, and an equivalent quantity of diphenylcarbamyl chloride (9.0 grams) added, and the mixture heated for four hours under reflux. The liquid was then filtered, the chloroform evaporated, and the residue crystallised from hot alcohol:

0.1964 gave 15.2 c.c. N_2 at 19° and 759 mm. $N=9.1$.

$C_{20}H_{16}O_2N_2$ requires $N=8.86$ per cent.

Diphenylcarbamylobenzsynaldoxime is obtained in this way as a white, crystalline solid, which melts over a range of about 10° according to the rate of heating, as do all the diphenylcarbamyloximes examined. By means of the Maquenne block, however, sharp and constant melting points could be obtained, and those given in this paper were determined by this method. The above compound melts on the Maquenne block at 163° .

* The authors hope to investigate the action of anhydrous isocyanic acid on the oximes and of carbamyl chloride on the sodium salts of the oximes.

The sodium salt of benzsynaldoxime was treated with diphenylcarbamyl chloride in dry ether in the cold for four days. The liquid was filtered, and the residue extracted with alcohol, from which crystals were obtained which proved to be identical with the compound described above.

Action of Alcoholic Potassium Hydroxide on Diphenylcarbamylbenzsynaldoxime.

The substance was heated under reflux for ten minutes with alcoholic potassium hydroxide, at the end of which time the liquid had a strong odour of benzonitrile. The alcohol was removed and the liquid filtered. The solid, after recrystallising, melted at 54° , and was diphenylamine. The filtrate was saturated with sulphur dioxide, to prevent benzaldehyde distilling should it have been formed, and distilled in a current of steam. The distillate still had a strong odour of benzonitrile. It was extracted with ether, and after evaporating off the ether an oil was left which, on boiling with potassium hydroxide, evolved ammonia, benzoic acid being recovered from the alkaline solution.

Preparation of the Sodium Salts of the Nitrobenzaldoximes.

It was found that the most convenient method for the preparation of the dry sodium salts of the nitrobenzaldoximes was to dissolve the oxime in much dry ether and add a slight excess of sodium ethoxide dissolved in the smallest possible quantity of alcohol. The solution was stirred vigorously for some minutes, when the sodium salt crystallised and could be easily collected. After being washed with dry ether and left on the filter for a few moments, the salt was quite dry.

Diphenylcarbamyl-p-nitrobenzsynaldoxime.—Equivalent quantities of diphenylcarbamyl chloride and of the sodium salt of *p*-nitrobenzantialdoxime were suspended in chloroform, and heated under reflux for four hours. The mixture was filtered, the chloroform evaporated, and the pale yellow residue of the carbamyl-oxime recrystallised from alcohol:

0.1386 gave 14.5 c.c. N_2 at 25° and 742 mm. $N=11.76$.

$C_{20}H_{15}O_4N_3$ requires $N=11.63$ per cent.

Diphenylcarbamyl-p-nitrobenzsynaldoxime forms colourless prisms melting at 174° .

Diphenylcarbamyl-m-nitrobenzsynaldoxime.—This compound may be obtained from *m*-nitrobenzantialdoxime in a similar way to the above. It has also been obtained by treating the sodium salt of *m*-nitrobenzsynaldoxime with diphenylcarbamyl chloride in

ethereal solution, the mixture being shaken for three hours. After filtering, the solid is washed with water and crystallised from alcohol:

0.1280 gave 13.1 c.c. N_2 at 21° and 743 mm. $N=11.68$.

$C_{20}H_{15}O_4N_3$ requires $N=11.63$ per cent.

Diphenylcarbamylo-nitrobenzsynaldoxime crystallises in colourless needles, melting at 175° .

Diphenylcarbamylo-o-nitrobenzsynaldoxime.—This was prepared in a similar way to the para-compound from the sodium salt of *o*-nitrobenzantialdoxime and diphenylcarbamylo chloride:

0.1444 gave 14.8 c.c. N_2 at 21° and 747 mm. $N=11.75$.

$C_{20}H_{15}O_4N_3$ requires $N=11.63$ per cent.

This compound crystallises in colourless needles, melting at 159° .

The diphenylcarbamylnitrobenzsynaldoximes all rapidly develop a yellow colour on exposure to light. They are soluble in hot alcohol, acetone, chloroform, benzene, or ethyl acetate, but insoluble or very sparingly soluble in water, cold alcohol, ether, or light petroleum.

Action of Alcoholic Potassium Hydroxide on the Diphenylcarbamylnitrobenzsynaldoximes.

The diphenylcarbamyloximes were heated with 2 per cent. alcoholic potassium hydroxide under reflux; at the end of half an hour, there was a plentiful evolution of ammonia. When the mixture had been gently boiling for an hour it was cooled, diluted, and filtered. The residue was washed with cold alcohol; from the alcoholic solution diphenylamine was isolated, and the substance insoluble in the cold alcohol proved to be diphenylurethane (m. p. 72°).

The alkaline filtrate was extracted with ether to remove traces of diphenylamine, etc., acidified, and again extracted with ether. After removing the ether and recrystallising the residue once from alcohol, the pure acid was obtained corresponding with the diphenylcarbamylnitrobenzsynaldoxime taken. This was identified by its melting point and the mixed melting point with the acid obtained by oxidising the corresponding nitrobenzaldehyde.

Action of Hydrochloric Acid on Carbanilino-p-nitrobenzantialdoxime.

Carbanilino-*p*-nitrobenzantialdoxime was heated for an hour with concentrated hydrochloric acid under reflux. The solution was diluted, made alkaline with potassium hydroxide, and filtered. On gently warming a portion of the alkaline liquid, there was a

copious evolution of ammonia, indicating the presence of an ammonium salt. The bulk of the alkaline liquid was extracted with ether to remove aniline, etc., acidified, and again extracted with ether. After removing the ether, a yellow solid remained, which, after recrystallising from alcohol, proved to be *p*-nitrobenzoic acid.

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