

XXXI.—*The Methylation of the Oximes of Benzil.*
*Part II. The Monomethyl Ethers of the Benzildioximes.**

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THE preparation of the monomethyl ethers of the benzildioximes was undertaken with a view to the study of their metallic complexes, which will be described in a subsequent paper. In addition it was hoped that it might be possible to prepare, through these compounds, the hitherto unknown dimethyl ethers of γ -benzildioxime and the *NN*-dimethyl- β -benzildioxime (Brady and Perry, J., 1925, **127**, 2874).

O-Methyl- α -benzilmonoxime (I) on oximation gives a mixture of *O*-monomethyl- α -benzildioxime (II) and α' -*O*-monomethyl- γ -benzildioxime (III). (The symbols α' and β' are used to indicate the oximino-group methylated in the γ -dioxime, α' being applied when the methylated hydroxyl group is vicinal and β' when it is remote from the phenyl group.)

α -Benzildioxime (IV) on monomethylation gives a mixture of the former compound (II) and *N*-monomethyl- α -benzildioxime (V). *O*-Monomethyl- α -benzildioxime (II) on further methylation yields *OO*-dimethyl- α -benzildioxime (VI) and *ON*-dimethyl- α -benzildioxime (VII). α' -Monomethyl- γ -benzildioxime (III) on further methylation gives *OO*-dimethyl- α -benzildioxime (VI) and *OO*-dimethyl- γ -benzildioxime (VIII), and *N*-monomethyl- α -benzildioxime (V) yields *ON*-dimethyl- α -benzildioxime (VII) and *NN*-dimethyl- α -benzildioxime (IX).

The dimethyl ethers of α -benzildioxime, described in Part I (Brady and Perry, *loc. cit.*), establish the configuration of the monomethyl ethers from which they can be prepared. *O*- and *N*-Ethers were distinguished by heating with hydriodic acid, methyl iodide and methylamine, respectively, being obtained. The configuration of α' -*O*-monomethyl- γ -benzildioxime will be discussed later.

O-Monomethyl- α -benzildioxime (II) was converted by boiling with aniline for 30 seconds into α' -*O*-monomethyl- γ -benzildioxime (III), the change being analogous to that of α -benzildioxime to β -benzildioxime under similar conditions (J., 1925, **127**, 2880); in the present case, however, brief treatment caused isomerisation of the unmethylated group only; more prolonged boiling with aniline or with hydrogen chloride in glacial acetic acid resulted in isomerisation of the methylated group also, giving *O*-monomethyl- β -benzildioxime (XII).

* The new configurations of Meisenheimer (*Ber.*, 1921, **54**, 3206) are used throughout this paper.

O-Methyl- β -benzilmonoxime (XI) does not react readily with hydroxylamine, it being necessary to heat it to 175–185° with hydroxylamine hydrochloride in alcohol; *O*-monomethyl- β -benzildioxime (XII) is then formed exclusively. If any of the β' -*O*-monomethyl- γ -benzildioxime (XVI) were formed, it would certainly undergo isomeric change under these conditions. The dichloride $\text{PhC}(\text{NOMe})\cdot\text{CCl}_2\text{Ph}$, which might react more readily, could not be prepared, since phosphorus pentachloride was without action on *O*-methyl- β -benzilmonoxime.

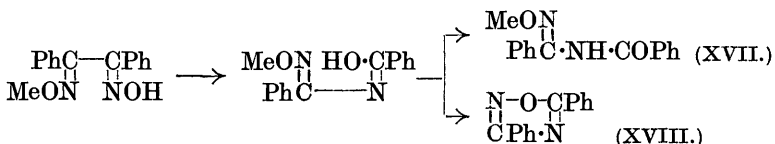
The monomethylation of β -benzildioxime (X) leads to the formation of *O*-monomethyl- β -benzildioxime (XII) and *N*-monomethyl- β -benzildioxime (XIII). *O*-Monomethyl- β -benzildioxime on further methylation gave *ON*- and *OO*-dimethyl- β -benzildioxime (XIV and XV), and *N*-monomethyl- β -benzildioxime gave *O*-methyl- β -benzilmonoxime (XI), formed probably by the hydrolysis of *ON*-dimethyl- β -benzildioxime.

From the monomethylation of γ -benzildioxime (XXII), only *N*-monomethyl- β -benzildioxime (XIII) could be isolated, isomeric change occurring. From the other liquid products of the reaction, no *O*- or *N*-monomethyl- γ -benzildioximes could be isolated.

When *N*-monomethyl- α -benzildioxime was boiled with aniline, the *N*-methyloximino-group was eliminated and replaced by the anil group, but if dimethylaniline was used, isomerisation occurred and *N*-monomethyl- β -benzildioxime was formed: this is the first example of such isomerisation of an *N*-ether.

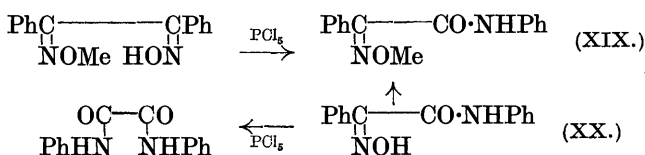
The results so far described are summarised in the diagram.

Unlike the *OO*-dimethyl ethers, the *O*-monomethyl ethers undergo the Beckmann rearrangement. *O*-Monomethyl- α -benzildioxime gives *N*-benzoyl-*O*-methylbenzamidoxime (XVII) at 0° and 3:5-diphenyl-1:2:4-oxadiazole (XVIII) at room temperature, methyl alcohol being eliminated in the latter case.

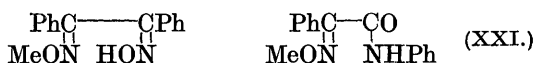


At room temperature, either the phosphorus pentachloride causes the isomerisation of the methylated oximino-group or *trans*-ring formation must take place; in the latter case, the usual explanation of salt formation between the two groups seems inadmissible, $\text{MeO} \cdot \text{N} \cdot \text{H} \cdot \text{O} \cdot \text{CPh}$, since *O*-methyl ethers are destitute of basic properties.

O-Monomethyl- β -benzildioxime in the Beckmann rearrangement gives β -*O*-methylphenylglyoxyylanilideoxime (XIX), which has been synthesised by the methylation of phenylglyoxyylanilideoxime (XX), whose orientation is known by its conversion into oxanilide in the Beckmann rearrangement.



α' -*O*-Monomethyl- γ -benzildioxime undergoes the Beckmann rearrangement with the formation of α -*O*-methylphenylglyoxyylanilideoxime (XXI).



It has not been possible to synthesise this compound, but the production of aniline by hydrolysis fixes the relative positions of hydroxyl and phenyl in the oximino-group and the formation of β -*O*-methylphenylglyoxyylanilideoxime (XIX) from *O*-monomethyl- β -benzildioxime eliminates the possibility of the methoxyl group being on the opposite side of the nitrogen atom in α' -*O*-monomethyl- γ -benzildioxime. Moreover, β -*O*-methylphenylglyoxyylanilideoxime (XIX) is readily converted by boiling concentrated hydrochloric acid (a reagent which commonly causes isomerisation of an NOME group) into the α -isomeride (XXI).

EXPERIMENTAL.

O-Methyl- α -benzilmonoxime.— α -Benzilmonoxime was prepared by a modification of the method of Auwers and Meyer (*Ber.*, 1889, 22, 540). A suspension of benzil (200 g.) in alcohol (700 c.c.), obtained by rapid cooling of the boiling solution, was cooled to 10° and treated below 15° with alternate small quantities of sodium hydroxide (100 g. in 100 c.c. of water) and hydroxylamine hydrochloride (66 g. in 100 c.c. of water). After being kept for 24 hours at room temperature, the mixture was diluted to 4 litres, a small quantity of benzil removed, and the oxime precipitated with concentrated hydrochloric acid or saturated ammonium chloride solution. The washed and dried precipitate was crystallised from benzene, which gave a much better separation of the α - and β -benzilmonoximes than the 30% alcohol used by Auwers and Meyer. Yield, 70%. The oxime was converted into *O*-methyl- α -benzilmonoxime by the method of Brady and Perry (*loc. cit.*).

Oximation of O-Methyl- α -benzilmonoxime.—Finely divided *O*-methyl- α -benzilmonoxime (20 g.) was suspended in alcohol (60 c.c.) and sodium hydroxide (8 g.) and hydroxylamine hydrochloride (7 g.), each dissolved in 8 c.c. of water, were added in small portions. The mixture became hot and the *O*-methyl- α -benzilmonoxime dissolved to give a dark yellow solution. After 2 hours, small crystals filled the liquid, and on the next day these were collected and washed with a little alcohol (A). The filtrate when diluted to 200 c.c. gave a crystalline precipitate (B) and saturation of the mother-liquor with carbon dioxide gave a further precipitate (C).

The precipitate A, consisting of a sparingly soluble sodium salt, was dissolved in hot 2*N*-sodium hydroxide, some unchanged *O*-methyl- α -benzilmonoxime removed, and the solution cooled and saturated with carbon dioxide; the precipitate, after crystallising three times from acetone, gave *O*-monomethyl- α -benzildioxime (II) in flat needles, m. p. 181—182° (Found: N, 11.4; OMe, 9.2. $C_{15}H_{14}O_2N_2$ requires N, 11.0; OMe, 12.2%). Low methoxyl values are usual with compounds of this type (compare Brady and Perry, *loc. cit.*).

When the above compound was boiled for 15 minutes with acetic anhydride, the mixture treated with water, and the product crystallised from alcohol, *acetyl-O*-monomethyl- α -benzildioxime was obtained in small plates, m. p. 107—108° (Found: N, 9.5. $C_{17}H_{16}O_3N_2$ requires N, 9.4%). *Benzoyl-O*-monomethyl- α -benzildioxime, prepared by the Schotten-Baumann reaction, crystallised from glacial acetic acid in needles, m. p. 167° (Found: N, 7.8. $C_{22}H_{18}O_3N_2$ requires N, 7.7%).

Fractions B and C when crystallised from various solvents gave a product, m. p. 157—160°, which was seen under the microscope to consist of approximately equal quantities of flat needles and small octahedra. When the mixture was dissolved in hot 2*N*-sodium hydroxide, and the solution cooled, the sodium salt of most of the *O*-monomethyl- α -benzildioxime separated; the mother-liquor, on saturation with carbon dioxide, gave a pasty solid which soon set to a brittle mass. Two crystallisations of this from glacial acetic acid gave a product, m. p. 165—167°; in later preparations, the separation was greatly assisted by seeding the acetic acid solution with these crystals and filtering the liquid before crystallisation was complete, whereby the bulk of the new compound was removed before the *O*-monomethyl- α -benzildioxime separated. Further crystallisation from acetic acid did not increase the purity of the product, as this treatment brought about partial conversion into a third isomeride, but crystallisation from chloroform and light

petroleum gave α' -*O*-monomethyl- γ -benzildioxime (III) in small octahedra, m. p. 172° (Found: N, 10.9; OMe, 9.6%).

Acetyl- α' -O-monomethyl- γ -benzildioxime crystallised from alcohol in needles, m. p. 80° (Found: N, 9.6%), and *benzoyl- α' -O-monomethyl- γ -benzildioxime* from glacial acetic acid in prisms, m. p. 79° (Found: N, 7.9%). Both compounds were prepared by the methods described above.

In the above oximation the final yields averaged 40–50% of the α - and 7–10% of the γ -benzildioxime derivative with about 25% of inseparable mixture. Many unsuccessful attempts were made to obtain larger yields of α' -*O*-monomethyl- γ -benzildioxime: oximation in hot solution with free hydroxylamine gave but a small yield of the mixture; in hot acid solution, or with hydroxylamine hydrochloride alone in alcohol, much of the product was converted into *O*-monomethyl- β -benzildioxime; in alkaline solution as above but at a higher temperature, much hydroxylamine was destroyed and a poor yield of the mixture obtained.

Oximation of O-Methyl- β -benzilmonoxime.—*O*-Methyl- β -benzilmonoxime, prepared by boiling *O*-methyl- α -benzilmonoxime with concentrated hydrochloric acid (Brady and Perry, *loc. cit.*), is unaffected by treatment with hydroxylamine in acid, alkaline, or neutral solution even at 100°. When, however, the compound (5 g.) was heated under pressure with hydroxylamine hydrochloride (1.8 g.) in alcohol (25 c.c.) at 175–185° for 10 hours, and the solution cooled, a solid separated on scratching which, after crystallising three times from glacial acetic acid, gave *O*-monomethyl- β -benzildioxime (XII) in stout prisms, m. p. 177° (Found: N, 11.1; OMe, 10.9%).

Mixtures of any two of the isomeric monomethylbenzildioximes obtained melted between 130° and 150°.

Acetyl-O-monomethyl- β -benzildioxime crystallised from alcohol in prisms, m. p. 81° (Found: N, 9.5%), and *benzoyl-O-monomethyl- β -benzildioxime* from glacial acetic acid in prisms, m. p. 162° (Found: N, 7.8%).

In this oximation no indication of β' -*O*-monomethyl- γ -benzildioxime was obtained. This result was, however, to be expected owing to the instability of the derivatives of γ -benzildioxime, which at high temperatures change to the β -isomerides.

Monomethylation of α -Benzildioxime.—A solution of α -benzildioxime (10 g.) in 4*N*-sodium hydroxide (200 c.c.) and methyl alcohol (5 c.c.) was cooled in ice, and methyl sulphate (15 g.) added slowly. The precipitate which formed was collected, washed with cold 2*N*-sodium hydroxide, and extracted with hot *N*/5-sodium hydroxide; a small quantity of oil remained consisting of dimethyl

ethers. The alkaline extract on saturation with carbon dioxide gave *O*-monomethyl- α -benzildioxime. The mother-liquor from the methylation was saturated with carbon dioxide, the precipitate obtained was extracted with hot alcohol, some undissolved α -benzildioxime removed, and the solid which separated on cooling was crystallised from alcohol, *N*-monomethyl- α -benzildioxime (V) being obtained in prisms, m. p. 168° (Found: N, 11.4. $C_{15}H_{14}O_2N_2$ requires N, 11.0%). This compound gave no methyl iodide on treatment with hydriodic acid, but methylamine was detected in the solution by Valton's method (J., 1925, 127, 40).

Monomethylation of β -Benzildioxime.—This was carried out in the same way as that of α -benzildioxime. The pasty precipitate of dimethyl ethers was removed and the filtrate diluted and saturated with carbon dioxide; the semi-solid precipitate obtained slowly hardened and after three crystallisations from alcohol gave a small yield of *O*-monomethyl- β -benzildioxime. The mother-liquors from the crystallisation were evaporated to dryness at room temperature and the residue was extracted several times with boiling light petroleum and once with hot benzene, a further quantity of the *O*-methyl ether thus being removed; the undissolved part, crystallised from alcohol, gave *N*-monomethyl- β -benzildioxime (XIII) in hexagonal prisms, m. p. 205° (decomp.) (Found: N, 11.2%). Hydriodic acid produced no methyl iodide from this compound, but methylamine was detected.

Monomethylation of γ -Benzildioxime.—The dioxime (5 g.) was dissolved in 2*N*-sodium hydroxide (100 c.c.), and a concentrated solution of sodium hydroxide (7 g.) added with cooling, followed by a little methyl alcohol (2.5 c.c.); the suspension of sodium salt obtained was cooled in ice, and methyl sulphate (4 g.) added. After 30 minutes, the mixture was diluted until solution was attained and an excess of a saturated solution of ammonium chloride was then added. The precipitate obtained, on crystallising twice from alcohol, gave *N*-monomethyl- β -benzildioxime (2 g.). The mother-liquors from the crystallisation were evaporated at room temperature and the residue was extracted with hot benzene; some *N*-ether remained undissolved. The benzene solution on evaporation yielded a considerable quantity of oil, but no pure compound could be obtained therefrom.

*Methylation of *O*-Monomethyl- α -benzildioxime.*—A solution of the compound (5 g.) in hot 2*N*-sodium hydroxide (120 c.c.) was quickly cooled and methyl alcohol (5 c.c.) added, followed by methyl sulphate (10 g.) in small portions with cooling in ice. After some hours, the pasty solid was collected and crystallised first from glacial acetic acid and then from acetone; the *OO*-dimethyl- α -benzil-

dioxime obtained was identified by comparison with a specimen prepared by Brady and Perry's method. When the acetic acid mother-liquor was diluted somewhat with water, more of the above compound separated; this was removed, excess of water added to the filtrate, the precipitate formed dissolved in the minimum quantity of glacial acetic acid, and concentrated hydrochloric acid added until no further precipitate was formed. The precipitated hydrochloride (m. p. 157—161°) was washed with concentrated hydrochloric acid, then with hot benzene, and decomposed with concentrated aqueous ammonia. The solid obtained, after crystallisation from alcohol, was identified as *ON*-dimethyl- α -benzildioxime.

Methylation of N-Monomethyl- α -benzildioxime.—The compound (1 g.) was dissolved in 2*N*-sodium hydroxide, the solution cooled in ice, and methyl sulphate (2 g.) added. The oil formed slowly solidified; when it was crystallised from alcohol, *NN*-dimethyl- α -benzildioxime separated. The alcoholic mother-liquor was concentrated somewhat, a further quantity of the *NN*-ether removed, and concentrated hydrochloric acid added to the filtrate; the precipitated hydrochloride, after being washed with concentrated hydrochloric acid and with ether, was decomposed with ammonia, and the solid crystallised from alcohol, *ON*-dimethyl- α -benzildioxime being obtained.

Methylation of O-Monomethyl- β -benzildioxime.—A solution of the compound (5 g.) in hot 2*N*-sodium hydroxide (120 c.c.) was cooled and treated with methyl sulphate (10 g.). The pasty precipitate was extracted with ether, and the solution dried with anhydrous sodium sulphate and saturated with dry hydrogen chloride. The oily hydrochloride precipitated was separated by decantation, united with a further quantity obtained by addition of light petroleum to the ethereal solution, and decomposed with concentrated aqueous ammonia. The oil obtained, after being kept in a vacuum over solid sodium hydroxide, solidified and then, on crystallising several times from light petroleum, gave *ON*-dimethyl- β -benzildioxime. The ether-light petroleum solution from which the hydrochloride had been removed was evaporated, and the residue crystallised twice from alcohol, *OO*-dimethyl- β -benzildioxime being obtained.

Methylation of α' -O-Monomethyl- γ -benzildioxime.—A mixture of the compound (2 g.), methyl iodide (1.5 g.), dry ether (20 c.c.), and dry silver oxide (2 g.) was boiled under reflux for 3 hours, cooled, and the liquid filtered. The solid was extracted with hot acetone; the extract on evaporation yielded *OO*-dimethyl- α -benzildioxime. The ethereal solution was evaporated at room temperature, and the

residue crystallised from acetone, a further quantity of the *OO*-ether being obtained. The acetone mother-liquor on evaporation at room temperature gave an oil which solidified when kept in an evacuated desiccator and scratched; crystallised from dilute alcohol and finally from 80% alcohol, this yielded *OO*-dimethyl- γ -benzildioxime (VIII) in plates, m. p. 59° (Found: N, 10.3; OMe, 18.1. $C_{16}H_{16}O_2N_2$ requires N, 10.4; OMe, 23.1%). The melting point of this compound was depressed by 30—40° by addition of an approximately equal quantity of *O*-methyl- α - or - β -benzilmonoxime or *OO*-dimethyl- β -benzildioxime, m. p.'s 61°, 62°, and 73° respectively.

Methylation of α' -*O*-monomethyl- γ -benzilmonoxime with methyl sulphate as described for *O*-monomethyl- α -benzildioxime gave an oil which did not solidify after several months. When, however, the above compound had been obtained and was used to seed this oil, crystallisation occurred, and recrystallisation from alcohol gave a fair yield of *OO*-dimethyl- γ -benzildioxime but no *OO*-dimethyl- α -benzildioxime.

Isomeric Changes of the Methyl Ethers of the Benzildioximes.—*O*-Monomethyl- α -benzildioxime (20 g.) was added to boiling, freshly distilled aniline (40 c.c.) and the mixture was boiled for 30 seconds and poured at once into ice-cold dilute hydrochloric acid. The precipitated mixture of the monomethyl ethers of α -, β -, and γ -benzildioximes, after being thoroughly washed with dilute hydrochloric acid, was separated by removal of unchanged *O*-monomethyl- α -benzildioxime as its sparingly soluble sodium salt and crystallisation of the remaining mixture from acetic acid and from chloroform and light petroleum (p. 220). About 5 g. of α' -*O*-monomethyl- γ -benzildioxime were obtained (this is the easiest way of preparing this compound in quantity). If the time of contact with boiling aniline exceeds 30 seconds, a larger quantity of *O*-monomethyl- β -benzildioxime is formed which is very difficult to separate. When *O*-monomethyl- α -benzildioxime (4 g.) was boiled for 5 minutes with aniline (10 c.c.) and cooled, a mass of crystals separated which gave 2 g. of *O*-monomethyl- β -benzildioxime after being washed with dilute acid and crystallised from glacial acetic acid.

A suspension of *O*-monomethyl- α -benzildioxime (8 g.) in glacial acetic acid (30 c.c.) was saturated with dry hydrogen chloride and the mixture was boiled under reflux for 30 minutes, cooled and poured into water. The solid obtained, on crystallising from glacial acetic acid, gave 5 g. of *O*-monomethyl- β -benzildioxime. Similarly α' -*O*-monomethyl- γ -benzildioxime gave *O*-monomethyl- β -benzildioxime.

OO-Dimethyl- γ -benzildioxime was boiled under reflux with con-

concentrated hydrochloric acid for an hour and the solution was diluted with water and extracted with ether; the product, crystallised from acetone, gave *OO*-dimethyl- α -benzildioxime.

N-Monomethyl- α -benzildioxime (1 g.) was added to boiling aniline (3 g.) and boiled for 5 minutes. The solution was poured into cold dilute hydrochloric acid, and the resulting precipitate crystallised from alcohol; benzilmonoxime anil, $\text{CPh}(\text{:NOH})\cdot\text{CPh}\cdot\text{NPh}$, thus obtained was identified by comparison with a specimen prepared by Auwers and Siegfeld's method (*Ber.*, 1893, **26**, 794). The readily hydrolysable $\text{NMe}\cdot\text{O}$ group was eliminated by this treatment, but when dimethylaniline was substituted for aniline *N*-monomethyl- β -benzildioxime was obtained.

Beckmann Rearrangement of O-Monomethyl- α -benzildioxime.—The compound (5 g.) was suspended in dry ether (20 c.c.) cooled in ice, and phosphorus pentachloride (4 g.) added. After 8 hours' keeping at room temperature, all the oxime had dissolved; the ether was then decanted, washed with ice-cold water, and dried over potassium carbonate; on evaporation an oil was obtained which slowly solidified in a vacuum. The solid, crystallised twice from alcohol, gave 3 : 5-diphenyl-1 : 2 : 4-oxadiazole, identified by comparison with a specimen prepared by Günther's method (*Annalen*, 1889, **252**, 48). The alcoholic mother-liquors from the crystallisation were diluted with water; the precipitate obtained, on crystallising twice from benzene, gave flat plates of *N*-benzoyl-*O*-methylbenzamidoxime (XVII), m. p. 151° (Found: N, 11.1; OMe, 11.9. $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$ requires N, 11.0; OMe, 12.2%). This compound (0.5 g.) was boiled under reflux with 30% sodium hydroxide solution (10 c.c.) for 1 hour: sodium benzoate separated; the alkaline solution, on extraction with ether, removal of the solvent, and crystallisation of the residue from light petroleum, gave *O*-methylbenzamidoxime, identified by comparison with a genuine specimen (Krüger, *Ber.*, 1885, **18**, 1053). Hydrolysis of *N*-benzoyl-*O*-methylbenzamidoxime with concentrated hydrochloric acid gave benzamide and benzoic acid.

In later experiments the oxime-ether-phosphorus pentachloride mixture was kept at 0° until the reaction was complete; a larger proportion of *N*-benzoyl-*O*-methylbenzamidoxime was then formed which could be isolated by direct crystallisation from alcohol and benzene.

Beckmann Rearrangement of α' -O-Monomethyl- γ -benzildioxime.—The reaction was carried out as above, but the temperature was kept below 0° by means of a freezing mixture. The solid from the ether, after crystallising three times from alcohol, gave α -*O*-methylphenylglyoxyylanilideoxime (XXI) in long needles, m. p. 118 — 120°

(Found: N, 11.2. $C_{15}H_{14}O_2N_2$ requires N, 11.0%). Hydrolysis of this compound with boiling concentrated hydrochloric acid and extraction with ether gave an oil, from which a solid (m. p. 57—60°) could be isolated, but in too small quantity for further investigation; the hydrochloric acid solution yielded aniline.

Beckmann Rearrangement of O-Monomethyl-β-benzildioxime.—The reaction was carried out at 0° as with the α-compound, the ether yielding a solid which, after crystallising twice from alcohol, gave β-O-methylphenylglyoxylanilideoxime (XIX) in needles, m. p. 152° (Found: N, 11.4%). Boiling concentrated hydrochloric acid converted it first into the α-isomeride; prolonged boiling gave results similar to those obtained with the latter compound. The constitution was proved by the following synthesis. A solution of phenylglyoxylanilide (2 g.), prepared from β-benzilmonoxime by the Beckmann rearrangement, in alcohol (15 c.c.) was cooled in ice, and hydroxylamine hydrochloride (0.7 g.) and sodium hydroxide (0.8 g.), each in 1 c.c. of water, were added slowly. After 2 hours, the whole was poured into water and the precipitated solid, after drying, was extracted with hot benzene, which removed a small quantity of benzanilide. The insoluble portion, together with the precipitate obtained by saturating the original alkaline filtrate with carbon dioxide was crystallised from alcohol, giving the β-phenylglyoxylanilideoxime of Beckmann and Köster (*Annalen*, 1893, **274**, 9). This oxime (1 g.) was boiled under reflux with methyl iodide (1 g.), dry silver oxide (0.5 g.), and dry ether (15 c.c.) for 2 hours. After filtration and evaporation of the ether the residual solid was crystallised first from alcohol and then from benzene and light petroleum, β-O-methylphenylglyoxylanilideoxime being obtained.

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