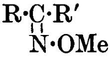
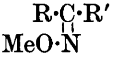
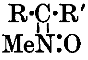
CXXVIII.—*The Isomerism of the Oximes. Part XXIX. Isomeric* p-*Nitrobenzyl and Methyl Ethers of Some Aldoximes.*

By Oscar L. Brady and Louis Klein.

The Hantzsch–Werner theory demands the existence of two isomeric *O*-ethers and two isomeric *N*-ethers corresponding to a pair of isomeric unsymmetrical oximes.

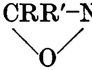

$\begin{array}{l}\mathrm{R{\cdot}C{\cdot}R'} \\ \quad\| \\ \quad\mathrm{N{\cdot}OMe}\end{array}$


$\begin{array}{r}\mathrm{R{\cdot}C{\cdot}R'} \\ \| \quad \\ \mathrm{MeO{\cdot}N}\quad\end{array}$


$\begin{array}{c}\mathrm{R{\cdot}C{\cdot}R'} \\ \| \\ \mathrm{MeN{:}O}\end{array}$


$\begin{array}{c}\mathrm{R{\cdot}C{\cdot}R'} \\ \| \\ \mathrm{O{:}NMe}\end{array}$

The Beckmann structural theory as extended by Atack (J., 1921, **119**, 1175) demands one *O*-ether and two *N*-ethers,



$$CRR'{:}N{\cdot}OMe, \quad \underset{\diagdown O \diagup}{CRR'{-}NMe}, \quad CRR'{:}NMe{:}O.$$

Four isomeric methyl ethers have been obtained from certain unsymmetrical ketoximes (Semper and Lichtenstadt, *Ber.*, 1918, **51**, 928; Plowman and Whiteley, J., 1924, **125**, 587; Brady and Mehta, *ibid.*, p. 2297) but, despite many attempts, only one *N*-ether has been obtained from any one aldoxime (Brady, Dunn, and Goldstein, J., 1926, 2386). Now the gravamen of Atack's charge against the Hantzsch–Werner theory was the paucity of evidence for the existence of two isomeric *O*-ethers of undoubted composition. The best authenticated cases are the pairs of *O*-methyl ethers of *p*-nitrobenzophenoneoxime (Brady and Mehta, *loc. cit.*), *m*-nitrobenzaldoxime, and 3-nitro-4-methoxybenzaldoxime (Goldschmidt, *Ber.*, 1890, **23**, 2170; Brady and Dunn, J., 1913, **103**, 1620; Brady, Dunn, and Goldstein, J., 1926, 2402). In other cases, one or both of the isomerides are uncrystallisable oils (methyl ethers of *p*-tolylphenoximes, benzaldoximes, *p*-methoxy- and *o*-nitro-benzaldoximes), or the unstable is much more fusible than the stable isomeride and a mixture of the two melts at an intermediate temperature, so there is no satisfactory criterion of purity of the lower-melting compound (methyl, ethyl, and benzyl ethers of *p*-nitrobenzaldoximes). Even the evidence that the α- and β-*O*-methyl-*m*-nitrobenzaldoximes * are truly *O*-ethers is not entirely satisfactory.

The objects of the work here presented were (1) to adduce further evidence of the constitution of the two *O*-methyl-*m*-nitrobenzaldoximes, (2) the preparation of a number of pairs of *O*-ethers from various oximes, and (3) a further search for a second *N*-ether of aldoximes. The last effort was unavailing and no evidence was obtained of the existence of more than one *N*-ether corresponding to any one aldoxime. It has been found that both *O*-methyl-*m*-nitrobenzaldoximes have normal molecular weights and give quantitative yields of methyl iodide when heated with hydriodic acid. Further, a mixture of the two *O*-ethers has been obtained by the action of *O*-methylhydroxylamine on *m*-nitrobenzaldehyde, the α-isomeride greatly preponderating.

The evidence for the constitution of these compounds as *O*-ethers is therefore (1) methoxyl determinations, (2) synthesis from *O*-methylhydroxylamine, (3) partial conversion of the α- into the β-form by ultra-violet light (Brady and McHugh, J., 1924, **125**,

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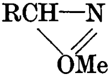
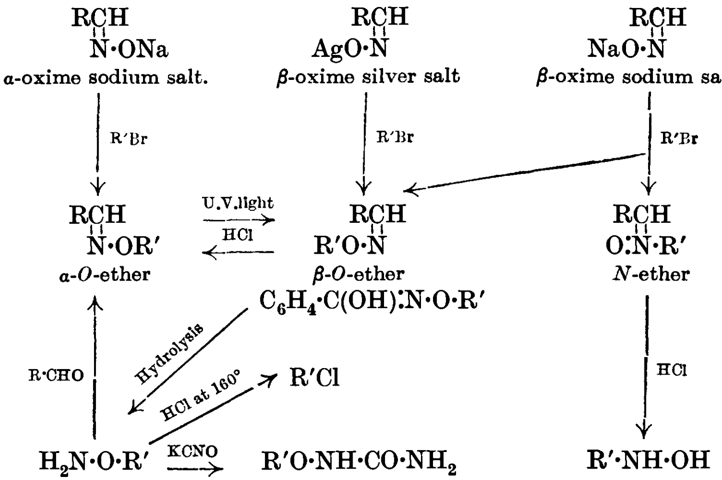
* The nomenclature used in this paper is that suggested by Brady and Bishop (J., 1925, **127**, 1361), and the new configurations have been adopted.

552), (4) complete conversion of the β- into the α-form by hydrogen chloride at room temperature (Goldschmidt and Kjellin, *Ber.*, 1891, **24**, 2555) and (5) normal molecular weights. None of this evidence rules out the structure  suggested as possible although unlikely by Atack, who states that a substance having this structure should be readily convertible into the more stable form, >C:N·O·R. He has overlooked the rather surprising stability of the β-*O*-ethers in the absence of acids; *e.g.*, β-*O*-methyl-*m*-nitrobenzaldoxime is not isomerised on melting and can be kept unchanged for 16 years, whereas β-*m*-nitrobenzaldoxime is completely converted into the α-isomeride after 4 years. Moreover, the isomeric *O*-methyl-*p*-nitrobenzophenoneoximes are not interconvertible by means of hydrogen chloride (Brady and Mehta, *loc. cit.*). The ring formula is, however, inadmissible until some evidence is adduced for the existence of compounds of this type in which none of the four oxygen valencies is attached to a negative group—the compounds instanced by Atack (Kehrmann and Bohn, *Ber.*, 1914, **47**, 3052) are all salt-like in structure.

The chief difficulty experienced in previous work on the ethers of the aldoximes was the low melting point of the methyl, ethyl, and benzyl compounds and for this reason the *p*-nitrobenzyl derivatives have been studied, since compounds containing this radical have usually a higher melting point. As a result, three isomeric ethers, derived from each of ten pairs of isomeric oximes, have been prepared. One of the three was an *N*-ether as shown by its ready hydrolysis by acids to the aldehyde and *N*-*p*-nitrobenzylhydroxylamine and by its synthesis from these two compounds, the constitution of the latter of which was proved by Behrend and Leuchs and by Behrend and König (*Annalen*, 1890, **257**, 243; 1891, **263**, 190). The other two were *O*-ethers. This was established as follows. The previously unknown O-p-*nitrobenzylhydroxylamine* was prepared by the hydrolysis of *O*-*p*-nitrobenzylbenzhydroxamic acid (Werner, *Ber.*, 1892, **25**, 44), and its constitution proved by its conversion into *p*-nitrobenzyl chloride by heating under pressure with hydrochloric acid, by its reaction with potassium cyanate to give *p*-nitrobenzyloxycarbamide and by its failure to reduce cold Fehling's solution. This compound reacted with aldehydes, giving ethers identical with those obtained by the action of *p*-nitrobenzyl bromide on the sodium salts of the α-aldoximes, *i.e.*, the α-*O*-ethers. In six cases these α-*O*-ethers were converted by ultra-violet light into the β-*O*-ethers identical with those obtained by the action of *p*-nitrobenzyl bromide on the silver salts of the β-aldoximes. In all ten cases the β-*O*-ethers were completely converted into the α-*O*-ethers by hydrogen chloride. These changes may be represented diagrammatically thus, R′ denoting $NO_2{\cdot}C_6H_4{\cdot}CH_2$:



The α-*O*-ethers are very stable towards hydrolysing agents, being unchanged by boiling with aqueous or alcoholic hydrochloric acid, hydrobromic acid, 60% sulphuric acid or 2*N*-sodium hydroxide.

The sodium salts of the α-oximes gave with *p*-nitrobenzyl bromide almost exclusively α-*O*-ethers; in only one case could any indication of the formation of the *N*-ether be detected (compare Brady, Dunn, and Goldstein, *loc. cit.*; Brady and Goldstein, J., 1926, 2403). The sodium salts of the β-oximes gave mainly the *N*-ethers, but small quantities of the β-*O*-ethers were also obtained in five cases. The β-*O*-ethers were generally prepared by the action of (1) *p*-nitrobenzyl bromide on either the β-aldoxime in the presence of dry silver oxide, or the silver salt of the β-aldoxime, (2) ultra-violet light on the α-*O*-ethers. The results are summarised in Table I.

As the melting points of the two isomeric *O*-ethers are frequently close together, the melting point of a mixture of approximately equal amounts of the two is given also; the figure for the two *O*-ethers of *p*-methoxybenzaldoxime is the m. p. of a mixture prepared by adding a very small quantity of the α- to the β-*O*-ether. That the β-*O*-ethers have been prepared by various methods is further evidence of their entity; a particular method was, however, not always equally successful and in some cases failed altogether.

The cases of Nos. 5 and 9 are of special interest, since all attempts to obtain the β-oximes have been unsuccessful (Brady and Dunn, J., 1923, **123**, 1787; Brady and Manjunath, J., 1924, **125**, 1066);

TABLE I.

p-Nitrobenzyl Ethers of Aldoximes.

	Oxime.	M. p. of *N*-ether.	M. p. of α-*O*-ether.	M. p. of β-*O*-ether.	Mixed m. p. of α- + β-*O*-ethers.	Methods of preparation of β-*O*-ethers.
1	Benzaldoxime	110°	60—61°	54°	37—38°	Ag salt.
2	*o*-Nitrobenzaldoxime	203	112	116	94—95	Ag_2O; Na salt; U.V. light.
3	*m*-Nitrobenzaldoxime	223	87—88	118	77—79	Ag_2O; Ag salt; Na salt; U.V. light.
4	*p*-Nitrobenzaldoxime	234—235	179	184	153—155	Ag_2O; Ag salt; Na salt; U.V. light.
5	*o*-Methoxybenzaldoxime	141	88	Oil.	—	U.V. light.
6	*p*-Methoxybenzaldoxime	150	122	74	69—70	Ag salt; Na salt; U.V. light.
7	3 : 4-Methylenedioxybenzaldoxime	144	110	125	95	Ag_2O; Ag salt; U.V. light.
8	3-Nitro-4-methoxybenzaldoxime	232	117	152	108—109	Ag_2O; Ag salt; Na salt; U.V. light.
9	5-Nitro-2-methoxybenzaldoxime	237	149	153	128—130	U.V. light.
10	Cinnamaldoxime	135	83	86	62—63	Ag_2O.

the U.V. light method was therefore the only one available for the preparation of the β-*O*-ethers. It is noteworthy that conversion occurs although U.V. light has no action upon the parent oximes (compare Brady and McHugh, J., 1924, **125**, 552, and experimental part). α-*O*-Methyl-6-nitro-3 : 4-methylenedioxybenzaldoxime also has been partly converted into the β-form by similar means ; only one form of the oxime is known.

The *N*-ethers of *o*-methoxy- and 5-nitro-2-methoxy-benzaldoximes were obtained from the aldehydes and *N*-*p*-nitrobenzylhydroxylamine, since the β-oximes are unknown.

The action of *p*-nitrobenzyl bromide on the sodium salt of β-cinnamaldoxime produced a viscous, brown oil which could not be purified. The *N*-ether was, however, easily prepared by the action of *N*-*p*-nitrobenzylhydroxylamine on the aldehyde. It behaved abnormally on hydrolysis, giving a product which could not be satisfactorily purified. This peculiar behaviour is being further investigated (compare Bamberger and Weitnauer, *Ber.*, 1922, **55**, 3376).

The *N*-*p*-nitrobenzyl ethers undergo the Beckmann change in the same way as the *N*-methyl ethers (Brady and Dunn, J., 1926, 2411).

Finally the binary fusion diagram for α-benzaldoxime and *p*-nitrobenzyl bromide was constructed, but no evidence of compound formation was forthcoming (compare Brady and Truszkowski, J., 1924, **125**, 1089 ; Brady and Klein, J., 1925, **127**, 852).

We consider that the results here described remove all doubt of the existence of two isomeric *O*-ethers. Any theory of the isomerism of the oximes must therefore provide for two such compounds and, so far, only that suggested by Hantzsch and Werner makes a serious attempt to do so.

EXPERIMENTAL.

Action of p-*Nitrobenzyl Bromide on Sodium Salts of α-Aldoximes.*

α-Benzaldoxime.—The oxime (8 g.) dissolved in alcohol (20 c.c.) was mixed with sodium ethoxide (from 1·53 g. of sodium in 40 c.c. of alcohol), and a hot solution of *p*-nitrobenzyl bromide (14·4 g.) in alcohol (100 c.c.) added. Having been heated on the water-bath for ½ hour, the mixture was diluted with water (250 c.c.) and cooled in ice. The α-*O*-*p*-nitrobenzylbenzaldoxime thus obtained, in 89% yield, crystallised from alcohol in almost white prisms, m. p. 60—61° (Found : N, 11·1 ; *M*, cryoscopic in benzene, 253. Calc. : N, 10·9%; *M*, 256). Schroeter and Peschkes (*Ber.*, 1900, **33**, 1982) described the compound as forming yellow prisms. The ether was unaffected by boiling with hydrochloric acid (aqueous or alcoholic), hydrobromic acid, 60% sulphuric acid or with sodium hydroxide solution.

The aqueous-alcoholic filtrate from the above preparation was extracted with chloroform, and the extract was washed with 2*N*-sodium hydroxide, to remove unchanged oxime, and with water, evaporated to small bulk, and dried over sodium sulphate. Treatment with dry hydrogen chloride for an hour produced a small precipitate (m. p. 172—173°) of *N*-*p*-nitrobenzylhydroxylamine hydrochloride, decomposition of which with aqueous sodium carbonate gave a small quantity of *N*-*p*-nitrobenzylhydroxylamine (m. p. 120°), identified by comparison with an authentic specimen.

α-Cinnamaldoxime.—By the above method (oxime, 2·72 g. in 15 c.c. of alcohol; sodium ethoxide from 0·43 g. of sodium and 20 c.c. of alcohol; *p*-nitrobenzyl bromide, 4 g. in 40 c.c. of alcohol) a 69% yield was obtained of α-O-p-*nitrobenzylcinnamaldoxime*, which crystallised from alcohol in buff leaflets, m. p. 83° (Found : N, 10·2; *M*, cryoscopic in benzene, 271. $C_{16}H_{14}O_3N_2$ requires N, 9·9%; *M*, 282).

*α-*o*-Nitrobenzaldoxime.*—Owing to the sensitiveness of this oxime to hot alkali, the reaction was carried out at room temperature. The oxime (5 g.) in 30 c.c. of cold alcohol was treated with sodium ethoxide (from 0·7 g. of sodium and 30 c.c. of alcohol), a warm solution of *p*-nitrobenzyl bromide (6·5 g. in 80 c.c. of alcohol) added, and the mixture immediately cooled; a yellow solid then separated. After 12 hours, the precipitate was collected (84% yield), and crystallised from alcohol, α-O-p-*nitrobenzyl*-o-*nitrobenzaldoxime* being obtained in pale yellow leaflets, m. p. 112° (Found : N, 13·9; *M*, cryoscopic in camphor, 295. $C_{14}H_{11}O_5N_3$ requires N, 14·0%; *M*, 301).

The alcoholic filtrate from the preparation was diluted and treated as described under benzaldoxime, but nothing crystalline was isolated.

α-m-*Nitrobenzaldoxime.*—The oxime (8 g., suspended in 25 c.c. of alcohol), sodium ethoxide (from 1·11 g. of sodium and 40 c.c. of alcohol), and *p*-nitrobenzyl bromide (10·4 g. in 75 c.c. of hot alcohol) were heated on the water-bath under reflux for 30 minutes. On cooling, an oil separated which soon solidified (yield 90%). This crystallised from alcohol containing a little acetone, α-O-p-*nitrobenzyl*-m-*nitrobenzaldoxime* being obtained in pale yellow prisms, m. p. 87—88° (Found : N, 14·1 ; *M*, cryoscopic in benzene, 284. $C_{14}H_{11}O_5N_3$ requires N, 14·0% ; *M*, 301). The compound is dimorphous, for when its concentrated alcoholic solution is slowly cooled without stirring, pale yellow prisms, m. p. 97°, are obtained and a solution of these in hot alcohol, on being cooled rapidly and stirred, deposits the lower-melting form. A mixture of approximately equal amounts of either form with β-*O*-*p*-nitrobenzyl-*m*-nitrobenzaldoxime melts at 77—79°.

α-p-*Nitrobenzaldoxime.*—The O-p-*nitrobenzyl ether*, prepared similarly to the *m*-compound in 88% yield, crystallises from acetone in glistening, pale yellow prisms, m. p. 179° (Found : N, 13·9. $C_{14}H_{11}O_5N_3$ requires N, 14·0%).

α-3 : 4-*Methylenedioxybenzaldoxime.*—The addition of *p*-nitrobenzyl bromide (10·5 g. in 100 c.c. of hot alcohol) to a solution of the oxime (8 g. in 60 c.c. of warm alcohol) mixed with sodium ethoxide (from 1·12 g. of sodium and 40 c.c. of alcohol) gave a precipitate which dissolved when the mixture was heated under reflux for 30 minutes. On cooling, a mass of yellow crystals separated and, after dilution with a little water, these were collected (yield 96%) and crystallised from acetone; α-O-p-*nitrobenzyl*-3 : 4-*methylenedioxybenzaldoxime* was then obtained in pale yellow prisms, m. p. 110° (Found : N, 9·4; *M*, cryoscopic in camphor, 315. $C_{15}H_{12}O_5N_2$ requires N, 9·3% ; *M*, 300).

α-p- *and* α-o-*Methoxybenzaldoximes.*—Treated as described above with sodium ethoxide (from 0·92 g. of sodium and 40 c.c. of alcohol) and *p*-nitrobenzyl bromide (8·58 g. in 80 c.c. of alcohol), these oximes (6 g. in 50 c.c. of alcohol) gave, respectively, an 84% yield of α-O-p-*nitrobenzyl*-p-*methoxybenzaldoxime*, pale yellow prisms from acetone, m. p. 122° (Found : N, 9·7. $C_{15}H_{14}O_4N_2$ requires N, 9·8%), and a 79% yield of α-O-p-*nitrobenzyl*-o-*methoxybenzaldoxime*, very pale yellow prisms from methyl alcohol, m. p. 88° (Found : N, 9·9%).

α-3-*Nitro*-4-*methoxy*- *and* α-5-*Nitro*-2-*methoxy-benzaldoximes.*—Treated as described above with sodium ethoxide (from 0·59 g. of sodium and 30 c.c. of alcohol) and *p*-nitrobenzyl bromide (5·51 g.

in 35 c.c. of hot alcohol), the oximes (5 g. in 40 c.c. of alcohol) gave, respectively, a 90% yield of α-O-p-*nitrobenzyl*-3-*nitro*-4-*methoxybenzaldoxime*, a pale yellow, micro-crystalline powder from amyl alcohol, m. p. 117° (Found : N, 12·8; *M*, cryoscopic in camphor, 340. $C_{15}H_{13}O_6N_3$ requires N, 12·7%; *M*, 331), and an 87% yield of α-O-p-*nitrobenzyl*-5-*nitro*-2-*methoxybenzaldoxime*, white, micro-crystalline needles from acetone, m. p. 149° (Found : N, 12·7%; *M*, cryoscopic in camphor, 328).

α-*O*-*p*-Nitrobenzyl-3-nitro-4-methoxybenzaldoxime is dimorphous like the derivative from *m*-nitrobenzaldoxime, separating from benzene in yellow prisms, m. p. 105°.

O-p-*Nitrobenzylhydroxylamine.*

Benzhydroxamic Acid.—Jeanrenaud (*Ber.*, 1889, **22**, 1272) obtained this compound in 40% yield, but more than 60% can be obtained by the following modification of his process. Hydroxylamine hydrochloride (23·2 g.) was dissolved in the minimum amount of water, and alcohol (50 c.c.) added followed by alcoholic sodium ethoxide (7·7 g. of sodium in 180 c.c. of alcohol). The precipitated sodium chloride was filtered off, and ethyl benzoate (50 g.) added followed by more sodium ethoxide (7·7 g. of sodium in 180 c.c. of alcohol). On cooling, the liquid set to a mass of crystals of sodium benzhydroxamate, which were collected, washed with alcohol, dried, and dissolved in the minimum of water. The solution was acidified with hydrochloric acid and extracted six times with chloroform; the extract on evaporation yielded benzhydroxamic acid sufficiently pure for the next preparation.

O-p-*Nitrobenzylbenzhydroxamic Acid*, $C_6H_5{\cdot}C(OH){:}N{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$ or $C_6H_5{\cdot}CO{\cdot}NH{\cdot}O{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2$.—A solution of benzhydroxamic acid (25 g.) in alcohol (80 c.c.) was mixed with a solution of potassium hydroxide (10·2 g.) in water (40 c.c.), *p*-nitrobenzyl bromide (39·4 g. in 300 c.c. of hot alcohol) added, and the mixture heated under reflux for 45 minutes. On cooling, *O*-*p*-nitrobenzylbenzhydroxamic acid separated and was crystallised from alcohol (compare Werner, *Ber.*, 1892, **25**, 44).

O-p-*Nitrobenzylhydroxylamine.*—*O*-*p*-Nitrobenzylbenzhydroxamic acid (15 g.) in hot alcohol (125 c.c.) was boiled under reflux for 25 minutes with concentrated hydrochloric acid (150 c.c.). The clear solution thus obtained was cooled somewhat and diluted with water (150 c.c.) and while still warm was extracted with chloroform (200 c.c.) to remove benzoic acid, etc. The extraction was carried out as rapidly as possible, since, when the liquid cooled, the sparingly soluble *O*-*p*-nitrobenzylhydroxylamine hydrochloride was apt to separate. The aqueous layer was evaporated to dryness on the water-bath; a 96% yield of the crude compound was then obtained. The residue was crystallised from hot 2*N*-hydrochloric acid and the crystals were washed with alcohol and then with ether, pure O-p-*nitrobenzylhydroxylamine hydrochloride* being obtained in white leaflets, m. p. 217° (decomp.) (Found : Cl, 17·9. $C_7H_8O_3N_2$,HCl requires Cl, 17·3%). Boiling with water produces partial hydrolysis, and, unlike *N*-*p*-nitrobenzylhydroxylamine, the compound does not reduce Fehling's solution. The hydrochloride was dissolved in a little hot water, containing hydrochloric acid, and a solution of potassium cyanate added; p-*nitrobenzyloxycarbamide* separated on cooling and crystallised from hot water in white prisms, m. p. 206° (decomp.) (Found : N, 20·1. $C_8H_9O_4N_3$ requires N, 19·9%).

O-*p*-Nitrobenzylhydroxylamine hydrochloride (0·5 g.) was heated in a sealed tube at 160—180° for 4 hours with concentrated hydrochloric acid (2 c.c.). After cooling, the liquid contained a few colourless plates of the unchanged compound and some brown lumps; the latter were crystallised from light petroleum, and the *p*-nitrobenzyl chloride thus obtained was identified by comparison with an authentic specimen and by conversion into *p*-nitrobenzyl iodide by boiling in alcohol with potassium iodide. The hydrochloric acid mother-liquor on evaporation yielded ammonium chloride. When a concentrated solution of the hydrochloride in hot water, containing hydrochloric acid, was poured with stirring into an excess of 2*N*-sodium carbonate, an emulsion was obtained which, on cooling in ice, deposited crystals of the free base; a further quantity was obtained by extracting the mother-liquor with chloroform. After crystallising from light petroleum containing a little benzene, O-p-*nitrobenzylhydroxylamine* was obtained in white prisms, m. p. 56° (Found : N, 16·9. $C_7H_8O_3N_2$ requires N, 16·7%).

Action of O-p-*Nitrobenzylhydroxylamine on Aldehydes.*

p-Nitrobenzaldehyde (1·5 g.) in hot alcohol was treated with a solution of *O*-*p*-nitrobenzylhydroxylamine hydrochloride (2 g.) in hot 2*N*-hydrochloric acid (20 c.c.); crystals of α-*O*-*p*-nitrobenzyl-*p*-nitrobenzaldoxime soon began to separate. After cooling, they were collected and washed with alcohol (yield 2 g.).

By similar methods, like results were obtained with *o*-nitrobenzaldehyde, 5-nitro-2-methoxybenzaldehyde, and 3 : 4-methylenedioxybenzaldehyde, except that in the last case the mixture was heated for a short time on the water-bath.

m-Nitrobenzaldehyde (0·9 g.) in warm alcohol (15 c.c.) was mixed with a solution of *O*-*p*-nitrobenzylhydroxylamine (1·05 g.) in warm alcohol (12 c.c.); after 3 days, crystals of α-*O*-*p*-nitrobenzyl-*m*-nitrobenzaldoxime had separated (yield 1·6 g.). The alcoholic mother-liquor was fractionally precipitated with water, but only a small amount of the α-*O*-ether was obtained and there was no indication of the presence of the β-*O*-ether. The α-*O*-ethers were similarly obtained from cinnamaldehyde and *p*-methoxybenzaldehyde and *O*-*p*-nitrobenzylhydroxylamine. In every case the *O*-ether was identified by the method of mixed melting points with that obtained by the action of *p*-nitrobenzyl bromide on the sodium salt of the α-oxime.

Action of Silver Oxide and p-*Nitrobenzyl Bromide on* β-*Aldoximes.*

β-*Cinnamaldoxime.*—The oxime (2·94 g.) and *p*-nitrobenzyl bromide (4·32 g.) were dissolved in hot benzene (30 c.c.), dry, finely powdered silver oxide (2·6 g.) was added, and the mixture was boiled under reflux for an hour. After silver oxide and bromide had been removed, the solution was allowed to evaporate spontaneously. The residual solid was pressed on a porous tile, washed with 2*N*-sodium hydroxide to remove unchanged oxime and with water, and crystallised twice from methyl alcohol; β-O-p-*nitrobenzylcinnamaldoxime* was then obtained in pale buff prisms, m. p. 86° (yield 1·5 g.) (Found: N, 10·0; *M*, cryoscopic in benzene, 280. $C_{16}H_{14}O_3N_2$ requires N, 9·9%; *M*, 282).

β-o- *and* β-m-*Nitrobenzaldoximes.*—The finely powdered oxime (1 g.) and *p*-nitrobenzyl bromide (1·3 g.) were dissolved in benzene (75 c.c.) at room temperature, dry silver oxide (1 g.) was added, and the mixture was kept for 5 days in the dark in a corked flask with occasional shaking. The mixture was then heated to boiling and filtered hot. The filtrate on spontaneous evaporation gave a sticky solid which, after being pressed on a porous tile and crystallised four times from alcohol, yielded β-O-p-*nitrobenzyl*-o-*nitrobenzaldoxime* in feathery needles, m. p. 116° (Found: N, 13·7; *M*, cryoscopic in camphor, 312. $C_{14}H_{11}O_5N_3$ requires N, 14·0%; *M*, 301). Similarly, β-O-p-*nitrobenzyl*-m-*nitrobenzaldoxime* was obtained, crystallising from methyl alcohol in white leaflets, m. p. 118° (Found: N, 14·0%; *M*, cryoscopic in ethylene dibromide, 326).

β-p-*Nitro- and* β-3 : 4-*Methylenedioxy-benzaldoximes.*—The finely powdered oxime (3 g.) and *p*-nitrobenzyl bromide (3·9 g.) were suspended in benzene (250 c.c.) at room temperature, dry silver oxide (3 g.) was added, and the mixture was kept in the dark in a corked flask for 6 days with occasional shaking. After being heated to boiling and filtered, the solution gave on evaporation a solid which was washed with 2*N*-sodium hydroxide, water, and a little warm acetone. The residue on crystallisation from acetone gave β-O-p-*nitrobenzyl*-p-*nitrobenzaldoxime* as a white, micro-crystalline powder,

m. p. 184° (Found : N, 13·8. $C_{14}H_{11}O_5N_3$ requires N, 14·0%). Similarly, β-O-p-*nitrobenzyl*-3 : 4-*methylenedioxybenzaldoxime* was obtained in yellow prisms, m. p. 125° (Found : N, 9·5; *M*, cryoscopic in camphor, 325. $C_{15}H_{12}O_5N_2$ requires N, 9·3%; *M*, 300).

β-3-*Nitro*-4-*methoxybenzaldoxime.*—By a similar method to the preceding, from the oxime (2·7 g.), *p*-nitrobenzyl bromide (2·97 g.), benzene (500 c.c.), and silver oxide (1·9 g.), β-O-p-*nitrobenzyl*-3-*nitro*-4-*methoxybenzaldoxime* was obtained; it crystallised from alcohol–acetone in white needles, m. p. 152° (Found : N, 12·8; *M*, cryoscopic in camphor, 348. $C_{15}H_{13}O_6N_3$ requires N, 12·7%; *M*, 331).

β-*Benzaldoxime and* β-p-*Methoxybenzaldoxime.*—β-Benzaldoxime gave only an uncrystallisable oil by the silver oxide method. β-*p*-Methoxybenzaldoxime gave only the α-*O*-*p*-nitrobenzyl ether, although various solvents and other modifications of procedure were tried. The β-*O*-ethers from these two oximes have, however, been prepared by another method (see below).

Action of p-*Nitrobenzyl Bromide on Silver Salts of* β-*Aldoximes.*

β-*Benzaldoxime,* β-p-*Methoxy-,* β-p-*Nitro-, and* β-3-*Nitro*-4-*methoxy-benzaldoximes.*—The silver salts were each prepared by suspending the oxime in alcohol, adding an alcoholic solution of sodium ethoxide prepared from a weighed quantity of sodium, shaking the mixture until a clear solution was obtained, and then adding in artificial light an aqueous-alcoholic solution of silver nitrate. The precipitated silver salt, which was usually difficult to filter off, was collected and washed first with absolute alcohol and then with dry chloroform. The quantities used for β-benzaldoxime, β-*p*-methoxybenzaldoxime, β-*p*-nitrobenzaldoxime and β-3-nitro-4-methoxybenzaldoxime, respectively, were oxime (7·2 g.; 5·5 g.; 1·45 g.; 4·35 g.), alcohol (50 c.c.; 50 c.c.; 20 c.c.; 60 c.c.), sodium (1·37 g. in 70 c.c. of alcohol; 0·83 g. in 50 c.c.; 0·2 g. in 15 c.c.; 0·51 g. in 30 c.c.), silver nitrate (11 g. in the minimum of water, and 80 c.c. of alcohol added; 6·5 g., and 75 c.c. of alcohol; 2 g., and 15 c.c. of alcohol; 4 g., and 30 c.c. of alcohol). The silver salt so obtained was suspended in a solution of *p*-nitrobenzyl bromide in chloroform and kept in a corked flask in the dark for a week with occasional shaking. The quantities were *p*-nitrobenzyl bromide (9 g.; 4 g.; 1·3 g.; 3·2 g.), chloroform (100 c.c.; 45 c.c.; 30 c.c.; 55 c.c.) respectively. The solution was then filtered, and the chloroform allowed to evaporate spontaneously. In the case of β-benzaldoxime, great difficulty was experienced at first in inducing the residual oil to crystallise. This was overcome by seeding the oil with a little of the crude product of the action of *p*-nitrobenzyl bromide on the sodium salt of β-benzaldoxime and keeping it in an evacuated desiccator for a week in an ice-chest; the pasty mass thus obtained was pressed on a porous tile. Later, when the pure β-*O*-ether was available, it was sufficient to seed the oil with this, keep it as before for 2 days, and press the solid on a tile. In this way, 3·6 g. of a nearly pure product were obtained. On crystallising from alcohol with seeding, β-O-p-*nitrobenzylbenzaldoxime* was obtained in pale yellow crystals, m. p. 54° (Found: N, 11·1; *M*, cryoscopic in benzene, 247. $C_{14}H_{12}O_3N_2$ requires N, 10·9%; *M*, 256). Similarly, after crystallising from acetone and water and then from methyl alcohol, β-O-p-*nitrobenzyl*-p-*methoxybenzaldoxime* was obtained in fine, white needles, m. p. 74° (Found: N, 9·9. $C_{15}H_{14}O_4N_2$ requires N, 9·8%).

The addition of a small amount of α-*O*-*p*-nitrobenzyl-*p*-methoxybenzaldoxime (m. p. 122°) lowered the melting point of the above compound to 69°; with somewhat larger quantities of the α-ether, the mixed melting point lay between 74° and 122°. The β-*O*-*p*-nitrobenzyl ethers of *m*-nitro-, *p*-nitro-, 3 : 4-methylenedioxy-, and 3-nitro-4-methoxy-benzaldoximes were prepared analogously from the silver salts of the respective β-oximes and found to be identical with the compounds obtained from these oximes by the silver oxide method.

Action of Ultra-violet Light on α-O-p-*Nitrobenzyl Ethers.*

The method consisted in exposing a solution of the α-*O*-*p*-nitrobenzyl ether in benzene in a silica vessel to the light of a quartz mercury-vapour lamp at a distance of about 5 inches. The exposure was usually continuous for 72 hours. The benzene was then removed and the crude product, after its melting point had been determined, was fractionally crystallised from suitable solvents. Unless the contrary is mentioned, the products were identified by the method of mixed melting points with ethers otherwise prepared, mixed melting points being taken with both α- and β-ethers.

α-O-p-*Nitrobenzyl*-o-*nitrobenzaldoxime* (m. p. 112°; 1 g. in 25 c.c. of benzene).—The crude product (m. p. 91—92°) was dissolved in the minimum of boiling alcohol; on cooling, crystals, m. p. 99—101°, separated which, on recrystallisation from alcohol, gave unchanged α-*O*-ether. The mother-liquor from the first crystallisation, on being diluted somewhat with water and scratched, gave crystals (m. p. 97—106°) which, recrystallised three times from alcohol, gave the pure β-*O*-ether (m. p. 116°).

α-O-p-*Nitrobenzyl*-m-*nitrobenzaldoxime* (m. p. 87—88°; 1·5 g. in 25 c.c. of benzene).—The crude product (m. p. 73—77°) was dissolved in a small quantity of hot alcohol, containing a little acetone, and the solution cooled with stirring; the product, m. p. 76—78°, thus obtained crystallised from a fairly large volume of alcohol, containing a little acetone, a compound, m. p. 103—104°, being obtained which, after two crystallisations from methyl alcohol, yielded the pure β-*O*-ether (m. p. 118°).

α-O-p-*Nitrobenzyl*-p-*nitrobenzaldoxime* (m. p. 179°; 2 g. in 150 c.c. of benzene).—The crude product (m. p. 150—151°) was treated with boiling acetone, partial solution occurring. The solution was decanted while hot, and the residue, after two crystallisations from much acetone, gave the pure β-*O*-ether (m. p. 184°). The acetone extract, on cooling, gave crystals (m. p. 156—158°) which, after repeated crystallisation from acetone, gave more β-*O*-ether. The mother-liquor from the crystals (m. p. 156—158°) was diluted with water and the precipitate produced was crystallised from acetone; the pure α-*O*-ether was then obtained.

α-O-p-*Nitrobenzyl*-3 : 4-*methylenedioxybenzaldoxime* (m. p. 110°; 1 g. in 40 c.c. of benzene; exposure, 68 hours).—The residue (m. p. 75—90°), after being pressed on a porous tile and washed with a little ether, was dissolved in a hot mixture of alcohol and acetone, and the solution, after cooling, was fractionally precipitated with water. The first and the second fraction, after crystallisation from acetone and water and then from acetone, gave unchanged α-*O*-ether. The third fraction, m. p. 80—85°, crystallised from acetone and water and then from alcohol, gave a very small quantity of somewhat impure β-*O*-ether (m. p. 120°).

α-O-p-*Nitrobenzyl*-p-*methoxybenzaldoxime* (m. p. 122°; 1·5 g. in 45 c.c. of benzene; exposure, 100 hours).—The residue (m. p. 100—105°), on crystallisation from acetone, gave unchanged α-*O*-ether; addition of a little water to the acetone filtrate gave another crop of this compound. The aqueous-acetone filtrate, on spontaneous evaporation, yielded a pasty solid which was pressed on a porous tile and crystallised twice from methyl alcohol; a very small yield of β-*O*-ether was then obtained.

α-O-p-*Nitrobenzyl*-3-*nitro*-4-*methoxybenzaldoxime* (m. p. 117°; 0·75 g. in 45 c.c. of benzene).—The crude product (m. p. 115—126°) was crystallised from benzene and then twice from acetone–alcohol, the pure β-*O*-ether being obtained. The benzene mother-liquor gave only impure β-*O*-ether.

α-O-p-*Nitrobenzyl*-o-*methoxybenzaldoxime* (m. p. 88°; 1·5 g. in 25 c.c. of benzene; exposure, 100 hours).—The crude product (m. p. 78—80°), on crystallisation from alcohol, gave the α-*O*-ether; a second crop of the same compound was obtained by diluting the filtrate with a little water. The aqueous-alcoholic filtrate, on spontaneous evaporation, gave an oil which would not crystallise on being seeded with the α-*O*-ether. It undoubtedly contained the unknown β-*O*-ether, for, after hydrogen chloride had been passed into its chloroform solution and the solvent evaporated, the residue immediately solidified on being scratched and was then found to be almost pure α-*O*-ether (compare below).

α-O-p-*Nitrobenzyl-5-nitro-2-methoxybenzaldoxime* (m. p. 149°; 3 g. in 150 c.c. of benzene; exposure, 96 hours).—The crude product (m. p. 123—126°) was dissolved in 40 c.c. of boiling acetone and, after cooling, fractionally precipitated with water. The first fraction (m. p. 132—139°), after three crystallisations from acetone–alcohol, gave 0·5 g. of β-O-p-*nitrobenzyl-5-nitro-2-methoxybenzaldoxime* in white needles, m. p. 153° (Found: N, 12·8; *M*, cryoscopic in camphor, 357. $C_{15}H_{13}O_6N_3$ requires N, 12·7%; *M*, 331). Admixture with the α-*O*-ether caused a depression of melting point to 128—130°.*

Action of Hydrogen Chloride on β-O-p-*Nitrobenzyl Ethers.*

Hydrogen chloride was passed for 10—20 seconds into a solution of a small quantity of the β-*O*-ether in a little chloroform. The solution was then evaporated, and the product (after crystallisation from alcohol in the case of the ether of cinnamaldoxime) identified as the corresponding α-*O*-ether by the method of mixed melting points. From the ether of benzaldoxime an oil was obtained which, however, immediately solidified on being seeded with a crystal of the α-*O*-ether. With the ethers of *m*-nitro- and 3-nitro-4-methoxybenzaldoximes the oils obtained solidified on being rubbed with a little alcohol. The results are in Table II.

TABLE II.

	Before HCl treatment.		After HCl treatment.		
O-*p*-Nitrobenzyl ether of	M. p.	Mixed m. p. with α-*O*-ether.	M. p.	Mixed m. p. with α-*O*-ether.	M. p. of α-*O*-ether.
β-Cinnamaldoxime	86°	62—63°	77—79°	81—82°	83°
β-Benzaldoxime	54	37—38	57—58	59	60—61
β-*o*-Nitrobenzaldoxime	116	94—95	107—108	110—111	112
β-*m*-Nitrobenzaldoxime	118	77—79	82—83	85—86	87—88
β-*p*-Nitrobenzaldoxime	184	153—155	174—175	177—178	179
β-3 : 4-Methylenedioxybenzaldoxime	125	95	105	107	110
β-*p*-Methoxybenzaldoxime	74	69—70	115—117	119—120	122
β-3-Nitro-4-methoxybenzaldoxime	152	108—109	105—106	111—112	117
β-*o*-Methoxybenzaldoxime	Oil.	—	74—76	78—80	88
β-5-Nitro-2-methoxybenzaldoxime	153	128—130	146	148	149

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* Exposure of a benzene solution of α-5-nitro-2-methoxybenzaldoxime to ultra-violet light for 48 hours did not result in its conversion into the β-isomeride.

Action of p-*Nitrobenzyl Bromide on Sodium Salts of* β-*Aldoximes.*

The general method was to suspend the β-oxime in alcohol and add a solution of sodium ethoxide in alcohol (the oxime then dissolved as the sodium salt) followed by a warm solution of *p*-nitrobenzyl bromide in alcohol. The mixture was at once cooled in running water and then treated as described below.

β-*Benzaldoxime* (6 g. in 25 c.c.; 1·14 g. of sodium in 40 c.c.; 10·71 g. of *p*-nitrobenzyl bromide in 100 c.c. of alcohol).—After being kept for 24 hours, the solution was diluted with water and cooled in ice with stirring. The yellow solid thus obtained was washed with water, dried in the air, and crystallised three times from small quantities of benzene, giving *N*-*p*-nitrobenzylbenzaldoxime, m. p. 110° (Found : N, 11·3. Calc. : N, 10·9%) (compare Behrend and König, *loc. cit.*). No β-*O*-ether could be isolated from the benzene mother-liquors.

The *N*-ether (1 g. in 20 c.c. of benzene) was exposed to ultra-violet light for 54 hours and the solvent was then removed; the residue had a faint odour of benzaldehyde or benzonitrile and consisted practically entirely of unchanged *N*-ether (compare Brady and McHugh, J., 1924, **125**, 553).

N-*p*-Nitrobenzylbenzaldoxime (1 g.) and pure acetic anhydride (5 c.c.) were gently heated together. A somewhat vigorous reaction occurred at the boiling point, and the liquid was immediately cooled, poured into excess of 2*N*-sodium carbonate, and shaken for some time until the odour of the anhydride disappeared. The solid that separated, after being washed with water and crystallised from alcohol, was found to be benzo-*p*-nitrobenzylamide by comparison with an authentic specimen. This amide has been described by Hafner (*Ber.*, 1890, **23**, 339), but several improvements in the method of preparation have been devised. Phthal-*p*-nitrobenzylimide (0·5 g.), prepared from potassium phthalimide and *p*-nitrobenzyl bromide (Hammick and Locket, J., 1922, **121**, 2362; Salkowski, *Ber.*, 1889, **22**, 2142), was heated under reflux for 4 hours with 60% sulphuric acid (30 c.c.)—an improvement on Gabriel's method (*Ber.*, 1887, **20**, 2227). After cooling, the liquid was diluted with water, made alkaline with sodium hydroxide, and extracted with chloroform. The liquid *p*-nitrobenzylamine obtained on removal of the solvent was suspended in 2*N*-sodium hydroxide (30 c.c.) and shaken with benzoyl chloride (1 c.c.) for 30 minutes. The precipitated benzo-*p*-nitrobenzylamide was collected and crystallised from alcohol.

β-o-*Nitrobenzaldoxime* (4 g. in 25 c.c.; 0·56 g. of sodium in 30 c.c.; 5·2 g. of *p*-nitrobenzyl bromide in 50 c.c. of alcohol).—After 12 hours, the yellow precipitate was collected, washed with a little alcohol, dried (yield, 3·7 g.; m. p. 170—175°), and extracted with warm ether; this removed 0·3 g. of material which, after crystallisation from alcohol, gave β-*O*-*p*-nitrobenzyl-*o*-nitrobenzaldoxime. The portion insoluble in ether, after three crystallisations from acetone, gave N-p-*nitrobenzyl*-o-*nitrobenzaldoxime* in long, pale yellow prisms, m. p. 203° (decomp.) (Found: N, 14·1. $C_{14}H_{11}O_5N_3$ requires N, 14·0%).

β-m-*Nitrobenzaldoxime* (7 g. in 30 c.c.; 0·97 g. of sodium in 50 c.c.; 9·11 g. of *p*-nitrobenzyl bromide in 120 c.c. of alcohol).—After 12 hours, the precipitate was collected, washed with alcohol and dried (yield, 12 g.; m. p. 215—218°). Crystallised from boiling glacial acetic acid, it gave N-p-*nitrobenzyl*-m-*nitrobenzaldoxime* in canary-yellow prisms, m. p. 223° (decomp.), which were very sparingly soluble in most organic solvents (Found: N, 14·2. $C_{14}H_{11}O_5N_3$ requires N, 14·0%). The alcoholic filtrate from the *N*-ether was largely diluted with water and after 12 hours 0·6 g. of impure β-*O*-ether had separated (m. p. 90—103°). This was extracted with hot methyl alcohol, a little insoluble *N*-ether separated, and the filtrate cooled and diluted with water. The precipitated compound was pressed on a porous tile, washed with a little ether, and crystallised from methyl alcohol; pure β-*O*-*p*-nitrobenzyl-*m*-nitrobenzaldoxime was then obtained.

β-p-*Nitrobenzaldoxime* (5·42 g. in 60 c.c.; 0·75 g. of sodium in 30 c.c.; 7·05 g. of *p*-nitrobenzyl bromide in 100 c.c. of alcohol).—After 12 hours, the precipitate was washed with alcohol, dried (yield, 9·8 g.; m. p. 216—221°), and extracted with boiling acetone. The filtered extract was evaporated on the water-bath, leaving a solid residue. This was boiled with acetone, and the cooled, filtered solution was diluted with water, producing a precipitate which, crystallised from acetone and water and then twice from acetone, gave a very small quantity of β-*O*-*p*-nitrobenzyl-*p*-nitrobenzaldoxime. The residue from the first acetone extraction, after crystallisation from boiling pyridine, gave *N*-*p*-nitrobenzyl-*p*-nitrobenzaldoxime, m. p. 234—235° (decomp.). This compound was prepared by Behrend and König (*loc. cit.*) by the oxidation of *NN'*-di-*p*-nitrobenzylhydroxylamine. They give m. p. 227—228°, and we have found that this is the maximum melting point attainable if acetic acid or nitrobenzene, the solvents used by those authors, is employed for crystallisation.

β-3 : 4-*Methylenedioxybenzaldoxime* (3·3 g. in 40 c.c.; 0·46 g. of sodium in 30 c.c.; 4·32 g. of *p*-nitrobenzyl bromide in 60 c.c. of alcohol).—The solid was crystallised from acetone and water and then twice from acetone–alcohol, N-p-*nitrobenzyl*-3 : 4-*methylene-*

dioxybenzaldoxime being obtained in deep canary-yellow leaflets, m. p. 144° (Found : N, 9·3. $C_{15}H_{12}O_5N_2$ requires N, 9·3%). No β-*O*-ether could be isolated from the various mother-liquors.

β-p-*Methoxybenzaldoxime* (7·65 g. in 60 c.c.; 1·17 g. of sodium in 60 c.c.; 10·94 g. of *p*-nitrobenzyl bromide in 100 c.c. of alcohol).—After 24 hours, water (700 c.c.) was added to the mixture, and the precipitated solid was collected and air-dried (yield, 13·85 g.; m. p. 90—100°). After two crystallisations from acetone, N-p-*nitrobenzyl*-p-*methoxybenzaldoxime* was obtained in yellow needles, m. p. 150° (Found : N, 9·8. $C_{15}H_{14}O_4N_2$ requires N, 9·8%). The acetone mother-liquor from the first crop of crystals of the *N*-ether gave, on dilution, a further crop of *N*-ether. The aqueous-acetone filtrate was allowed to evaporate spontaneously and the solid obtained was extracted with boiling ether (100 c.c.), some *N*-ether remaining undissolved. Light petroleum (75 c.c.) was added to the solution; a sticky precipitate was then obtained which was rejected. The ether–light petroleum filtrate, on evaporation in a current of air, gave 0·9 g. of material which yielded, after crystallisation from methyl alcohol, β-*O*-*p*-nitrobenzyl-*p*-methoxybenzaldoxime.

β-3-*Nitro*-4-*methoxybenzaldoxime* (3·55 g. in 40 c.c.; 0·42 g. of sodium in 30 c.c.; 3·91 g. of *p*-nitrobenzyl bromide in 40 c.c. of alcohol).—After 12 hours, the yellow precipitate was collected (yield 6 g.) and crystallised twice from acetone, giving N-p-*nitrobenzyl*-3-*nitro*-4-*methoxybenzaldoxime* in bright yellow needles, m. p. 232° (decomp.) (Found : N, 12·8. $C_{15}H_{13}O_6N_3$ requires N, 12·7%). The acetone mother-liquor from the first crystallisation was evaporated to dryness, and the residue extracted with boiling chloroform. The extract was separated from undissolved *N*-ether and evaporated to dryness; the residue (0·8 g.), after two crystallisations from alcohol–acetone, gave β-*O*-*p*-nitrobenzyl-3-nitro-4-methoxybenzaldoxime.

Hydrolysis of N-p-*Nitrobenzyl Ethers.*

N-*p*-Nitrobenzyl-*p*-methoxybenzaldoxime (4·3 g.) was triturated with 160 c.c. of concentrated hydrochloric acid; the mixture was then boiled under reflux for an hour, diluted with a little water, cooled, and extracted with chloroform. The extract, on evaporation, gave an oil which was identified as *p*-methoxybenzaldehyde by conversion into the semicarbazone, the yield of this compound being 2·8 g. (calc., 2·9 g.). The aqueous layer was evaporated to dryness on the water-bath; the *N*-*p*-nitrobenzylhydroxylamine hydrochloride that remained (yield, 2·7 g.; calc., 3·1 g.), on crystallisation from absolute alcohol by addition of ether, gave the pure compound, m. p. 179—181° (compare Behrend and König, *Annalen*, 1891, **263**, 190). By addition of 2*N*-sodium carbonate to a concentrated aqueous solution of the hydrochloride, the free base was obtained, m. p. 120—122° after crystallisation from hot water (Behrend and König, *loc. cit.*). This method of preparing *N*-*p*-nitrobenzylhydroxylamine from *p*-methoxybenzaldoxime *N*-*p*-nitrobenzyl ether is preferable to that described by the above authors, since β-*p*-methoxybenzaldoxime is one of the easiest β-aldoximes to obtain pure and in quantity and the *N*-*p*-nitrobenzyl ether is more easily hydrolysed than that of *p*-nitrobenzaldoxime owing to the very sparing solubility of the latter.

The *N*-*p*-nitrobenzyl ethers of benzaldoxime, 3 : 4-methylenedioxy-, *o*-methoxy-, and 5-nitro-2-methoxy-benzaldoximes were hydrolysed in an analogous way; benzaldehyde and *o*-methoxybenzaldehyde were identified as semicarbazones and 3 : 4-methylenedioxy- and 5-nitro-2-methoxy-benzaldehydes as α-oximes.

N-*p*-Nitrobenzyl-*m*-nitrobenzaldoxime (8 g.) was triturated with 200 c.c. of boiling concentrated hydrochloric acid, and steam was rapidly passed through the mixture for 5 hours. The distillate on extraction with chloroform gave 3·9 g. of *m*-nitrobenzaldehyde (calc., 4·0 g.). The liquid in the flask on evaporation to dryness on the water-bath gave 5·2 g. of crude *N*-*p*-nitrobenzylhydroxylamine (calc., 5·4 g.), which was identified as before.

The *N*-*p*-nitrobenzyl ethers of *o*- and *p*-nitro- and 3-nitro-4-methoxy-benzaldoximes were hydrolysed similarly to the *m*-nitro-derivative. In the case of *N*-*p*-nitrobenzyl-*p*-nitrobenzaldoxime, hydrobromic acid proved more satisfactory than hydrochloric acid. 3-Nitro-4-methoxybenzaldehyde was obtained as an oil and identified by conversion into the α-oxime.

Action of N-p-*Nitrobenzylhydroxylamine on Aldehydes.*

An alcoholic solution of the aldehyde was treated successively with alcoholic solutions of *N*-*p*-nitrobenzylhydroxylamine hydrochloride and potassium acetate, and the mixture kept for a definite time.

Cinnamaldehyde (1·9 g. in 4 c.c.; *N*-*p*-nitrobenzylhydroxylamine hydrochloride, 3·2 g., in 24 c.c.; potassium acetate, 2 g., in 20 c.c.).—After 12 hours, the precipitate was washed with a little alcohol and with water; 2·6 g. were then obtained. A further crop of 1·4 g. was obtained by diluting the mother-liquors.

N-p-*Nitrobenzylcinnamaldoxime* crystallises from benzene in lemon-yellow needles, m. p. 135° (Found : N, 9·9. $C_{16}H_{14}O_3N_2$ requires N, 9·9%). This compound could not be prepared by the action of *p*-nitrobenzyl bromide on the sodium salt of β-cinnamaldoxime, the products under various conditions being brown tars from which nothing crystalline could be isolated. On hydrolysis with hydrochloric acid, the *N*-ether behaved abnormally, giving a yellow, crystalline substance mixed with a resinous material from which it could not be separated.

o-*Methoxybenzaldehyde* (0·5 g. in 5 c.c.; hydrochloride, 0·83 g., in 5 c.c.; acetate, 0·5 g., in 5 c.c. of alcohol).—0·72 G. of crude *N*-ether crystallised and a further 0·12 g. was obtained by diluting the mother-liquor. N-p-*Nitrobenzyl*-o-*methoxybenzaldoxime* crystallises from alcohol in very pale yellow, fern-like crystals, m. p. 141° (Found : N, 10·2. $C_{15}H_{14}O_4N_2$ requires N, 9·8%).

5-*Nitro-2-methoxybenzaldehyde* (2 g. in 25 c.c. of warm alcohol; hydrochloride, 2·3 g., in 20 c.c.; acetate, 1·4 g., in 20 c.c. of alcohol). —After being kept in cold water for an hour, the precipitate was collected and washed with water and with alcohol (yield 3·2 g.). N-p-*Nitrobenzyl-5-nitro-2-methoxybenzaldoxime* crystallises from nitrobenzene in yellow prisms, m. p. 237° (decomp.) (Found : N, 13·3. $C_{15}H_{13}O_6N_3$ requires N, 12·7%).

m-*Nitrobenzaldehyde* (0·37 g. in 5 c.c.; hydrochloride, 0·6 g., in 10 c.c.; acetate, 0·35 g., in 5 c.c.).—The reaction mixture was kept for 30 minutes and then diluted with water; an almost quantitative yield of *N*-*p*-nitrobenzyl-*m*-nitrobenzaldoxime was obtained identical with that prepared from the sodium salt of the β-oxime. There was no indication of the formation of a second isomeride.

*The System α-Benzaldoxime–*p*-Nitrobenzyl Bromide.*

The α-benzaldoxime was crystallised from benzene and light petroleum; it melted in a capillary tube at 34° and froze in bulk at 32·9°. The *p*-nitrobenzyl bromide was crystallised first from light petroleum and then from alcohol; it melted in a capillary tube at 100° and froze in bulk at 97·9°. Cooling curves were constructed for mixtures of the two compounds in a vacuum-lagged silica vessel. It was found necessary to seed mixtures containing more than 87% of α-benzaldoxime with a crystal of α-benzaldoxime in order to induce crystallisation. The freezing points are given in Table III (*a* = molecular percentage of α-benzaldoxime).

TABLE III.

a.	F. p.	*a*.	F. p.	*a*.	F. p.	Eutectic.
0	97·9°	54·3	72·5°	85·6	37·8°	
4·3	96·1	61·1	67·7	88·9	27·8	27·2°
8·2	94·3	67·0	63·6	91·1	27·4	27·3
11·8	93·0	74·0	57·2	94·7	29·4	
18·1	89·2	78·1	51·7	97·3	30·8	
37·3	80·9	81·6	45·4	98·9	31·7	
47·2	76·5	83·6	41·2	100	32·9	

No indication of the formation of a compound was obtained. Equimolecular quantities of α-benzaldoxime and *p*-nitrobenzyl bromide dissolved in the minimum quantity of dry benzene were kept for 6 months. On removing the benzene, an oily solid was obtained which had the characteristic odour of α-benzaldoxime and, after being pressed on a porous tile, left a residue of *p*-nitrobenzyl bromide.

O-*Methyl Ethers of* m-*Nitrobenzaldoxime.*

Methoxyl Content and Molecular Weights.—The ethers employed were those prepared by Brady, Dunn, and Goldstein (J., 1926, 2398, 2402). α-*O*-Methyl-*m*-nitrobenzaldoxime has m. p. 63° (Found: OMe, 16·7; *M*, microcryoscopic in camphor, 181. Calc.: OMe, 17·2%; *M*, 180). β-*O*-Methyl-*m*-nitrobenzaldoxime has m. p. 75° (Found: OMe, 16·8%; *M*, microcryoscopic in camphor, 174).

Action of O-*Methylhydroxylamine on* m-*Nitrobenzaldehyde.*—The pure aldehyde (10 g.), dissolved in alcohol (150 c.c.), was mixed with *O*-methylhydroxylamine (3·3 g.) in alcohol (15 c.c.) and kept for 65 hours in a corked flask in the dark. The products were then precipitated in three fractions by very gradual addition of water with thorough stirring; in order to induce the third fraction to crystallise it was necessary to cool the mixture in ice. Fractions 1 and 2, constituting the bulk of the product (about 9 g.), were almost pure α-*O*-methyl-*m*-nitrobenzaldoxime (m. p. 63°). Fraction 3 (m. p. 42—44°) was redissolved in a small quantity of hot alcohol; from the cooled solution, more of the α-*O*-ether separated. The mother-liquor was cooled in ice and a little water added; a mixture then separated (m. p. 43—45°). After removal of this, further dilution followed by cooling in ice gave a product, m. p. 55—60°, which, after crystallisation from light petroleum, yielded a small quantity of nearly pure β-*O*-methyl-*m*-nitrobenzaldoxime, m. p. 70—71°; this melted at 73—74° and 45—50° when mixed with equal amounts of pure β-*O*-ether and α-*O*-ether, respectively. A similar result had previously been obtained by one of us using *O*-methylhydroxylamine hydrochloride, decomposed by sodium ethoxide in alcohol, and considerably smaller quantities of material.

*Action of Ultra-violet Light on Some α-*O*-Methyl Ethers.*

α-O-*Methyl*-6-*nitro*-3 : 4-*methylenedioxybenzaldoxime.*—The ether was prepared by methylation of the oxime (Brady, Dunn, and Goldstein, *loc. cit.*). The same compound is formed when 6-nitro-3 : 4-methylenedioxybenzaldehyde (1 g.) in warm alcohol (40 c.c.) is mixed with a solution of *O*-methylhydroxylamine hydrochloride (0·5 g.) in a little water which has been treated with sodium ethoxide in alcohol (0·14 g. of sodium in 25 c.c. of alcohol); after a few hours crystals of the α-*O*-ether separate. The α-*O*-ether (2·5 g.), dissolved in benzene (100 c.c.), was exposed in a quartz flask to ultra-violet light for 72 hours. A small amount of brown, flocculent precipitate was removed, the solution evaporated, and the residue, m. p. 99—104°, dissolved in warm acetone (40 c.c.). The cold solution was then fractionally precipitated with water. The first fraction was the α-*O*-ether (m. p. 147°). The second and third fractions (m. p. 100—105°) were combined and crystallised four times from alcohol; 0·2 g. of β-O-*methyl*-6-*nitro*-3 : 4-*methylenedioxybenzaldoxime* was then obtained in long, straw-coloured needles, m. p. 122° (Found : N, 12·7. $C_9H_8O_5N_2$ requires N, 12·5%). A mixture of approximately equal quantities of the α- and β-*O*-ethers melted at 107—108°. The β-*O*-ether, when dissolved in chloroform and treated for a few seconds with hydrogen chloride, is converted into the α-*O*-ether, the solution on evaporation giving a product which melts at 146°, and at 147° when mixed with α-*O*-ether.

α-O-*Methyl*-3-*nitro*-4-*methoxybenzaldoxime*.—Similar treatment of this compound resulted in partial inversion, but the product (m. p. 103—104°) could not be separated into its components. When it was dissolved in chloroform and treated with hydrogen chloride, and the solution was evaporated to dryness, the mixture was reconverted into the α-ether.

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