726. *The Isomerism of the Oximes. Part XLIV.* Alkylcinnamaldoximes, Aroylaldoximes, and the Action of Potassium Cyanide and Sodium Sulphite on Aldoximes and their* O*-Methyl Ethers.*

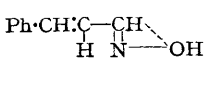
By M. Benger and O. L. Brady.

A number of α-alkylcinnamaldoximes have been studied; unlike the cinnamaldoxime and other substituted derivatives thereof these compounds could be obtained in only one form which probably has the α-configuration. Various aroyl derivatives of aldoximes have been prepared and their hydrolysis investigated.

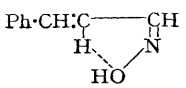
This communication deals with a variety of experimental observations to which reference will be made in subsequent papers but which did not, when first made, seem worthy of further development.

Cinnamaldehyde, unlike aldehydes in which the CHO group is attached directly to the benzene ring, on oximation in alkaline solution gives a mixture of the α- and β-isomerides in which the β-isomeride predominates (Bamberger and Goldschmidt, *Ber.*, 1894, **27**, 3429). On the other hand *o*-, *m*-, and *p*-nitro- and *o*-methoxy-cinnamaldehydes under these conditions give mainly the α-aldoximes (Brady and Thomas, *J.*, 1922, **121**, 2098; Brady and Grayson, *J.*, 1924, **125**, 1418).

It was thought that the behaviour of cinnamaldehyde was associated with the possibility in the cinnamaldoximes of a lone pair of electrons of the oxygen atom being associated with one or other of two methine-hydrogen atoms :



α-Cinnamaldoxime

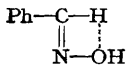


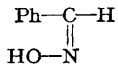
β-Cinnamaldoxime

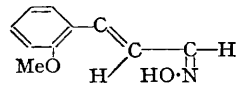
Since the hydrogen bonding here implied is now generally regarded as an electrostatic effect the consideration of ring size is not critical but the influence of the lone pair of electrons of the oxygen in, for example, α-benzaldoxime will be small owing to the distance between the oxygen and the methine hydrogen yet, nevertheless, it may be enough, in

* Part XLIII, *J.*, 1950, 1243.

the absence of other possibilities of hydrogen bonding, to stabilise the α- relative to the β-isomeride. It will, at least, help to account for the fact that the α-aldoxime is a considerably stronger acid than the β-aldoxime.


α-Benzaldoxime


β-Benzaldoxime


β-*o*-Methoxycinnamaldoxime

This view will be developed in subsequent communications.

In the case of β-cinnamaldoxime the distance between the oxygen and the second methine-hydrogen atom can be less and consequently the β-isomeride is stabilised. In the nitrocinnamaldoximes the electron-withdrawing influence of the nitro-group will militate against hydrogen bonding, and in *o*-methoxycinnamaldoxime the oxygen of the methoxyl group can act as a competitor with the oximino-oxygen for the hydrogen bonding in the β-isomeride.

It is noteworthy that the ratio of the dissociation constants of the α- and the β-isomerides of benzaldoxime and of substituted benzaldoximes is about 4·5, whereas the ratio for α- and β-cinnamaldoximes is about 2·1 or much the same as that for α- and β-*p*-nitrobenzophenone oximes (Brady and Chokshi, *J.*, 1929, 946; Brady and Goldstein, *J.*, 1926, 1918). In the case of α- and β-benzaldoximes the higher dissociation constant of the α-isomeride indicates a lower electron density at its oxygen atom than at that of the β-isomeride, and this may be due to potential hydrogen bonding in the α-isomeride which is absent in the β-isomeride and in both α- and β-unsymmetrical benzophenoneoximes. The dissociation constants of α-benzaldoxime and α-cinnamaldoxime are about the same, but that of β-cinnamaldoxime is about three times that of β-benzaldoxime, which may be due to hydrogen bonding in the case of β-cinnamaldoxime.

In order to test this hypothesis the α-alkylcinnamaldoximes have been investigated as in their β-isomerides hydrogen bonding could not arise. Unfortunately the α-alkylcinnamic aldehydes on oximation gave one form of oxime only, and attempts to obtain the other isomeride by the usual methods were unsuccessful.

In the absence of the second isomeride one cannot decide with certainty the configuration of these compounds since the standard method depends on the relative ease of attack of OH^- on the methine-hydrogen atom or on the carbonyl group of the acetyl derivatives of the two isomerides, to give either nitrile or the original oximes; it does not, as often assumed, depend on an absolute difference in behaviour of the two isomerides (Hauser, Jordan, and O'Connor, *J. Amer. Chem. Soc.*, 1935, **57**, 2456; Benger and Brady, *J.*, 1950, 1221). For this reason the results give no certain support for our hypothesis, but the oximes behave more like α- than like β-aldoximes. For example, their acetyl derivatives on hydrolysis give mainly the original oxime; they give benzoyl derivatives which are hydrolysed to the original oxime instead of to the stereoisomeride (Brady and Thomas, *loc. cit.*; Brady and McHugh, *J.*, 1925, **127**, 2414); and α-methyl- and α-phenyl-cinnamaldoxime with 1-chloro-2 : 4-dinitrobenzene give dinitrophenyl ethers, but α-*n*-amylcinnamaldoxime resembles a β-oxime, giving dinitrophenol and α-*n*-amylcinnamaldehyde (Brady and Truszkowski, *J.*, 1924, **125**, 1087). On the other hand, the electron supply from the groups in the α-position may so stabilise the methine-hydrogen atom against removal by OH^- that even if the oximes have the β-configuration their acetyl derivatives may give but little nitrile on hydrolysis. Against this, however, is the fact that the acetyl derivatives of acetaldoxime and β-phenylpropaldoxime give mainly nitrile on alkaline hydrolysis.

Some approximate experiments have been performed on the relative amounts of oxime and nitrile formed in the alkaline hydrolysis of the acetyl derivatives, by determining the oxime formed by treatment with dinitrophenylhydrazine in ethanolic sulphuric acid (Brady and Peakin, *J.*, 1929, 478). The acetyl derivative of α-*n*-amylcinnamaldoxime gave 98% of oxime, of α-ethylcinnamaldoxime 71%, of α-phenylcinnamaldoxime 62%, of β-cinnamaldoxime 16%, of β-phenylpropaldoxime 19%, and of acetaldoxime 25%, on hydrolysis with ethanolic potassium hydroxide at room temperature.

Benger and Brady (*loc. cit.*) showed that, if the group attached to the oximino-oxygen atom was sufficiently electron-attracting, nitrile was obtained in appreciable quantities on alkaline hydrolysis at low temperatures even from the α-isomeride, *e.g.*, α-trichloroacetyl-*p*-nitrobenzaldoxime with 2N-sodium hydroxide at 0° gave 35% of nitrile. We have prepared the *o*-nitro-, *p*-nitro-, 3 : 5-dinitro-, and *p*-methoxy-benzoyl derivatives of a number of α-aldoximes and the phenylacetyl derivative of α-*p*-nitrobenzaldoxime to find out how far such substituents would favour nitrile formation on alkaline hydrolysis. At room temperature with ethanolic potassium hydroxide the *o*-nitrobenzoyl, *p*-nitrobenzoyl, and 3 : 5-dinitrobenzoyl derivatives of α-*o*-nitrobenzaldoxime gave mainly *o*-nitrobenzonitrile and a little α-*o*-nitrobenzaldoxime, but the α-*p*-methoxybenzoate gave mainly *o*-nitrobenzaldoxime and a little *o*-nitrobenzonitrile. These results are as expected, since the *o*-nitro-group greatly activates the methine-hydrogen atom, only *o*-nitro-substituted α-aldoximes are converted into nitriles by alkali, in other cases the oxime must be suitably acylated first (Reissert, *Ber.*, 1908, **41**, 3815; Brady and Goldstein, *J.*, 1926, 1918). The substituted benzoyl derivatives of other aldoximes regenerated the original oxime, as also did α-*p*-nitrobenzaldoxime phenylacetate.

Passerini (*Gazzetta*, 1926, **56**, 274) has stated that α- and β-*p*-methoxybenzaldoximes, among others, are converted into nitriles by boiling ethanolic potassium cyanide, but we have been unable to repeat his results with α-aldoximes except in the case of α-*o*-nitrobenzaldoxime.

The action of aqueous sodium sulphite on some α-aldoximes and their *O*-methyl ethers has also been investigated. When the aldoxime contained a nitro-group in the *o*-position amides were obtained, but not in other cases. It is probable that these amides were formed through the nitrile, as it has been found that benzonitrile and nitrobenzonitriles give amides more or less readily in boiling aqueous sodium sulphite but that such compounds as *p*-methoxy- and 3 : 4-methylenedioxy-benzonitrile do not do so even after 8 hours' boiling.

The action of sodium sulphite on *O*-methyl ethers is interesting. α-*O*-Methyl-*o*-nitro- and α-*O*-methyl-3 : 4-methylenedioxy-6-nitro-benzaldoxime gave good yields of the amide, but α-*o*-methoxy-*O*-methyl- and α-*O*-methyl-3 : 4-methylenedioxy-benzaldoxime were unaffected. α-*O*-Methyl-*p*-nitrobenzaldoxime yielded a considerable amount of α-*p*-nitrobenzaldoxime, and α-*O*-methyl-*m*-nitrobenzaldoxime a small amount of α-*m*-nitrobenzaldoxime. It seems probable therefore that the sodium sulphite surprisingly acts in the first instance as a demethylating agent to *O*-methyl ethers of oximes containing a nitro-group, and that, if the nitro-group is in the *o*-position, the resulting oxime is converted, as before, into the amide.

Experimental

α-*Alkylcinnamaldoximes* *.—α-Methyl-, α-ethyl-, α-*n*-amyl-, and α-phenyl-cinnamaldehydes were prepared by a Claisen condensation of benzaldehyde with propaldehyde, *n*-butyraldehyde, heptaldehyde, and phenylacetaldehyde respectively. α-*Phenylcinnamaldehyde* formed colourless plates (from ethanol), m. p. 95°, b. p. 208°/16 mm. (Found: C, 86·1; H, 5·8. $C_{15}H_{12}O$ requires C, 86·5; H, 5·8%). The following were prepared by the action of dinitrophenylhydrazine sulphate in ethanol: α-*methylcinnamaldehyde* 2 : 4-*dinitrophenylhydrazone*, red plates (from benzene), m. p. 208° (Found: C, 58·6; H, 4·2. $C_{16}H_{14}O_4N_4$ requires C, 58·9; H, 4·0%); α-ethylcinnamaldehyde 2 : 4-dinitrophenylhydrazone, dark red prisms (from benzene), m. p. 188°; α-n-*amylcinnamaldehyde* 2 : 4-*dinitrophenylhydrazone*, red plates (from benzene), m. p. 168° (Found: C, 62·0; H, 5·8. $C_{20}H_{22}O_4N_4$ requires C, 62·8; H, 5·7%); and α-*phenylcinnamaldehyde* 2 : 4-*dinitrophenylhydrazone*, vermilion prisms (from xylene), m. p. 239° (Found: C, 64·4; H, 4·1. $C_{21}H_{16}O_4N_4$ requires C, 64·9; H, 4·1%).

The oximes were prepared by mixing an ethanolic solution of 1 mol. of the aldehyde with ethanolic solutions of 1½ mols. each of hydroxylamine hydrochloride and sodium hydroxide. After a few minutes' warming the clear solution was decanted from the precipitated sodium chloride into a large volume of dilute hydrochloric acid, and the precipitated oxime collected, washed with water, and crystallised. Thus were obtained: α-*methylcinnamaldoxime*,* silky

* In all cases the α indicates the position of the alkyl group and not the configuration of the aldoxime.

needles (from ethanol), m. p. 130° (Found: C, 73·8; H, 6·8. $C_{10}H_{11}ON$ requires C, 74·4; H, 6·8%); α-*ethylcinnamaldoxime*, stout needles (from light petroleum), m. p. 103° (Found: C, 75·4; H, 7·4. $C_{11}H_{13}ON$ requires C, 75·4; H, 7·4%); α-n-*amylcinnamaldoxime*, plates (from light petroleum), m. p. 70° (Found: C, 77·7; H, 8·6. $C_{14}H_{19}ON$ requires C, 77·4; H, 8·8%); and α-*phenylcinnamaldoxime*, prisms (from ethanol), m. p. 165° (Found: C, 80·9; H, 5·6. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·8%).

α-Methylcinnamaldoxime was acetylated by the standard method, giving an uncrystallisable oil which on hydrolysis with alcoholic 0·5N-potassium hydroxide regenerated the original oxime in good yield. As the oxime is insoluble in 2N-alkali it was dissolved in 4 times its weight of cold benzoyl chloride, kept for 1 hr., and shaken with a large excess of 2N-sodium carbonate. Crystallising the precipitate from benzene gave α-*methylcinnamaldoxime benzoate* in colourless prisms, m. p. 77° (Found: C, 77·1; H, 5·7. $C_{17}H_{15}O_2N$ requires C, 77·0; H, 5·6%). Hydrolysis with alcoholic potassium hydroxide regenerated the original oxime. Ethanolic solutions of equimolecular amounts of the oxime, 1-chloro-2 : 4-dinitrobenzene, and sodium were mixed and warmed; O-2 : 4-*dinitrophenyl*-α-*methylcinnamaldoxime* separated slowly and crystallised from benzene in very pale greenish-yellow needles, m. p. 162° (Found: C, 58·5; H, 3·7. $C_{16}H_{13}O_5N_3$ requires C, 58·7; H, 4·0%). A solution of the oxime is dry ether, on saturation with hydrogen chloride, gave α-methylcinnamaldoxime hydrochloride as a bright yellow powder, m. p. 145°, which with 2N-sodium carbonate regenerated the original oxime.

α-*n*-Amylcinnamaldoxime, acetylated by the standard method, gave its *acetate* as colourless needles (from benzene), m. p. 37° (Found: C, 73·9; H, 8·0. $C_{16}H_{21}O_2N$ requires C, 74·1; H, 8·1%). Alkaline hydrolysis of this compound gave a good yield of the original oxime. Its *benzoate*, prepared as above, separated as an oil which crystallised after 10 weeks in a desiccator as colourless needles, m. p. 36°, but could not be recrystallised (Found: C, 79·8; H, 7·2. $C_{21}H_{23}O_2N$ requires C, 78·5; H, 7·2%). Alkaline hydrolysis regenerated the original oxime. α-*n*-Amylcinnamaldoxime hydrochloride, m. p. 82°, was formed as a white precipitate by passing hydrogen chloride into a dry ethereal solution of the oxime and regenerated the original oxime with 2N-sodium carbonate. When α-*n*-amylcinnamaldoxime was treated with 1-chloro-2 : 4-dinitrobenzene and sodium ethoxide in ethanol, only sodium dinitrophenoxide and α-*n*-amylcinnamaldehyde, identified after steam-distillation as its dinitrophenylhydrazone, could be isolated. α-*n*-Amylcinnamaldoxime (10 g.) was boiled under reflux with acetic anhydride (25 c.c.) for 2 hr., excess of anhydride removed with 2N-sodium carbonate, and the oil extracted with ether and distilled under reduced pressure; α-n-*amylcinnamonitrile* was obtained as a yellow liquid, b. p. 174—176°/16 mm. (Found: C, 83·9; H, 8·6. $C_{14}H_{17}N$ requires C, 83·9; H, 8·5%). On hydrolysis with ethanolic potassium hydroxide it gave α-n-*amylcinnamic acid*, colourless needles (from ethanol), m. p. 118° (Found: C, 77·3; H, 8·6. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·3%).

α-Phenylcinnamaldoxime, treated as above, gave its *acetate* as colourless crystals (from ethanol), m. p. 105° (Found: C, 76·7; H, 5·5. $C_{12}H_{15}O_2N$ requires C, 77·0; H, 5·7%), which on alkaline hydrolysis gave the original oxime; and the 2 : 4-*dinitrophenyl ether* as pale yellow needles (from acetone), m. p. 194° (Found: C, 64·3; H, 4·0. $C_{21}H_{15}O_5N_3$ requires C, 64·8; H, 3·9%). A solution of the oxime in ether gave no precipitate with hydrogen chloride; evaporating the ether in a current of dry air gave a yellow gum which effervesced with sodium carbonate and gave the original oxime.

Solutions of the above oximes in benzene were exposed in a quartz vessel to ultra-violet light for 72 hr., but no indication of isomerisation was observed (cf. Brady and McHugh, *J.*, 1924, **125**, 547).

Quantitative Hydrolysis of Acetyl Derivatives.—A weighed quantity of the oxime was dissolved at 20° in about double of the amount of pure acetic anhydride required to acetylate it, then kept for 5 min., and the solution was added to twice the amount of ethanolic 2N-potassium hydroxide required to neutralise the total acetic anhydride employed; this avoided the troublesome isolation of liquid acetyl derivatives (cf. Benger and Brady, *J.*, 1950, 1221). The solution was kept for 1 hr. with occasional shaking and acidified with dilute sulphuric acid, the potassium sulphate which crystallised removed, and a slight excess of an ethanolic solution of 2 : 4-dinitrophenylhydrazine sulphate added. The solution was warmed, then kept for 2 hr., and the precipitated dinitrophenylhydrazone collected, washed with a little ethanol, then with water, dried, and weighed. In the case of acetaldoxime, since acetonitrile is miscible with water, and acetaldehyde dinitrophenylhydrazone is appreciably soluble in alcohol, a dilute solution of 2 : 4-dinitrophenylhydrazine hydrochloride in 2N-hydrochloric acid was used instead of the sulphate. The results are recorded above.

Substituted Benzoyl Derivatives of Substituted Benzaldoximes.—The *products* listed in the Table were prepared by shaking a solution of the oxime in excess of 2N-sodium hydroxide with a solution of a slight excess of the appropriate acid chloride dissolved in the minimum amount of ether or chloroform, the mixture being kept alkaline throughout the reaction; as the products were sparingly soluble in ether or chloroform they could be collected by filtration.

α-p-*Nitrobenzaldoxime O-phenylacetate* was prepared by treating α-*p*-nitrobenzaldoxime (3 g.) with a solution of phenylacetic anhydride (8 g.) in the minimum of dry ether at room temperature. After 1 hr. the ether was removed by a current of air, and the oily residue shaken with 2N-sodium carbonate, and the solid obtained crystallised from benzene–light petroleum as colourless plates, m. p. 109° (Found: C, 63·0; H, 4·2. $C_{15}H_{12}O_4N_2$ requires C, 63·4; H, 4·2%).

The acyl derivatives (1 g. each) were hydrolysed by being kept for 12 hr. at room temperature with ethanolic 0·5N-potassium hydroxide (60 c.c.), and the mixtures were poured into a slight excess of saturated ammonium chloride solution. Most of the alcohol was removed on the water-bath, and the product examined for oxime, nitrile, or amide. *o*-Nitrobenzaldoxime *o*- and *p*-nitro- and 3 : 5-dinitro-benzoate gave mainly *o*-nitrobenzonitrile and a little α-*o*-nitrobenzaldoxime, whereas the *p*-anisoate gave mainly α-*o*-nitrobenzaldoxime and a little *o*-nitrobenzonitrile. The other compounds gave the corresponding α-aldoxime, except *p*-dimethylaminobenzaldoxime 3 : 5-dinitrobenzoate which yielded only a tar.

Substituted α-O-*acylbenzaldoximes*, Ar·CH:N·OAr'.

Substituents in Ar	Substituents in Ar'	M. p.	Solvent for crystn.*	Found (%) C	Found (%) H	Formula	Reqd. (%) C	Reqd. (%) H
o-NO_2	*o*-NO_2	142°	AcOH	53·3	2·7	$C_{14}H_9O_6N_3$	53·3	2·9
,,	*p*-NO_2	178	,,	53·3	2·8	,,	,,	,,
,,	3 : 5-$(NO_2)_2$	184	,,	46·5	2·3	$C_{14}H_8O_8N_4$	46·6	2·2
,,	*p*-MeO	125	,,	60·2	4·0	$C_{15}H_{12}O_5N_2$	60·0	4·0
p-NO_2	*p*-NO_2	193	,, [a]	53·2	3·0	$C_{14}H_9O_6N_3$	53·3	2·9
,,	*o*-NO_2	178	,, [b]	53·3	2·9	,,	,,	,,
,,	3 : 5-$(NO_2)_2$	180	,, [a, b]	46·5	2·4	$C_{14}H_8O_8N_4$	46·6	2·2
,,	*p*-MeO	179	EtOH [c]	60·2	4·0	$C_{15}H_{12}O_5N_2$	60·0	4·0
p-MeO	*p*-NO_2	164	,, [d]	60·2	4·0	,,	,,	,,
,,	*p*-MeO	150	C_6H_6	67·4	5·3	$C_{16}H_{15}O_4N$	67·4	5·3
3 : 4-$(MeO)_2$	*p*-NO_2	178	$COMe_2$ [e]	57·2	3·2	$C_{15}H_{10}O_6N_2$	57·3	3·2
,,	*o*-NO_2	128	EtOH	57·5	3·4	,,	,,	,,
,,	3 : 5-$(NO_2)_2$	193	$COMe_2$–EtOH [f]	50·0	2·7	$C_{15}H_9O_8N_3$	50·1	2·5
,,	*p*-MeO	188	C_6H_6	64·4	4·4	$C_{16}H_{13}O_5N_3$	64·2	4·4
p-NMe_2	*o*-NO_2	122	C_6H_6–Pet [e, g]	61·6	4·7	$C_{16}H_{15}O_4N_3$	61·4	4·8
,,	*p*-NO_2	170	C_6H_6–EtOAc [h]	61·5	4·8	,,	,,	,,
,,	3 : 5-$(NO_2)_2$	151	EtOAc [i]	53·6	3·8	$C_{16}H_{14}O_6N_4$	53·6	3·9

* Colourless needles unless otherwise stated. Pet. = light petroleum.

[a] Leaflets. [b] Buff. [c] Plates. [d] Pale yellow. [e] Canary-yellow. [f] Cadmium-yellow. [g] Orange plates. [h] Vermilion prisms. [i] Scarlet.

Action of Aqueous Potassium Cyanide and Sodium Sulphite on Aldoximes and their O-*Methyl Ethers.*—The oxime (5 g.) and potassium cyanide (3 g.) were heated under reflux for 3 hr. in ethanol, and most of the solvent was removed on the water-bath. The remaining solution was treated with excess of 2N-sodium hydroxide, to convert unchanged oxime into sodium salt, and extracted with ether. The extract was examined for nitrile, and the aqueous layer acidified for recovery of oxime. With α-*m*-nitro-, α-*p*-nitro-, α-*o*-methoxy-, α-*p*-methoxy-, α-3 : 4-methylenedioxy-, and α-3 : 4-methylenedioxy-6-nitro-benzaldoxime most of the oxime was recovered unchanged and no nitrile could be detected.

When α-*o*-nitrobenzaldoxime (5 g.) was heated with ethanolic potassium cyanide as above and the solution evaporated to small bulk, 3 g. of *o*-nitrobenzonitrile crystallised.

The *O*-methyl ether (5 g.) and potassium cyanide (3 g.) were heated under reflux for 5 hr. in ethanol, and most of the solvent was removed; with α-*O*-methyl-*o*-nitrobenzaldoxime, *o*-nitrobenzamide (2 g.) crystallised, but with α-*O*-methyl-*p*-nitro-, α-*O*-methyl-*m*-nitro-, α-*O*-methyl-3 : 4-methylenedioxy-6-nitro-, and α-*p*-methoxy-*o*-methyl-benzaldoximes unchanged *O*-ether was recovered in good yield.

The oxime (5 g.) was boiled with water (250 c.c.) and sodium sulphite (5 g.) for various times, evaporated to small bulk, and cooled. α-*o*-Nitrobenzaldoxime boiled for 1 hr. gave almost pure *o*-nitrobenzamide (3·5 g.); α-*p*-nitro-, α-3 : 4-methylenedioxy-, α-4-methoxy-3-nitro-, and α-*o*-methoxy-benzaldoxime gave unchanged oxime after 7 hr.' boiling; α-3 : 4-

methylenedioxy-6-nitrobenzaldoxime was boiled for 6 hr., a deep red solution being obtained, which was evaporated to dryness and extracted with boiling ethanol; the solid which separated on cooling was crystallised again from alcohol, giving 3 : 4-*methylenedioxy*-6-*nitrobenzamide* in buff-coloured needles, m. p. 198° (Found: C, 45·9; H, 2·9. $C_8H_6O_5N_2$ requires C, 45·7; H, 2·9%). Mixed with the oxime (m. p. 203°) it melted at 161°. Similarly treated α-3 : 4-dimethoxy-6-nitrobenzaldoxime gave 3 : 4-*dimethoxy*-6-*nitrobenzamide*, yellow needles (from benzene), m. p. 184° (Found: C, 47·6; H, 4·5. $C_9H_{10}O_5N_2$ requires C, 47·8; H, 4·4%).

α-*O*-Methyl-*o*-nitrobenzaldoxime (5 g.) was boiled with sodium sulphite (5 g.) and water (200 c.c.) for 20 min., all the ether dissolving; on evaporation to small bulk and cooling, *o*-nitrobenzamide (3·5 g.) crystallised. Similarly, α-3 : 4-dimethoxy-*O*-methyl-6-nitrobenzaldoxime after 2 hr.' boiling gave the amide, but the *O*-methyl ethers of α-3 : 4-methylenedioxy- and α-*o*-methoxy-benzaldoxime were recovered unchanged after such treatment. α-*O*-Methyl-*p*-nitrobenzaldoxime dissolved to a red solution after 6 hr.' boiling; evaporation to dryness gave a red solid from which no amide could be extracted, but addition of hydrochloric acid yielded α-*p*-nitrobenzaldoxime; similarly, α-*O*-methyl-*m*-nitrobenzaldoxime gave a small amount of α-*m*-nitrobenzaldoxime.

Action of Sodium Sulphite on Nitriles.—The nitrile (1 g.) was boiled with sodium sulphite (1 g.) in water (150 c.c.), and the solution evaporated to small bulk and cooled. *o*- and *p*-Nitrobenzonitrile gave the amides after 30 min.' boiling, *m*-nitrobenzonitrile after 90 min.' boiling, and benzonitrile after 8 hr.' boiling, but *p*-methoxy- and 3 : 4-methylenedioxy-benzonitrile gave no amide after 8 hr.' boiling.

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