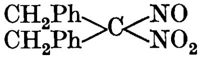
4. *The Nitration of Oximes.*

By William Charlton, John Campbell Earl, James Kenner, and Albert Anthony Luciano.

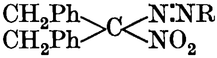
In previous papers it has been shown that the tendency of nitroso- and phenylazo-compounds to pass into oximino-derivatives and phenylhydrazones, respectively, is such that it may cause the displacement not only of carboxylic and similar unsaturated groups, but also of saturated alkylol groups (compare Jones and Kenner, J., 1930, 919). Moreover, these changes proceed without the aid of alkali, which is requisite for a similar transformation of the corresponding nitro-compounds. Apparently the sharing of two electrons with a co-ordinated oxygen atom causes the nitrogen atom of a nitro-group to exercise a greater restraint on the four electrons it shares with the doubly bound oxygen atom than it does in the nitroso-group.

It therefore appeared to be of interest to compare the nitroso- and the nitro-group in respect of their relative ease of displacement by means of alkali or other reagents when attached to the same carbon atom, as in ψ-nitroles. For this purpose dimethyl-ψ-nitrole was originally selected, but at an early stage in our work Rheinboldt and Dewald (*Ber.*, 1927, **60**, 249) showed that dibenzyl-ψ-nitrole (I) is easily accessible by the action of alkyl nitrite and nitric acid on dibenzyl ketoxime. It has the further advantage, for our purpose, of existing in the unimolecular condition.

(I.)



$$\begin{matrix}CH_2Ph\\CH_2Ph\end{matrix}\!>\!C\!<\!\begin{matrix}NO\\NO_2\end{matrix}$$

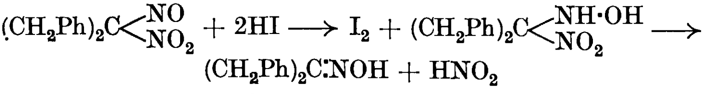


$$\begin{matrix}CH_2Ph\\CH_2Ph\end{matrix}\!>\!C\!<\!\begin{matrix}N{:}NR\\NO_2\end{matrix}$$

(II.)

The ψ-nitrole exhibited the characteristic behaviour of nitroso-compounds towards aniline and *m*-toluidine, and furnished well-crystallised yellow azo-derivatives (II; $R = C_6H_5$ or C_7H_7). The remainder of our experiments with basic reagents were, however, vitiated by the marked tendency of the ψ-nitrole to undergo oxidation in alcoholic solution to dibenzyldinitromethane. Rheinboldt and Dewald record the same behaviour in ethereal or benzene solution, and the formation of bromonitrocamphane from the green product of the action of potassium hypobromite on camphoroxime by exposure to air is doubtless yet another instance of the way in which nitroso-compounds reproduce the behaviour of nitric oxide in this respect (Forster, J., 1899, **75**, 1144; 1900, **77**, 255).

Rheinboldt and Dewald also record the liberation of iodine when their ψ-nitrole is treated with dilute hydriodic acid. It would be anticipated that the reaction would pursue the following course (compare Earl and Kenner, J., 1927, 2139) : *



$$(CH_2Ph)_2C\!<\!\begin{matrix}NO\\NO_2\end{matrix} + 2HI \longrightarrow I_2 + (CH_2Ph)_2C\!<\!\begin{matrix}NH{\cdot}OH\\NO_2\end{matrix} \longrightarrow$$
$$(CH_2Ph)_2C{:}NOH + HNO_2$$

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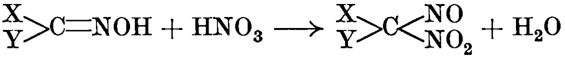
* In this paper, it was pointed out that in general the carbonyl group, in contradistinction from the nitroso-group, does not undergo reduction by cold dilute hydriodic acid, but it was nevertheless later emphasised that the difference between the two is one of degree (J., 1928, 2701) arising from the greater tendency of the nitrogen atom to acquire electrons. This property of the carbon atom in the carbonyl group can, however, be intensified by exposing it to a separate demand for electrons. Accordingly quinone can be estimated quantitatively by means of dilute hydriodic acid (compare Willstätter and Magiora, *Ber.*, 1910, **43**, 1172) and the quinols are reduced by both hydriodic and hydrobromic acids (Auwers, *Ber.*, 1912, **35**, 443). Similarly the elimination of the methylol group under the influence of the nitroso- and phenylazo-groups (J., 1930, 989) finds an exact parallel in the formation of 5-nitro-*m*-4-xylenol by nitration of *o*-oxymesityl alcohol, an *o*-quinitrole being doubtless an intermediate product (Fries and Kann, *Annalen*, 1907, **353**, 340).

The oxime is in fact the ultimate product, and the amount of iodine liberated is in agreement with this scheme. Similarly, bromonitrosodimethylbutane was largely converted by treatment with excess of hydrobromic acid into pinacolin oxime and bromine : $\mathrm{CMe_3{\cdot}CMeBr{\cdot}NO + HBr = CMe_3{\cdot}CMe{:}NOH + Br_2}$. Further, the hydrobromide of camphoroxime was prepared from the blue ethereal solution extracted from an early stage of the reaction between potassium hypobromite and camphoroxime (compare also Forster, J., 1897, **71**, 1045).

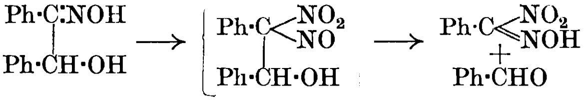
Prior to Rheinboldt and Dewald's publication, however, we had found it necessary to examine the modes of preparing *ψ*-nitroles. Their formation by the action of nitrogen peroxide on ketoximes (Scholl, *Ber.*, 1888, **21**, 508) is not particularly satisfactory, and has been regarded as an indirect reaction, depending on the oxidation of the oxime to the *aci*-nitro-compound, followed by interaction of this with the resulting nitrous anhydride (compare Born, *Ber.*, 1896, **29**, 90; Bamberger, *Ber.*, 1900, **33**, 1781; Schöfer, *Ber.*, 1901, **34**, 1910). It therefore appeared worth while to adapt Piloty's procedure in preparing bromonitroso-derivatives by the bromination of oximes (*Ber.*, 1898, **31**, 452) and to attempt their nitration :



$$\begin{matrix}\mathrm{X}\\\mathrm{Y}\end{matrix}\!>\!\mathrm{C{=}NOH} + \mathrm{HNO_3} \longrightarrow \begin{matrix}\mathrm{X}\\\mathrm{Y}\end{matrix}\!>\!\mathrm{C}\!<\!\begin{matrix}\mathrm{NO}\\\mathrm{NO_2}\end{matrix} + \mathrm{H_2O}$$

Wolff had already briefly recorded the formation of propyl-*ψ*-nitrole from acetoxime by this method (*Annalen*, 1895, **288**, 32, footnote), but, in spite of numerous attempts under a variety of conditions, we were able at best to obtain only very small yields by nitration in glacial acetic acid solution. The difficulty arose from a further reaction involving profound decomposition, and this was even more pronounced when the oximes of methyl ethyl ketone, diethyl ketone, and *cyclo*hexanone, respectively, were treated in the same manner. But very satisfactory yields of *ψ*-nitrole were obtained from dibenzyl ketoxime and from camphoroxime. In the latter case, however, its instability renders the product difficult of isolation in the pure condition.

A very smooth reaction occurred in the case of benzoin oxime, and resulted in the immediate formation of benzaldehyde and phenylnitrolic acid :



$$\begin{array}{l}\mathrm{Ph{\cdot}C{:}NOH}\\ \quad|\\ \mathrm{Ph{\cdot}CH{\cdot}OH}\end{array} \longrightarrow \left[\begin{array}{l}\mathrm{Ph{\cdot}C}\!<\!\begin{matrix}\mathrm{NO_2}\\\mathrm{NO}\end{matrix}\\ \quad|\\ \mathrm{Ph{\cdot}CH{\cdot}OH}\end{array}\right. \longrightarrow \begin{array}{l}\mathrm{Ph{\cdot}C}\!<\!\begin{matrix}\mathrm{NO_2}\\\mathrm{NOH}\end{matrix}\\ \quad +\\ \mathrm{Ph{\cdot}CHO}\end{array}$$

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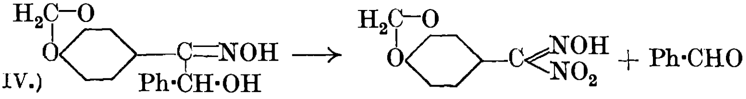
o-Oxy*iso*duryl alcohol behaves similarly and its conversion into *o*-di-*ψ*-cumenolemethane (Zincke and Hohorst, *ibid.*, p. 363) can also be regarded from this point of view.

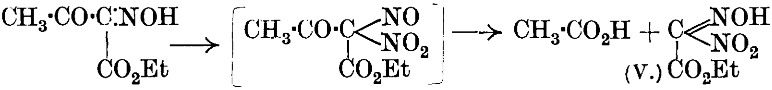
Similarly, the odour of benzaldehyde was at once perceptible when the oxime was treated with bromine. The reaction is a particular case of the elimination of alkylol groups referred to at the outset, and represents a means of determining the constitution of α-hydroxy-ketones. Thus, benzpiperoin, from the condensation of benzaldehyde with piperonal (Hörbye, *Dissert.*, Dresden, 1917; compare Brass, *Ber.*, 1930, **63**, 2617), was converted through its *oxime* into benzaldehyde and piperonylnitrolic acid :

(IV.)



Hörbye also deduced the constitution (IV), since he obtained benzaldehyde and piperonylic acid by applying Zincke's procedure of oxidative degradation to benzpiperoin (*Annalen*, 1882, **211**, 228).

Our method is, however, subject to limitations. It does not, for example, apply to glucoseoxime, since the alcoholic hydroxyl groups react preferentially to that of the oximino-group with nitric acid. Again, the oxime of 2-hydroxy*cyclo*hexanone suffers immediate decomposition. A similar reaction has already been recorded in the case of the monoximes of α-diketones, for Jovitschitsch showed that the nitrolic acid (V) resulted from the nitration of ethyl *iso*nitrosoacetoacetate :



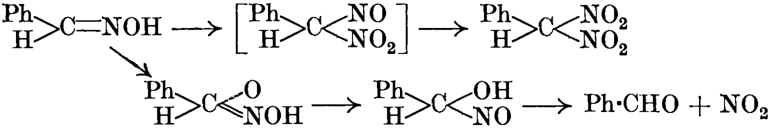
$$CH_3\cdot CO\cdot \underset{CO_2Et}{\underset{|}{C}}{:}NOH \longrightarrow \left[CH_3\cdot CO\cdot \underset{CO_2Et}{\underset{|}{C}}{<}^{NO}_{NO_2} \right] \longrightarrow CH_3\cdot CO_2H + \underset{CO_2Et}{\underset{|}{C}}{<}^{NOH}_{NO_2}$$

(V.)

Similarly, the chloro-derivative (V, with Cl in place of NO_2) resulted from the action of potassium chlorate and hydrochloric acid (*Ber.*, 1895, **28**, 1213, 2675; 1902, **35**, 151; 1906, **39**, 784).

A nitrolic acid was also obtained from *o*-nitrobenzaldoxime, and converted into *o*-nitrobenzoic acid, whilst *p*-nitrobenzoic acid was isolated directly from the nitration of *p*-nitrobenzaldoxime, presumably owing to the instability of the nitrolic acid.

The behaviour of benzaldoxime on nitration differs from that of the nitrobenzaldoximes in that the blue colour first produced does not immediately disappear, but only very gradually changes through green to yellow, and, in place of the nitrolic acid, phenyldinitromethane is the chief product, accompanied by a sensible proportion of benzaldehyde. It would seem that in virtue of its *o,p*-directive capacity, the phenyl group is able in some measure to meet the demand of the nitroso-group for electrons, and thus sufficiently to stabilise the ψ-nitrole first formed to allow of its oxidation :

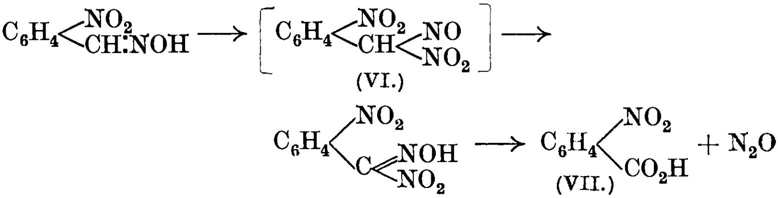


$$\mathrm{{Ph \atop H}{>}C{=}NOH \longrightarrow \left[{Ph \atop H}{>}C{<}{NO \atop NO_2}\right] \longrightarrow {Ph \atop H}{>}C{<}{NO_2 \atop NO_2}}$$

$$\mathrm{\searrow\ {Ph \atop H}{>}C{<}{O \atop NOH} \longrightarrow {Ph \atop H}{>}C{<}{OH \atop NO} \longrightarrow Ph{\cdot}CHO + NO_2}$$

The formation of free aldehyde can reasonably be attributed to the same influence, permitting an initial co-ordination of oxygen, followed by rearrangement as indicated (compare Bamberger, *loc. cit.*; Jones and Kenner, *loc. cit.*). We have also examined the nitration of the isomeric chloro- and methoxy-benzaldoximes, and of the tolualdoximes, obtaining in every case a nitrolic acid or a dinitromethane derivative. Usually, however, the isolation of these more or less unstable products in a state of purity involved some difficulty and consequent loss, so that it does not appear justifiable to attempt any detailed correlation of the results with the influence of the nuclear substituents. It may, however, be noted that in every case the *o*-derivative yielded a nitrolic acid, so that the *o*-effect observed by Lapworth and Manske (J., 1928, 2533) may possibly have asserted itself in this series also.

Aromatic aldoximes are also readily amenable to the same process of nitration. The first case studied was that of *m*-nitrobenzaldoxime, from which the corresponding nitrolic acid (VI) was readily obtained, and identified by its decomposition on heating into *m*-nitrobenzoic acid and nitrous oxide :



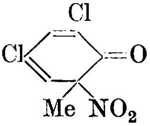
$$\mathrm{C_6H_4{<}{NO_2 \atop CH{:}NOH} \longrightarrow \left[C_6H_4{<}{NO_2 \atop CH{<}{NO \atop NO_2}}\right] \longrightarrow}$$

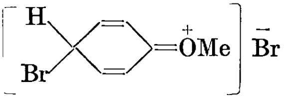
(VI.)

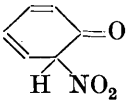
$$\mathrm{C_6H_4{<}{NO_2 \atop C{<}{NOH \atop NO_2}} \longrightarrow C_6H_4{<}{NO_2 \atop CO_2H} + N_2O}$$

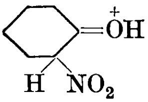
(VII.)

The formulation of the ψ-nitrole (VI) as an intermediate product is justified by the transient blue colour which is easily visible during the reaction. This observation is of importance, since the relationship between oxime and nitrolic acid is that of phenol to its *o*-nitro-derivative, whilst the formation of ψ-nitroles corresponds to that of the quinitrole (VIII) from, *e.g.*, 3 : 5-dichloro-*o*-cresol. The current view as to the mechanism of the bromination of anisole postulates formation of the oxonium derivative (IX), followed by extrusion of proton from the 4-position (compare Robinson, *J. Soc. Chem. Ind.*, 1925, 456T). But the blue colour noted above is experimental support (well adapted, it may be remarked, to purposes of lecture demonstration) for the view that the quinitrole (X) precedes the nitrophenol as a product of the nitration of phenol, which usually occurs in the form of the phenoxide ion. It would also represent the most direct mode of depolarisation of (XI), the analogue of (IX), which would result when the process of substitution is retarded by repression of ionisation in presence of strong mineral acid (compare Hewitt, Kenner, and Silk, J., 1904, **85**, 1225). The recent observation of the formation of 2 : 6-dichloro-4-nitrophenol even from 2 : 6-dichloro-4-methylquinitrole in warm methyl-alcoholic solution (Jones and Kenner, J., 1931, 1943) shows, if indeed such demonstration is necessary, that (XI) could readily pass into *o*-nitrophenol.


(VIII.)

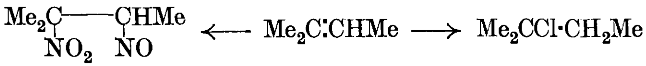

(IX.)


(X.)


(XI.)

By contrast with the preceding results, the formation of 3-nitro-4-hydroxybenzaldehyde and its oxime from the nitration under the same conditions of *p*-hydroxybenzaldoxime is noteworthy. Not only does it support the suggestion that the nitration of the oxime group is comparable with that of the phenol, but it illustrates the manner in which, in presence of a weak acid which does not repress its ionisation too strongly, aromatic hydroxyl exerts a stronger directive influence than aromatic methoxyl, whilst oximino-hydroxyl is intermediate in strength between the two. The present experiments may thus be regarded as supplementary to those of Wieland in illustrating the relationship between aromatic substitution and the reactions of open-chain unsaturated compounds. In this connexion, it is apposite to recall the α-nitration of urethane, urea, and guanidine (Thiele and Lachman, *Ber.*, 1894, **27**, 1520) and of acetic anhydride (Chattaway, J., 1910, **97**, 2099) as comparable with the *m*-nitration of benzoic acid.

Finally, it should be mentioned that Ruggeri has extended Scholl's work on the nitration of ketoximes by nitrogen peroxide, and in this way prepared *m*-nitro- and *p*-chloro-phenylmethylnitrolic acids from the corresponding oximes (*Gazzetta*, 1923, **53**, 691). Again, the formation of phenyldinitromethane, under similar conditions, from the monoxime of benzoylcarbinol and of acetylbenzoyl (Ponzio, *Gazzetta*, 1901, **31**, i, 262; 1909, **39**, i, 326) is exactly analogous to the behaviour of benzoinoxime and ethyl *iso*nitrosoacetoacetate already discussed. The correspondence with the results of simple nitration suggests, however, that Bamberger's view, already mentioned, is an unnecessarily complicated explanation, and it is more satisfactory to regard the action of nitrogen peroxide as a process of nitration exactly comparable with that of bromination by bromine. In such substitution reactions, and their additions to ethylenic compounds, nitrogen tri- and tetr-oxides exhibit definite polar properties. Thus in ψ-nitrosite formation, the nitrogen of the nitro-group conforms to Markownikow's rule in regard to the halogen atom in hydrogen halide additions, *e.g.* (Wieland, *Annalen*, 1921, **424**, 73),



$$\underset{NO_2}{Me_2C}\text{——}\underset{NO}{CHMe} \longleftarrow Me_2C{:}CHMe \longrightarrow Me_2CCl{\cdot}CH_2Me$$

This and the familiar nitration of amines and phenols by nitrogen trioxide are in agreement with the considerations advanced at the outset of this paper, as also is the formation of α-nitrostilbene by the action of alcoholic potassium hydroxide on stilbene ψ-nitrosite (Wallach, *Annalen*, 1900, **363**, 349).

EXPERIMENTAL.

In order to avoid constant repetition of the same phrase in the following account, it is to be understood that identification of known compounds included not merely the determination of melting point as quoted, but also direct comparison with an authentic specimen.

Dimethyl-ψ-nitrole.—When fuming nitric acid (2·3 c.c.; *d* 1·46) was gradually added to a solution of acetoxime (5 g.) in glacial acetic acid (5 g.) at 50°, a blue distillate was collected which crystallised when cooled and treated with ligroin. Yield, 0·2 g.; m. p. 76°. In another experiment, fuming nitric acid (1·1 c.c.) and acetic anhydride (3 c.c.) were successively added to a solution of the oxime (1 g.) in glacial acetic acid (5 c.c.) below 4°. After 1 hour, the blue solution was diluted with ice-water (40 c.c.). Yield, 0·05 g. Nitration in carbon tetrachloride solution led to a similar result.

Dibenzyl-ψ-nitrole.—Fuming nitric acid (6·5 c.c.; *d* 1·48) was added gradually to a solution of dibenzyl ketoxime (10 g.) in glacial acetic acid (150 c.c.). After the mixture had been kept for 10 minutes in the dark, the blue solution was diluted with water (500 c.c.). Crystallisation of the blue precipitate by cautious addition of water to its solution in glacial acetic acid yielded in the most favourable case 7·3 g. of ψ-nitrole, m. p. 72—73° (Found: N, 10·5. Calc. for $C_{15}H_{14}O_3N_2$: N, 10·4%). Rheinboldt and Dewald (*loc. cit.*) give m. p. 88°. When an alcoholic solution of the ψ-nitrole was boiled for one hour, it was decolorised, and the solid recovered after dilution with water, and recrystallisation from alcohol, melted at 127·5° (Found : N, 9·5. Calc. for $C_{15}H_{14}O_4N_2$: N, 9·8%). It was therefore dibenzyldinitromethane, for which Rheinboldt and Dewald record m. p. 132°.

A solution of the ψ-nitrole (1·785 g.) in benzene was shaken for 7 hours with an aqueous solution of potassium iodide (1·93 g.) and sulphuric acid (1 mol.). The benzene layer contained iodine (1·24 g., estimated, after removal, with excess of standard sodium thiosulphate solution), and dibenzyl ketoxime (0·5 g., m. p. 119°. Found : N, 6·3%). A mixture of the ψ-nitrole (1·72 g.) with redistilled aniline (10 g.) yielded a yellow crystalline separation (0·48 g.) after 24 hours at 0°. A further quantity (1·9 g.) remained after the liquor had been treated with dilute acetic acid (40%). By crystallisation from alcohol, bright yellow prisms, m. p. 108°, were obtained (Found : C, 73·3; H, 5·6; N, 12·1. $C_{21}H_{19}O_2N_3$ requires C, 73·0; H, 5·6; N, 12·2%). A similar product from *m*-toluidine formed small lemon-yellow prisms, m. p. 109—110° (Found : N, 11·5. $C_{22}H_{21}O_2N_3$ requires N, 11·7%).

Camphor-ψ-nitrole.—This was precipitated when water (50 c.c.) was added to a mixture of fuming nitric acid (0·65 c.c.) with a solution of camphoroxime (1 g.) in glacial acetic acid (15 c.c.), after 10 minutes in the dark. The blue crystalline precipitate was dried on porous earthenware in a vacuum for 2½ hours (Found : N, 13·4. $C_{10}H_{16}O_3N_2$ requires N, 13·2%). The melting point of this material had fallen over-night from 60° to 52°.

Reduction of Bromonitroso-derivatives by Hydrobromic Acid.—An ethereal solution of bromonitrosodimethylbutane, m. p. 127° (Piloty and Stock, *Ber.*, 1902, **35**, 309) became homogeneous and yellowish-green when shaken with hydrobromic acid. By dilution a red ethereal solution was obtained, from which tribromophenol, m. p. 88°, was obtained by treatment with phenol. From the aqueous acid liquor, pinacolin oxime, m. p. 75—79°, was isolated by treatment with alkali and extraction with ether. Similar results were obtained with a blue ethereal extract obtained after 10 minutes from the product of interaction of potassium hypobromite solution and camphoroxime (Forster, *loc. cit.*).

Nitration of Benzoinoxime.—When nitric acid (1·1 c.c.; *d* 1·5) was added to a solution of benzoinoxime (4·5 g.; m. p. 150—154°) in glacial acetic acid (90 c.c.), a transient green colour was observed, and the odour of benzaldehyde was at once apparent. After 8 minutes, the mixture was poured into ice-water (300 c.c.) and extracted thrice with ether. The combined extracts, having been washed once with water, were shaken with successive small volumes of ice-cold 2% aqueous ammonia, until an orange-coloured extract was obtained. The process of extraction was then continued, and the united coloured extracts (160 c.c.) were extracted once with ether and then acidified with cold oxalic acid solution. The dried ethereal solution from two extractions yielded, after crystallisation from chloroform–light petroleum, a yellow crystalline product, m. p. 58—59°, which did not depress the melting point of phenylmethylnitrolic acid, m. p. 59—60°, prepared according to the directions of Wieland and Semper (*Ber.*, 1906, **39**, 2524).

From the ethereal solution left after removal of the nitrolic acid, benzaldehydephenylhydrazone (3·3 g.), m. p. 155°, was prepared.

Constitution of Benzpiperoin (compare Brass, *loc. cit.*)—The *oxime*, prepared in the usual manner, was purified by trituration successively with a mixture of light petroleum and benzene, then with benzene, and finally by crystallisation from methyl alcohol. It melted at 153—154° (Found : N, 5·35. $C_{15}H_{23}O_4N$ requires N, 5·16%). The benzene washings contained a second impure substance, m. p. 105—111°, possibly the isomeric oxime, which was not examined further. A solution of the oxime (5·4 g.) in glacial acetic acid (130 c.c.) was treated with nitric acid (1·7 c.c.; *d* 1·48) and worked up as in the case of benzoinoxime. Crude benzaldehydephenylhydrazone (4·1 g.) was obtained, and readily identified after purification, but the instability of piperonylnitrolic acid, m. p. 88°, prevented its analysis and it was identified by its decomposition product, piperonylic acid, m. p. 225°. It could be separated from the latter by solution in chloroform.

*Attempted Nitration of 2-Hydroxy*cyclo*hexanoneoxime.*—The hydroxy-ketone, prepared as described by Kötz (*Annalen*, 1913, **400**, 55), melted at 131—132° after crystallisation from ethyl alcohol (Found : C, 63·3; H, 9·0. Calc. : C, 63·1; H, 8·8%). Previously recorded melting points are 92—93° (Kötz and Goethe, *J. prakt. Chem.*, 1909, [2], **80**, 488), 98° (Kötz, *loc. cit.*), and 113° (Bouveault and Chereau, *Compt. rend.*, 1906, **142**, 1086). The oxime (Kötz, *loc. cit.*) is more expeditiously prepared by boiling the ketone (22·8 g.) with ethyl alcohol (200 c.c.), and solutions of hydroxylamine hydrochloride (42 g.) and sodium hydroxide (24 g.) in the minimum amounts of water, for 5 hours (m. p. 105—106°. Found : N, 10·9%). It yielded a dark green salt, soluble in chloroform, when shaken with a solution of copper acetate, and imparted a purplish-red colour to a solution of nickel sulphate to which a trace of ammonia had been added. The oxime reacted vigorously with nitric acid under the conditions applied to benzoinoxime, and an apple-green solution resulted, but no definite products could be isolated.

Nitration of Aldoximes.—A solution of *m*-nitrobenzaldoxime (2 g.) in cold glacial acetic acid (30 c.c.) was gradually treated with nitric acid (1·0 c.c.; *d* 1·5). After a few seconds the deep green solution deposited a white substance (0·2 g.), which was collected when, after 6 minutes, the whole was poured into a mixture of sodium hydroxide solution (40%, 60 c.c.) and ice-water (240 c.c.). After being washed with acetic acid and with ether, it melted at 131° (decomp.) (Found: C, 50·6; H, 3·2; N, 17·2. Calc. for $C_{14}H_{10}O_6N_4$: C, 50·9; H, 3·1; N, 17·0%), and did not depress the melting point of a sample of *m*-nitrobenzaldoxime peroxide prepared by the action of nitrogen peroxide on the oxime (Ruggeri, *loc. cit.*). The alkaline solution, acidified at 0° by dilute sulphuric acid and extracted with ether, yielded *m*-nitrophenylmethylnitrolic acid (1·1 g.), which was purified by addition of water to its solution in glacial acetic acid. Thus prepared, it melted at 82° (Ruggeri, *loc. cit.*, gives m. p. 89°) (Found: N, 19·9. Calc. for $C_7H_5O_5N_3$: N, 19·9%), but this rose comparatively rapidly owing to decomposition of the nitrolic acid into nitrous oxide and *m*-nitrobenzoic acid, m. p. 138° (Found: N, 8·4%): this reaction was shown in a special experiment to occur quantitatively.

o-Nitrobenzaldoxime (2 g.) similarly yielded 0·25 g. of material, m. p. 120° (decomp.) (Robin, *Ann. Chim. Phys.*, 1921, **16**, 77, quotes 117° as the melting point of *o*-nitrobenzaldoxime peroxide), and *o*-nitrophenylmethylnitrolic acid (1·35 g.), m. p. 84° (Found: N, 19·9%). By boiling with water the acid yielded a tarry product and an aqueous solution of salicylic acid, m. p. 155°, which responded to the usual colour reaction with ferric chloride.

p-Nitrobenzaldoxime (2 g.) in the same way furnished the peroxide (0·25 g.), m. p. 143° (decomp.) (Found: C, 51·2; H, 3·3; N, 16·9%), but apparently the nitrolic acid is very unstable and only *p*-nitrobenzoic acid (0·75 g.), m. p. 235°, could be isolated.

α-Benzaldoxime (5 g.) in glacial acetic acid (75 c.c.) yielded a brown solution 10 minutes after being treated with fuming nitric acid (2·5 c.c.; *d* 1·5), and this was poured into excess of ice-cold dilute ammonia solution. Benzaldehyde was removed by ether and estimated as phenylhydrazone (1·25 g., m. p. 155°), and acidification of the residual alkaline solution yielded phenyldinitromethane (0·9 g.), m. p. 78—80° (Found: N, 15·2. Calc.: N, 15·4%). Ponzio (*Atti R. Accad. Lincei*, 1906, **15**, ii, 118) records m. p. 79°.

m-Tolualdoxime (2·7 g.) similarly yielded a yellow oil, from which after some days m-*tolyldinitromethane* (0·3 g.) crystallised; after being crystallised from acetic acid by addition of water, this melted at 53° (Found: N, 14·4. $C_8H_8O_4N_2$ requires N, 14·3%). The small proportion of free aldehyde produced in the reaction was characterised as phenylhydrazone, m. p. 88—90°.

p-Tolualdoxime (5·4 g.) also yielded the corresponding dinitromethane (1·6 g.), m. p. 78—79° (Found : N, 14·2%). Ponzio (*loc. cit.*) records m. p. 77°. Free aldehyde (1·1 g.) was also isolated as phenylhydrazone, m. p. 114—115°.

o-Tolualdoxime (5·4 g.) furnished a small proportion of free aldehyde, characterised as phenylhydrazone, m. p. 114—115°, but as chief product o-*tolylmethylnitrolic acid* (1·5 g.), m. p. 64° (decomp.) (Found : C, 52·8; H, 4·5; N, 15·7. $C_8H_8O_3N_2$ requires C, 53·3; H, 4·5; N, 15·6%). Over-night the melting point had fallen to 58° (decomp.), and the nitrolic acid was only isolated by working at low temperatures throughout.

o-Chlorobenzaldoxime (2·9 g.) in glacial acetic acid (45 c.c.) and nitric acid (0·9 c.c.; *d* 1·48) yielded traces of free aldehyde and o-*chlorophenylnitrolic acid* (2·2 g.), which separated in pale yellow crystals, m. p. 72°, when light petroleum was added to its solution in chloroform (Found : C, 41·9; H, 2·5; N, 13·8. $C_7H_5O_3N_2Cl$ requires C, 41·9; H, 2·5; N, 14·0%). It was comparatively stable and furnished *o*-chlorobenzoic acid, m. p. 139—140°, when boiled with water, but no salicylic acid.

m-Chlorobenzaldoxime (2·7 g.) similarly yielded m-*chlorophenylnitrolic acid* (0·8 g.), m. p. 61°. Owing to its rapid decomposition, unsatisfactory analytical results were repeatedly obtained (Found : N, 13·0, 13·3%). Free *m*-chlorobenzaldehyde (identified as phenylhydrazone, m. p. 133—134°) and its *peroxide* (0·25 g.), m. p. 111° (decomp.) (Found : N, 9·1. $C_{14}H_{10}O_2N_2Cl_2$ requires N, 9·1%), also resulted from the nitration.

p-Chlorobenzaldoxime (1 g.) in glacial acetic acid (15 c.c.), with nitric acid (0·5 c.c.; *d* 1·48), yielded *p*-chlorophenyldinitromethane (0·5 g.), m. p. 53°, after crystallisation from warm light petroleum (Found: N, 12·7. Calc.: N, 12·8%). Ruggeri (*loc. cit.*) records m. p. 55°. Free *p*-chlorobenzaldehyde was also formed and identified as phenylhydrazone, m. p. 126—128°.

o-Methoxybenzaldoxime (3 g.) yielded o-*methoxyphenylmethylnitrolic acid* (1·7 g.), m. p. 68° (Found : N, 14·0. $C_8H_8O_4N_2$ requires N, 14·3%), from which *o*-anisic acid, m. p. 100°, was obtained by boiling it with water.

m-Methoxybenzaldoxime was only obtained as an oil, from which indefinite oily products were obtained by nitration.

Anisaldoxime (3 g.) yielded an oily nitration product, from which were separated anisic acid (0·1 g.), m. p. 180—182°, and anisyldinitromethane (0·2 g.), m. p. 32—33° after crystallisation from light petroleum (Found : N, 13·6%). Ponzio (*loc. cit.*) records m. p. 34°. A large proportion of free aldehyde was also formed and isolated as phenylhydrazone (3 g.), m. p. 120—121° after crystallisation from alcohol.

Piperonaldoxime (5 g.) yielded a small amount of piperonal, detected by its odour, and piperonyldinitromethane (2 g.), m. p. 70—72° after crystallisation from light petroleum (Found : N, 12·6. Calc. for $C_8H_6O_6N_2$: N, 12·6%). Ponzio (*loc. cit.*) records m. p. 72°.

p-Hydroxybenzaldoxime (1·4 g.) yielded a mixture of 3-nitro-4-hydroxybenzaldehyde and its oxime (1·8 g.), which was identified by complete conversion into the oxime, m. p. 168—169°, and hydrolysis of this to the free aldehyde, m. p. 142—143°. The oximes of *m*-hydroxybenzaldehyde and protocatechuic aldehyde underwent a vigorous reaction on nitration under the above conditions, but no definite products were isolated.

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