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Oxidation with Nickel Peroxide. VII.[1] Oxidation of Aromatic Aldoxime with Nickel Peroxide

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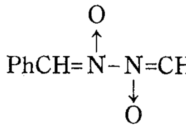
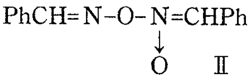
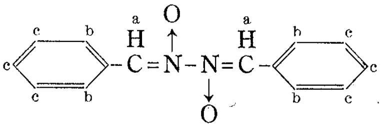
The action of many oxidants upon benzaldoxime has been reported and a number of proposals[3] for the structure of the product have also been made. The two most acceptable are aldazine-bis-N-oxide (I) and aldoxime anhydride-N-oxide (II).


$\mathrm{PhCH{=}}\overset{\displaystyle O}{\overset{\uparrow}{N}}\mathrm{{-}}\underset{\displaystyle O}{\underset{\downarrow}{N}}\mathrm{{=}CHPh}$ I


$\mathrm{PhCH{=}N{-}O{-}}\underset{\displaystyle O}{\underset{\downarrow}{N}}\mathrm{{=}CHPh}$ II

However, available experimental data do not permit rigorous exclusion of either structure as was indicated by G. Just in his report on the oxidation of aldoximes with lead tetraacetate.[4] We have examined the oxidative behaviour of nickel peroxide upon aromatic aldoximes and obtained the same product as reported for I or II. This product showed the same infrared (IR) spectrum and melting point. The dipole moment of the product obtained from the oxidation of α- or β-benzaldoxime was 1.135D. If the structure was II, its dipole moment should show 5D or over.

The nuclear magnetic resonance (NMR) spectrum suggested the structure of I and showed three types of protons: singlet at 1.07 τ due to proton (a), multiplet at 1.85 τ due to proton (b) and multiplet at 2.50 τ due to proton (c).



A formulation as benzaldazine-bis-N-oxide (I) is in accord with these data. L. Horner, *et al.*[5] reported that benzaldazine-bis-N-oxide was obtained by treating phenyldiazomethane with nitrogen monoxide or benzaldoxime with a mixture of nitrogen oxides. They determined its structure by the following experiments: (a) it was reduced with triphenylphosphine to give benzaldazine and triphenylphosphine oxide; (b) it was treated with alcoholic ammonium sulfide to give benzaldoxime in good yield. In the course of the oxidation reaction of p-chlorobenzaldoxime with nickel peroxide in benzene, an electron spin resonance (ESR) spectrum of the iminoxy–radical having hyperfine splitting constants of $a^{N}=30.90$, $a^{H}=5.82$ (1H) and $a^{H}=1.32$ (2H) was observed.[6] This observation leads us to believe that the iminoxy–radical may be produced during the first step of oxidation and that the subsequent coupling of two radicals yields product (I).

This reaction proceeds to a good yield with aromatic aldoximes and the results are summarized in Table, including the oxidation with lead tetraacetate, nitrogen monoxide, and a mixture of nitrogen oxides.

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[1] Part VI: K. Nakagawa, H. Onoue and K. Minami, *Chem. Pharm. Bull.* (Tokyo), **17**, 835 (1969).
[2] Location: *Fukushima-Ku, Osaka.*
[3] W. Emmons, *J. Am. Chem. Soc.*, **78**, 6208 (1956); L. Horner, L. Hockenberger and W. Kirmse, *Chem. Ber.*, **94**, 290 (1961); H. Kropf and R. Lambeck, *Liebigs Ann. Chem.*, **700**, 18 (1966); G. Just and K. Dahl, *Tetrahedron*, **24**, 5251 (1968).
[4] G. Just and K. Dahl, *Tetrahedron*, **24**, 5251 (1968).
[5] L. Horner, L. Hockenberger and W. Kirmse, *Chem. Ber.*, **94**, 290 (1961).
[6] Unpublished work with Dr. R. Konaka and Mr. S. Terabe.

Experimental

Solid nickel peroxide was prepared by the treatment of an aqueous solution of nickel sulfate with sodium hypochloride in an alkaline solution as described in Part I.[7] The quantity used in stoichiometric oxidation was calculated on the basis of the active oxygen content, determined by iodometry. It contained about 3.5 mg–atom active oxygen per gram. Usually 1.1 times as much as the theoretical amount of nickel peroxide was used for the oxidation.

Oxidation of α-Benzaldoxime——To a solution of 3.63 g (0.03 mole) of α-benzaldoxime in 50 ml of ether, 9.6 g of nickel peroxide (containing 0.03 g–atom of active oxygen) was added and the mixture stirred for 3 hr at −20°. The reaction mixture was filtered and washed with ether. The residue was treated with 50 ml of dil. hydrochloric acid at 0° to dissolve the oxidant, yielding 3.22 g of gray colored powder, mp 107—108°. The crude product was dissolved in chloroform at 50° and white small needles were obtained by the addition of alcohol, mp 108°. *Anal.* Calcd. for $C_{14}H_{12}O_2N_2$: C, 70.00; H, 5.04; N, 11.67. Found: C, 70.03; H, 4.93; N, 11.68.

Oxidation of α-*p*-Chlorobenzaldoxime——To a solution of 4.67 g (0.03 mole) of *p*-chlorobenzaldoxime in 150 ml of ether was added 10.25 g of nickel peroxide (0.033 g–atom of active oxygen) and the mixture stirred for 3 hr at −20°. The reaction mixture was filtered, washed with ether, and the residue was stirred in 150 ml of dil. hydrochloric acid at 0° to dissolve the oxidant. The crude product obtained (4.29 g) by filtration of the mixture was purified from chloroform solution by the addition of alcohol, mp 215°. *Anal.* Calcd. for $C_{14}H_{10}O_2N_2Cl_2$: C, 54.39; H, 3.26; N, 9.06. Found: C, 53.39; H, 3.43; N, 9.05.

Oxidation of α-*p*-Nitrobenzaldoxime——To a solution of 3.32 (0.02 mole) of α-*p*-nitrobenzaldoxime in 150 ml of ether was added 6.83 g of nickel peroxide (0.022 g–atom of active oxygen) and the mixture stirred for 3 hr at −20°. The reaction mixture was filtered and washed with ether. The residue was treated with 150 ml of dil. hydrochloric acid at 0° to dissolve the oxidant and the remaining pale yellow crystals were filtered and washed with water, yielding 3.18 g of an almost pure product, mp 141°. *Anal.* Calcd. for $C_{14}H_{10}O_6N_4$: C, 50.91; H, 3.06; N, 16.97. Found: C, 50.59; H, 3.07; N, 16.61.

Oxidation of Cinnamaldoxime——To a solution of 7.36 g (0.05 mole) of cinnamaldoxime in 200 ml of ether was added 17.1 g of nickel peroxide (0.055 g–atom of active oxygen) and the mixture stirred for 4 hr at −20°. The crude product was obtained by the same procedure as for α-benzaldoxime, 5.86 g. After the purification from chloroform and alcohol, yellow plates were obtained ,mp 123.5°. *Anal.* Calcd. for $C_{18}H_{16}O_2N_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.63; H, 5.61; N, 9.67.

TABLE I

Oxime	Solvent	Temp. (°C)	Reac. time (hr.)	Yield[d] (%)	mp[e] (decomp.) (°C)
α-Benzaldoxime	ether	−20	3	89.3	108
α-Benzaldoxime	ether	20	2	88.9	108
β-Benzaldoxime	ether	−20	2	96.5	108
α-*p*-Chlorbenzaldoxime	ether	−20	3	92.7	125
α-*p*-Nitrobenzaldoxime	ether	−20	3	96.4	141
α-Furfulaldoxime	ether	−20	3	77.9	127
α-Cinnamaldoxime	ether	−20	4	80.2	123.5
α-Benzaldoxime[a]	ether	5—10	0.5	91.0	108
α-Benzaldoxime[b]	ether	room temp.	short time	35—40	106—107
Phenyldiazomethane[c]	benzene cyclohexane	room temp.	0.5	82.0	108

a) Oxidized with lead tetraacetate. b) Oxidized with a mixture of nitrogen oxides.
c) Oxidized with nitrogen monoxide. d) of crude products e) Determined after the purification.

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[7] K. Nakagawa, R. Konaka and T. Nakata, *J. Org. Chem.*, 27, 1957 (1962).