used. For analysis a sample of the material was dried at 56°, 0.3 mm., for one hour.

N-(3-Chloromercuri-2-piperidinopropyl)-phthalamic Acid.—The procedure described for IV was followed for the reaction of 46.8 g. (0.25 mole) of N-allylphthalimide[15] and 124 ml. (1.25 mole) of piperidine with 67.9 g. (0.25 mole) of mercuric chloride. After the addition of the mercuric chloride, stirring was continued for 2 hours while the reaction mixture was attaining room temperature. After shaking for 4 days the solution was filtered and the filtrate was added dropwise while stirring to 2.5 l. of water, and thereafter stirring was continued for one day. The solution was clarified by filtration and the filtrate was extracted with 3 portions of 200 ml. of ether. The *p*H of the aqueous layer was adjusted to 6.5 by adding 350 ml. of 1 *N* acetic acid. After standing for a few days in the cold room the product separated in crystalline form.

N-(3-Chloromercuri-2-piperidinopropyl)-nicotinamide.—To a solution of 8.1 g. (0.05 mole) of N-allylnicotinamide[16] in 49.5 ml. (0.50 mole) of piperidine was added 13.6 g. (0.05 mole) of pulverized mercuric chloride in small portions and with shaking. After the addition of mercuric chloride was complete shaking was continued for one day. Then 200 ml. of ethyl acetate was added and the precipitate was filtered off. The filtrate was evaporated to dryness *in vacuo* (bath 25–30°) and the material was further dried over concd. sulfuric acid *in vacuo*. It was dissolved in 77 ml. of 2 *N* hydrochloric acid at 25° and filtered through charcoal. Addition of acetone to the filtrate yielded the crystalline hydrochloride, which was recrystallized from aqueous alcohol.

N-(3-Chloromercuri-2-pyrrolidinopropyl)-isonicotinamide.—The preceding procedure was employed using 8.1 g. (0.05 mole) of N-allylisonicotinamide,[17] 41.7 g. (0.50 mole) of pyrrolidine and 15.0 g. (0.055 mole) of mercuric chloride. Upon addition of 100 ml. of ether to the reaction mixture 2 layers were formed. The upper layer was decanted and the remaining oil was triturated 5 times with 50 ml. each of ether. The sirup was dried over phosphorus pentoxide. The product (25 g.) was dissolved in 84 ml. of 1 *N* hydrochloric acid and the solution clarified by filtration. The volume of the filtrate was reduced to 50 ml. *in vacuo*. When a solution of 29 g. of benzilic acid in 84 ml. of 1 *N* sodium hydroxide was added, a brown gum precipitated which was washed twice with 50 ml. of water. On triturating the gum with 100 ml. of acetone a white crystalline product was obtained. It was collected and washed with 100 ml. of acetone, yielding 7.9 g.

Acknowledgment.—The authors are indebted to Drs. J. Seifter and R. Tislow and their associates for the pharmacologic results and to Dr. G. Ellis and his staff for the analyses reported herein.

(15) B. R. Baker, M. V. Querry, R. Pollikoff, R. E. Schaub and J. H. Williams, *J. Org. Chem.*, **17**, 74 (1952); it was recrystallized from *n*-heptane, m.p. 70–71°; [O. Wallach and I. Kamenski, *Ber.*, **14**, 162 (1881)].

(16) M. Hartmann and L. Panizzon, U. S. Patent 2,136,501 (1938).

(17) Since we had little success with the procedure described by J. H. Billman and J. L. Rendall (THIS JOURNAL, **66**, 540 (1944)), we synthesized the compound in good yields by treating isonicotinyl chloride hydrochloride in benzene with allylamine and triethylamine; b.p. 152–154° (0.25 mm.).

RADNOR, PA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, TULANE UNIVERSITY]

Aldoximes and Dinitrogen Tetroxide[1]

BY J. H. BOYER AND H. ALUL

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Dinitrogen tetroxide nitrates and/or oxidizes aldoximes. With each oxime tested, nitration increases with temperature whereas oxidation is most effective at 0° and below. Nitrolic acids (II), the nitration products, are stable when R is alkyl but readily lose the elements of nitrous acid with furoxane (IV) formation when R is aryl or acyl. *aci*-Nitroalkanes (III), the oxidation products, are pyrolyzed readily into aldehydes when R is alkyl. *aci*-Nitroethane has been isolated.

The action of dinitrogen tetroxide upon aldoximes has been investigated heretofore with benzaldoxime[2] and isonitrosoacetone[3] from which diphenyl- and diacetylfuroxanes (IV), respectively, were obtained. The effect of this reagent upon acetaldoxime and propionaldoxime is described here together with a reinvestigation of the reaction with benzaldoxime.

From a 2:1 molar ratio of either α- or β-benzaldoxime and dinitrogen tetroxide from 36 to −60°, phenylnitrolic acid (II, R = C_6H_5), diphenylfuroxane (IV, R = C_6H_5), benzaldoxime anhydride N-oxide[4] (V, R = C_6H_5) and benzaldehyde are obtained. At the higher temperatures with short reaction times the best yields of II (R = C_6H_5) are observed, whereas at lower temperatures, product V (R = C_6H_5) predominates. Since phenylnitrolic acid upon standing at 0°, or more rapidly at its melting point, is transformed into benzoic acid (8%) and diphenylfuroxane (57%),[5] the best yield of IV (R = C_6H_5) was obtained from the reaction mixture stored at 0° for 72 hours. An excess of dinitrogen tetroxide converts the oxime into dinitrophenylmethane in high yield,[6] whereas a deficient amount of dinitrogen tetroxide allows appreciable recovery of oxime (Table I).

From acetaldoxime and dinitrogen tetroxide at −60°, a colorless solid, apparently the *aci*-form of nitroethane (III, R = CH_3) is obtained in 65% yield. In water, alcohol or ether it is converted into acetaldehyde. Careful neutralization of the reaction mixture at −60° and subsequent acidification with carbonic acid affords nitroethane (V, R = CH_3). Other products obtained from the oxime and dinitrogen tetroxide under a variety of condi-

(1) Financial assistance under National Science Foundation grant NSF-G4240 is gratefully acknowledged.

(2) R. Scholl, *Ber.*, **23**, 3496 (1890).

(3) W. S. Mills, *Chem. News*, **88**, 228 (1903).

(4) Three structures have been proposed for V, formerly known as "benzaldoxime peroxide." R. Cuisa and E. Parisi, *Gazz. chim. ital.*, **55**, 416 (1925), suggested RCH=NOH·RC≡N→O. L. I. Smith, *Chem. Revs.*, **23**, 239 (1938), discusses two additional ones, RCH=NOON=CHR and V. Infrared absorption data (see Experimental) eliminate the first proposed structure as a result of no triple bond absorption in the 2200 to 2100 cm.$^{-1}$ region and contain many similarities with absorption data for diphenylfuroxane (IV, R = C_6H_5).

(5) H. Wieland and L. Semper, *Ber.*, **39**, 2522 (1906). Compare with N. Kornblum and W. M. Weaver, THIS JOURNAL, **80**, 4334 (1958), who found that phenylnitrolic acid in the presence of sodium nitrite in dimethylformamide at −16° is changed into diphenylfuroxane (74%) and benzoic acid (8%), whereas at 25° the yields were diphenylfuroxane (3%) and benzoic acid (81%).

(6) L. F. Fieser and W. v. E. Doering, THIS JOURNAL, **68**, 2252 (1946).

TABLE I

REACTIONS OF BENZALDOXIME WITH DINITROGEN TETROXIDE

Products	M.p., °C.	Yield, %,[a] for reactions run at 36° 6 min.	0° 1 hr.	0°[b] 1 hr.	0°[c] 72 hr.	−60° 72 hr.
Phenylnitrolic acid	56–57	50	22	14	18	8
Diphenylfuroxane	112–114	10	18	7	42	20
Benzaldoxime anhydride N-oxide	112–114	0	42	25	8	45
Benzaldehyde (or der.)		Trace[d]		25[e]		

[a] Based on aldoxime. [b] The reaction was run at 0° with a molar ratio of oxime to dinitrogen tetroxide of 4:1 instead of 2:1, the ratio used in all other experiments. [c] Materials combined at −60° were then raised to 0°. [d] Isolated as its dinitrophenylhydrazone, m.p. 235°. [e] Starting material was β-benzaldoxime. In this experiment α-benzaldoxime, b.p. 125° (12 mm.) (C. M. Luxmore, *J. Chem. Soc.*, 69, 178 (1896), reports b.p. 123–124° (14 mm.) and 118–119° (12 mm.)), was recovered.

tions include ethylnitrolic acid (II, R = CH_3) in best yield from reaction run at 100° and acetaldehyde in best yield from reaction run at 0 to −60° (Table II). From propionaldoxime under similar conditions, propylnitrolic acid (II, R = C_2H_5) and propionaldehyde are obtained. Undetected *aci*-nitropropane apparently is transformed into propionaldehyde.

TABLE II

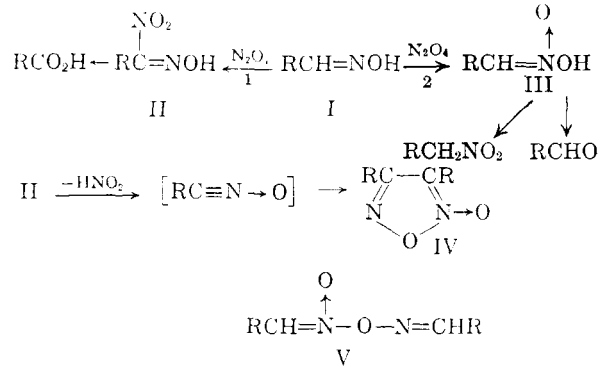
REACTIONS OF ACETALDOXIME WITH DINITROGEN TETROXIDE

Products	M.p., °C.	Yield, %,[a] for reactions run at 100° 6 min.	36° 6 min.	0° 40 min.	−60° 1 hr.
Acetaldehyde[b]	..	40	55	78	85[c]
Methylnitrolic acid	86[d]	36[e]	18	4	
aci-Nitroethane					65[f]

[a] Based on aldoxime. [b] Isolated as its dinitrophenylhydrazone, m.p. 147°. [c] This yield was obtained by allowing the reaction mixture to warm up to −20° at which temperature *aci*-nitroethane, which had been insoluble at −60°, went into solution. Upon treating the ether solution with a solution of dinitrophenyl-hydrazine the only product isolated was the DNP of acetaldehyde. [d] Mixture m.p. 86° (G. Ponzio, *Gazz. chim. ital.*, **33**, I, 508 (1903)). Acetic acid is formed upon melting (v. Meyer, *Ann.*, **175**, 88 (1875)). [e] When equimolar quantities of reactants were used this yield was reduced to 8%. [f] See text for isolation.

Apparently dinitrogen tetroxide nitrates (1) and/or oxidizes (2) aldoximes (I). Nitration is predominant at higher temperatures, oxidation at lower temperatures. Depending upon their stability, nitrolic acids (II) are isolated or converted into furoxanes (IV) presumably through dimerization of intermediate unisolated nitrile oxides. They also undergo pyrolysis with the formation of corresponding acids. The initial oxidation products are *aci*-nitroalkanes (III) which may be pyrolyzed into corresponding aldehydes, or transformed into mixed anhydrides with the original aldoxime, or be isomerized into nitroalkanes. Each of these three possible reactions has been detected.

In contrast to the behavior of benzaldoxime, neither furoxanes nor oxime anhydride N-oxides are detected from alkyl aldoximes with dinitrogen tetroxide. Absence of furoxane formation is consistent with the observation that alkyl nitrolic acids



are more stable than phenylnitrolic acid (they may be stored for several days at room temperature before noticeable decomposition) and supports the hypothesis that *aci*-nitro alkanes are not precursors of nitrile oxides.[7]

The available data indicate that stability of nitrolic acids (II) is increased when R is electron donating, *e.g.*, methyl or ethyl, and is decreased when R is electron withdrawing, *e.g.*, phenyl or acetyl.

Experimental

Reaction of Benzaldoxime with Dinitrogen Tetroxide at 36°.—To 5.0 g. (0.042 mole) of β-benzaldoxime, m.p. 130°, dissolved in 200 ml. of boiling anhydrous ether, a solution of 2.1 g. (0.022 mole) of dinitrogen tetroxide in 10 ml. of anhydrous ether was added dropwise with stirring at a rate which maintained a gentle reflux (3 minutes). Stirring was continued for an additional three minutes, 50 g. of ice was added, the ether layer was separated, washed once with water and extracted with ice-cold 4% ammonium hydroxide solution until the extracts were no longer colored. The red alkaline solution was washed with 100 ml. of ether, placed in a beaker and covered with 50 ml. of ether. Upon careful neutralization at 0° with aqueous oxalic acid the red color disappeared. The aqueous solution then was extracted with 50 ml. of ether, the combined ether extracts were washed once with ice-cold water and dried for 10 minutes with anhydrous magnesium sulfate. Ether was removed *in vacuo* and/or by evaporation in a stream of dry air. Phenylnitrolic acid crystallized as pale yellow needles, m.p. 56–57° dec. (lit.[8] 57–58° dec.), 3.5 g. (50%). The product was stable at −20° for several weeks, but decomposed within a few hours at room temperature.

The original ether solution after extraction with ammonium hydroxide was washed with 10% sodium hydroxide to remove benzaldoxime. Evaporation of the ether left impure diphenylfuroxane, 0.5 g. (10%), as short needles, m.p. and mixture m.p. 112–114° (lit.[9] m.p. 114–115°), after recrystallization from methanol. On treatment of the methanol mother liquor with 2,4-dinitrophenylhydrazine, the hydrazone of benzaldehyde was precipitated, m.p. 235°.

The reaction was repeated with 12.1 g. (0.10 mole) of β-benzaldoxime and 4.6 g. (0.05 mole) of dinitrogen tetroxide at 0° for 1 hour. A white precipitate of benzaldoxime anhydride N-oxide was washed with ether and with alcohol and weighed 5.1 g. (42.5%), m.p. 112–114° (lit.[8] 114–116°). The identity of the product was established by its conversion to 3,5-diphenyl-1,2,4-oxadiazole,[9] m.p. 108–109° (lit.[10] 109–110°) upon warming with chloroform and slowly evaporating the solvent.

Infrared absorption ($cm.^{-1}$) for benzaldoxime anhydride N-oxide was obtained from a potassium bromide wafer:

(7) E. R. Alexander, M. R. Kinter and J. D. McCollum, THIS JOURNAL, **72**, 801 (1950), converted ω-nitroacetophenone into dibenzoylfuroxane using red fuming nitric, oxide-free nitric or concentrated sulfuric acids, but not weaker acids such as hydrochloric or phosphoric. Their explanation did not require dehydration of *aci*-ω-nitroacetophenone into benzoyl nitrile oxide.

(8) H. Wieland and L. Semper, *Ber.*, **39**, 2522 (1906).

(9) E. Beckmann, *ibid.*, **22**, 1588 (1889).

(10) H. Wieland, *ibid.*, **40**, 1673 (1907).

3067(s), 1961(m), 1898(m), 1689(m), 1613(w), 1577(s), 1486(m), 1447(s), 1420(s), 1340(m), 1319(m), 1290(m), 1205(m), 1182(m), 1147(m), 1085(s), 1066(s), 1028(m), 998(m), 918(m), 866(m), 855(m), 843(s), 754(s), 741(s), 683(s). Possible assignments are 1689, 1613, C=N; 1447, 1420, O—N→O[11]; 1340, 1319 or 1290, N→O[11]; 1182, 1028, 918 and 843 appear related to corresponding bands at 1174(m), 1029(w), 919(w) and 838(s) found in diphenylfuroxane and are in regions characteristic of furoxanes.[11] We are indebted to Mr. R. T. O'Connor, Southern Regional Research Laboratory, for these infrared absorption data.

Other products were isolated from the reaction mixture as previously described. These results as well as those for reactions carried out at −60° for 72 hr. are found in Table I.

Pyrolysis of Phenylnitrolic Acid.—Phenylnitrolic acid, (2.0 g., 0.012 mole), m.p. 55–57°, in a 50-ml. beaker covered with 5 ml. of ligroin (b.p. 50–60°) was warmed on a water-bath until the acid had melted. It then was stored at room temperature for 48 hours. The crystalline product was taken up in ether and washed with dilute sodium hydroxide. Upon evaporation diphenylfuroxane, 0.82 g. (57%), m.p. and mixture m.p. 114° after recrystallization from methanol, was obtained. From the alkali wash, 0.12 g. (8%) of benzoic acid, m.p. 120°, was obtained after neutralization. Phenylnitrolic acid at room temperature for several hours changed into an oil from which crystalline diphenylfuroxane (50–65%) slowly separated.

Reaction of Acetaldoxime and Propionaldoxime with Dinitrogen Tetroxide at 0°.—Using the procedure described above, 10.0 g. (0.17 mole) of acetaldoxime[12] (b.p. 114°) in 200 ml. of anhydrous ether was treated with a solution of 7.7 g. (0.084 mole) of dinitrogen tetroxide in 20 ml. of anhydrous ether at 0° (10 minutes). Stirring was continued for another 30 minutes, the ether solution was washed several times with water, the aqueous washings were combined and their volume was made up to 400 ml. Twenty ml. of the aqueous solution was diluted with 20 ml. of alcohol and a freshly prepared solution of 2,4-dinitrophenylhydrazine was added to precipitate acetaldehyde DNP, 1.48 g. (78%), m.p. 147° after recrystallization from alcohol. In similar reactions with acetaldoxime at other temperatures and with propionaldoxime the products were isolated by methods already described. Results are found in Tables II and III.

Isolation of Nitroethane.—A reaction mixture of 10.0 g. (0.17 mole) of acetaldoxime and 7.6 g. (0.083 mole) of dinitrogen tetroxide in 120 ml. of ether was prepared and stored at −60° for 1 hour. A colorless precipitate of *aci*-nitroethane began to appear soon after mixing the reagents and was separated by filtration of the cold solution and washing with ether precooled to −60°. The precipitate, 7.9 g. (64%), was stored at −60°. Upon dissolving in water, alcohol or ether it was transformed into acetaldehyde isolated as its DNP derivative, m.p. 147°. A fresh aqueous solution of *aci*-nitroethane gave an intense red-brown color with ferric chloride.[13] After a few minutes at room temperature it violently decomposed apparently into acetaldehyde, detected by its odor. It melts between 60–70° with violent decomposition leaving no residue.

Attempts to dissolve it in alkaline solutions resulted in extensive decompositions; however, it was converted into nitroethane as follows. The original reaction mixture while still at −60° was neutralized carefully with a saturated solution of ammonia in ether at such a rate that the temperature remained below −50°. When all the acid had been neutralized the mixture was allowed to warm to room temperature and sufficient water was added to dissolve all solid material. A stream of carbon dioxide then was passed through the mixture until the aqueous layer was no longer alkaline. The aqueous layer was extracted with ether, the combined ether extracts were dried with calcium chloride and the solvent was removed on a water-bath. Impure nitroethane, 3.8 g. (30%), was left as a light yellow oil, $n^{25}D$ 1.4010.[14]

To 1.0 g. (0.013 mole) of nitroethane in 10 ml. of 20% sodium hydroxide solution, 1 g. of sodium nitrite was added. The mixture was cooled in an ice-bath and an ice-cold 6 *N* solution of sulfuric acid was added slowly until the mixture was acidic. When the solution again was made alkaline it gave an intense red-blood color which disappeared upon acidification. The red alkaline solution was washed with ether, acidified with a saturated solution of oxalic acid and extracted with ether from which methylnitrolic acid, 0.65 g. (55%), m.p. 86°, was isolated as described previously.

TABLE III

REACTIONS OF PROPIONALDOXIME WITH DINITROGEN TETROXIDE

Products	M.p., °C.	Yield, %,[a] for reactions run at 100° 6 min.	36° 6 min.	0° 40 min.
Propionaldehyde[b]		38	61	81
Ethylnitrolic acid	66[c]	28	16	3

[a] Based on aldoxime. [b] Isolated as its dinitrophenylhydrazone, m.p. 152–154°. [c] G. Ponzio, *Gazz. chim. ital.*, **33**, I, 508 (1903). Propionic acid is formed upon melting (v. Meyer, *Ann.*, **175**, 88 (1875)).

(11) N. E. Boyer, G. M. Czerniak, H. S. Gutowsky and H. R. Snyder, THIS JOURNAL, **77**, 4238 (1955); J. H. Boyer, U. Toggweiler and G. A. Stoner, *ibid.*, **79**, 1748 (1957).

(12) H. Wieland, *Ber.*, **40**, 1677 (1907).

(13) H. B. Hass and E. B. Wiley, *Chem. Revs.*, **32**, 395 (1943).

(14) Reference 13, p. 387, records $n^{25}D$ 1.3916.

NEW ORLEANS, LA.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE TEST STATION]

The Reactions of Some Polynitrobenzenes with 2-Cyano-2-propyl Radicals[1]

BY WILLIAM P. NORRIS

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2-Cyano-2-propyl radicals (generated in refluxing benzene from α,α'-azobisisobutyronitrile) react with *o*- and *p*-dinitrobenzene to give N-(*o*-nitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine (I) and N-(*p*-nitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine (II), respectively. In addition *p*-dinitrobenzene gave some N-[2-(2-cyano-2-propoxy)-4-nitrophenyl]-O,N-bis-(2-cyano-2-propyl)-hydroxylamine (III). 1,3,5-Trinitrobenzene gave N-(3,5-dinitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine. The order of reactivity of the nitro compounds toward free radical attack was: 1,3,5-trinitrobenzene > *p*-dinitrobenzene > *o*-dinitrobenzene. The structures of I, II and III were assigned on the basis of elemental analyses, molecular weight determinations and degradation studies.

Reactions of free radicals with aromatic nitro compounds are of two types. In one case, with highly reactive radicals like methyl, there is apparently only nuclear substitution. Fieser[2] found that mono-, di- and trinitrobenzenes could be methylated on the ring once and sometimes twice. Trinitro-*m*-xylene resisted attack by methyl radicals both on the ring and on the nitro groups.

Less reactive radicals such as 2-cyano-2-propyl react with the nitro group but do not give nuclear substitution. Nitrobenzene and *m*-dinitrobenzene

(1) Presented before the Pacific Southwest Regional Meeting of the American Chemical Society, Redlands, Calif., October 25, 1958.

(2) L. F. Fieser, R. C. Clapp and W. H. Daudt, THIS JOURNAL, **64**, 2052 (1942).