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

(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).

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)).

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.

(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.

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

BY WILLIAM P. NORRIS

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
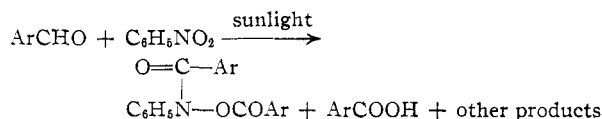
(1) Presented before the Pacific Southwest Regional Meeting of the American Chemical Society, Redlands, Calif., October 25, 1958.
(2) L. F. Fieser, R. C. Clapp and W. H. Daudt, THIS JOURNAL, **64**, 2052 (1942).

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

reacted with 2-cyano-2-propyl radicals to give N-phenyl-O,N-bis-(2-cyano-2-propyl)-hydroxylamine and N-(m-nitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine.[3] Another example of similar behavior of radicals toward aromatic nitro compounds is the reaction of aromatic aldehydes with nitrobenzene under the influence of sunlight.[4]

$$ArCHO + C_6H_5NO_2 \xrightarrow{\text{sunlight}}$$

$$\underset{\underset{|}{O=C-Ar}}{}$$

$$C_6H_5N-OCOAr + ArCOOH + \text{other products}$$

A related reaction is the photolysis of o-nitrobenzaldehyde to give o-nitrosobenzoic acid in high yield.[5] Here the reaction stops after loss of the oxygen by the nitro group. Due to the favorable steric relationship of the nitro and carbonyl groups the activated molecule transfers the oxygen without actually going through a free radical intermediate.
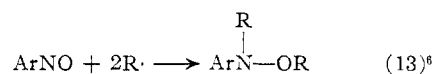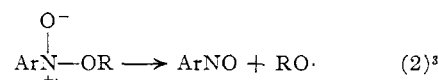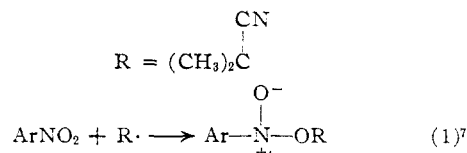
In the present work the reactions of 2-cyano-2-propyl radicals (from the thermal decomposition of α,α'-azobisisobutyronitrile) with o- and p-dinitrobenzene and 1,3,5-trinitrobenzene were investigated. This work was done several years ago as part of an investigation into how polynitroaromatic compounds act as free radical polymerization inhibitors. The publication by Inamoto and Simamura[3] prompted this publication which serves to confirm and extend considerably the work of the latter authors.

Using about a three and one-half to one molar ratio of α,α'-azobisisobutyronitrile to o-dinitrobenzene in refluxing benzene solution 33% of the o-dinitrobenzene reacted from which a 28% yield (with respect to the consumed o-dinitrobenzene) of N-(o-nitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine (I) was isolated. Under the same conditions p-dinitrobenzene gave a 58% conversion, a 29% yield of N-(p-nitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine (II) and a 9% yield of a compound, $C_{18}H_{21}N_5O_4$, m.p. 179–180°, which has been assigned the structure of N-[2-(2-cyano-2-propoxy)-4-nitrophenyl]-O,N-bis-(2-cyano-2-propyl)-hydroxylamine (III). There were additional small amounts of solids isolated in both cases in the chromatographic separation of the products but not in sufficient quantities to permit characterization. 1,3,5-Trinitrobenzene gave a 75% conversion of nitro compound and a 2% yield of N-(3,5-dinitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine (IV). This is in contrast to the statement by Gingras and Waters[6] that 1,3,5-trinitrobenzene does not react with 2-cyano-2-propyl radicals. The major part of the product consisted of highly colored materials which would not crystallize.

In view of the clean separation of the unreacted aromatic nitro compounds in the chromatographic separation of the reaction mixture components the percentage conversion figures, 75 for 1,3,5-trinitrobenzene, 58 for p-dinitrobenzene and 33 for o-dinitrobenzene, are significantly different. Using the conversion figures as an index of reactivity to-

ward 2-cyano-2-propyl radicals the nitro compounds fall into the same order as that observed for their chain-stopping capacity in polymerizing allyl acetate, i.e., 1,3,5-trinitrobenzene > p-dinitrobenzene > o-dinitrobenzene.[7] The greater reactivity of the trinitro compound is attributed, by Hammond and Bartlett, to some unspecified type of resonance stabilization of their proposed initial radical intermediate. The reason for the difference in reactivity between p- and o-dinitrobenzene is more apparent.

The greater reactivity of p-dinitrobenzene toward 2-cyano-2-propyl radicals

$$\underset{\underset{|}{R = (CH_3)_2C}}{\overset{CN}{|}}$$

$$ArNO_2 + R\cdot \longrightarrow \underset{\underset{+\cdot}{Ar-N-OR}}{\overset{O^-}{|}} \qquad (1)^7$$

$$\underset{+\cdot}{\overset{O^-}{|}}{ArN-OR} \longrightarrow ArNO + RO\cdot \qquad (2)^3$$

$$ArNO + 2R\cdot \longrightarrow \underset{|}{\overset{R}{|}}ArN-OR \qquad (13)^6$$

is consistent with the proposed first step, namely, the addition of a radical to the oxygen of nitro. The contributions from resonance structures involving the free nitro group will be more important in stabilizing the radical in the case of the p-isomer than for the o-isomer because the p-nitro group can readily assume the requisite coplanar configuration with respect to the ring and the other nitro group while the o-nitro group will encounter considerable steric hindrance from its neighbor when assuming the coplanar attitude.[8]

p-Dinitrodurene is another compound in which the nitro groups are sterically hindered from assuming a coplanar configuration with respect to the ring and the chain-stopping capacity of this compound is only two-thirds as much as p-dinitrobenzene in polymerizing allyl acetate.[7]

Step 2 is able to account for all the products actually isolated and identified. Some alternative routes for step 2 will be mentioned later. The addition of two 2-cyano-2-propyl radicals to the nitroso group to give a trisubstituted hydroxylamine (step 3) already has been observed by Gingras and Waters.[6] The 2-cyano-2-propoxy radical (step 2) reacts, for the most part, to give acetone and hydrogen cyanide.

The isolation of N-[2-(2-cyano-2-propoxy)-4-nitrophenyl]-O,N-bis-(2-cyano-2-propyl)-hydroxylamine is the first instance where the 2-cyano-2-propoxy radical has reacted and retained its identity. The 2-cyano-2-propoxy group may not actually separate as a free radical and then attack the ring because attack ortho to the free nitro group would be likely to occur too and this was not observed. Also, no 1-(2-cyano-2-propoxy)-2,5-dinitrobenzene was found and since p-dinitrobenzene was always present in much higher concentration

(3) N. Inamoto and O. Simamura, J. Org. Chem., **23**, 408 (1958).

(4) G. Ciamician and P. Silber, Ber., **38**, 3813 (1905).

(5) P. A. Leighton and F. A. Lucy, J. Chem. Phys., **2**, 756, 760 (1934).

(6) B. A. Gingras and W. A. Waters, J. Chem. Soc., 1920 (1954).

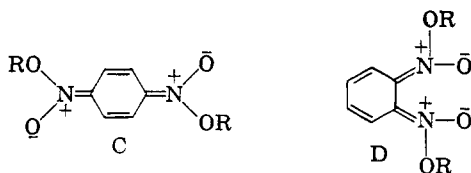(7) G. S. Hammond and P. D. Bartlett, J. Polymer Sci., **6**, 617 (1951).

(8) G. W. Wheland, "The Theory of Resonance and Its Applications to Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 136–138.

than any of the products or intermediates, and should be equal or superior in reactivity toward nuclear free radical substitution, it indicates that 2-cyano-2-propoxy radicals are probably very short lived and react with other substances only within the initial solvent sphere if at all.
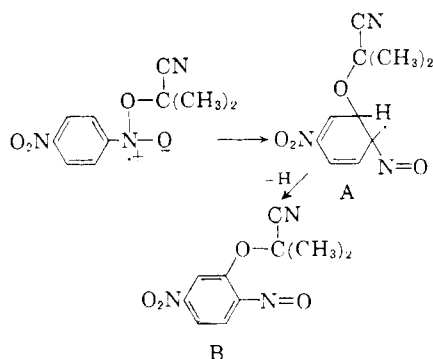
An intramolecular migration, perhaps involving a cyclic mechanism, may account for the transfer of the 2-cyano-2-propoxy group from nitrogen to the *ortho* carbon. The intermediate radical A would be stabilized by the ring unsaturation and by conjugation with the nitroso group. Hydrogen atom abstraction by another radical would give B which readily would add two 2-cyano-2-propyl radicals to give III. A careful investigation of the *o*-dinitrobenzene reaction mixture failed to produce a substitution product comparable to III.

Alternative possibilities for step 2 are coupling of the radical formed in step 1 with another 2-cyano-2-propyl radical on the oxygen or nitrogen of the initially attacked nitro group. In these two cases loss of a 2-cyano-2-propoxy radical followed by coupling with another 2-cyano-2-propyl radical could give the trisubstituted hydroxylamine. At the present there is nothing to recommend either possibility over the one previously proposed in step 2. A third possibility is that dinitronic esters, C and D, might be formed by another 2-cyano-2-propyl radical coupling with the free nitro group of the initial radical formed in step 1. Because of the unstable character of other nitronic esters[9] these prob-

ably would not survive and indeed may have contributed to the formation of the highly colored residues encountered in product workup.

The structures of the trisubstituted hydroxylamines I, II and III were established by elemental analysis, molecular weight determinations and degradation studies.

The *o*-nitroaniline and *p*-nitroaniline obtained from I and II, respectively, are as expected and confirm the *ortho* and *para* relationships of the nitro and hydroxylamine groups of I and II. Bromination occurred in each case from bromine formed
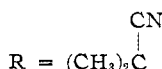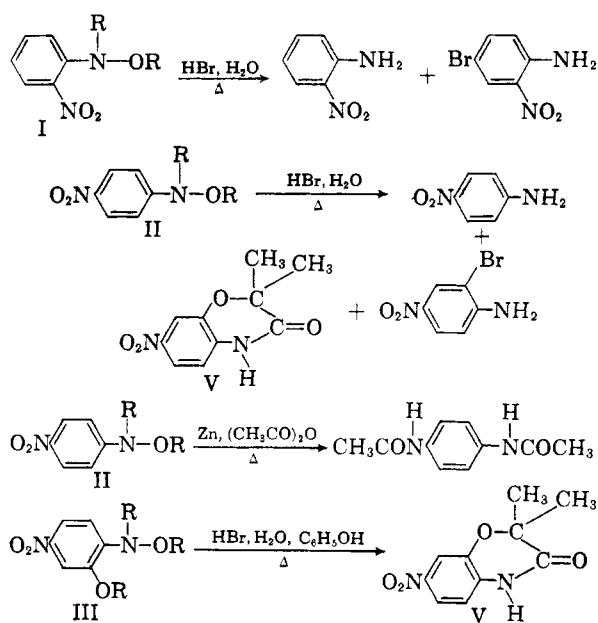
when bromide was oxidized and hydroxylamine reduced.[10] Phenol was used with III to take up the bromine thereby reducing the number of side products and simplifying product separation.

The sole product, V, isolated from the reaction of III with aqueous hydrogen bromide is identical with V, a minor product isolated from the reaction of II with aqueous hydrogen bromide. The elemental analysis of V agrees with the formula $C_{10}H_{10}N_2O_4$ and the infrared absorption spectrum shows a strong carbonyl band at 5.93 μ. One of the products obtained when N-phenylhydroxylamine is treated with acid is the rearranged material, *p*-aminophenol, in which an hydroxyl group has migrated from nitrogen to the *p*-position on the ring.[10] It therefore seems quite possible that a trisubstituted hydroxylamine such as II, under acidic conditions, would undergo a similar rearrangement to give an ether.
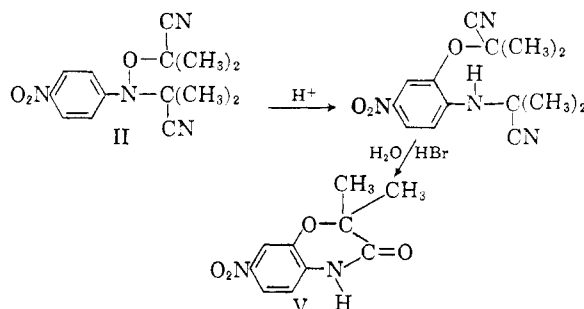
In this case *ortho* nuclear substitution would occur since the *p*-position is blocked by nitro. Cleavage of the 2-cyano-2-propyl group from nitrogen and cyclization to the amide would give V. The possibility that 2-cyano-2-propyl was cleaved from the ether oxygen with cyclization following to give a lactone isomeric with V was discounted on the basis of the position of the infrared absorption band for

(9) R. Arndt and J. D. Rose, *J. Chem. Soc.*, 1 (1935).

(10) E. Bamberger, *Ann.*, **424**, 233, 297 (1921).

the carbonyl. The carbonyl absorption band of V at 5.93 μ is much closer to the 5.95–6.15 μ carbonyl region of secondary amides[11] than to the 5.66–5.75 μ carbonyl region of esters.[12,13] Hence V is considered to have the structure shown. With the *ortho* relationship between the ether oxygen and amido nitrogen established in V, the position of the 2-cyano-2-propoxy group in III is established as *ortho* to the hydroxylamino group. Thus, III is N-[2-(2-cyano-2-propoxy)-4-nitrophenyl]-O,N-bis-(2-cyano-2-propyl)-hydroxylamine.

The structure of N-(3,5-dinitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine was assigned on the basis of elemental analysis and the analogous formation of trisubstituted hydroxylamines from other aromatic nitro compounds and 2-cyano-2-propyl radicals.

A table in the Experimental section lists some of the more distinctive absorption bands of the various hydroxylamines prepared here plus N-(*m*-nitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine.[14]

Experimental

Reaction of *p*-Dinitrobenzene with 2-Cyano-2-propyl Radicals.—Thirty-five grams (0.21 mole) of α,α'-azobisisobutyronitrile and 9.8 g. (0.058 mole) of *p*-dinitrobenzene,[15] m.p. 171–173°, were dissolved in 100 ml. of benzene and heated to reflux for 12 hr. The benzene was evaporated and the residue subjected to steam distillation to remove the large amount of tetramethylsuccinonitrile. The residue remaining was dissolved in 150 ml. of benzene and fractionated by elution chromatography on a 1:4 Celite–silicic acid column which measured 7.5 cm. by 18 cm. and contained 300 g. adsorbent using benzene as the eluting solvent. The reaction mixture components came off in the order given in the amounts shown: *p*-dinitrobenzene, m.p. 171–173°, 4.1 g. (42% of starting material); N-(*p*-nitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine (II), m.p. 147–150°, 2.8 g. (29% yield based on converted *p*-dinitrobenzene); and N-[2-(2-cyano-2-propoxy)-4-nitrophenyl]-O,N-bis-(2-cyano-2-propyl)-hydroxylamine (III), m.p. 170–175°, 1.1 g. (9% yield). Further elution using ether and benzene removed small amounts of other materials from the column, but none of these was investigated.

Recrystallization from carbon tetrachloride raised the melting point of N-(*p*-nitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine to 152–153°.

Anal. Calcd. for $C_{14}H_{16}N_4O_3$: C, 58.32; H, 5.59; N, 19.43; mol. wt., 288. Found: C, 58.13; H, 5.34; N, 19.06; mol. wt., 290.

Recrystallization of N-[2-(2-cyano-2-propoxy)-4-nitrophenyl]-O,N-bis-(2-cyano-2-propyl)-hydroxylamine from methanol and then ethanol raised the melting point to 179–180°.

Anal. Calcd. for $C_{18}H_{21}N_5O_4$: C, 58.20; H, 5.70; N, 18.86; mol. wt., 371. Found: C, 58.24; H, 5.66; N, 19.30; mol. wt., 374.

Reaction of *o*-Dinitrobenzene[15] with 2-Cyano-2-propyl Radicals.—The reaction was carried out and the product was worked up in exactly the same fashion as in the previous experiment to give 6.6 g. (67% recovery) of *o*-dinitrobenzene and 1.5 g. (28% yield based on converted *o*-dinitrobenzene) of N-(*o*-nitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine, m.p. 116–120°. Recrystallization from carbon tetrachloride and then from methanol raised the melting point to 119–120°.

(11) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954, p. 176.

(12) L. J. Bellamy, *ibid.*, p. 153

(13) E. J. Hartwell, R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1436 (1948).

(14) A sample of this compound was kindly provided by N. Inamoto, Department of Chemistry, Faculty of Science, Tokyo University, Japan.

(15) Prepared by the method of W. D. Emmons, THIS JOURNAL, **76**, 3470 (1954).

Anal. Calcd. for $C_{14}H_{16}N_4O_3$: C, 58.32; H, 5.59; N, 19.43; mol. wt., 288. Found: C, 58.26; H, 5.84; N, 19.94; mol. wt., 287.

Reaction of 1,3,5-Trinitrobenzene with 2-Cyano-2-propyl Radicals.—Two and one-tenth grams (0.010 mole) of 1,3,5-trinitrobenzene and 5.9 g. (0.036 mole) α,α'-azobisisobutyronitrile were dissolved in 20 ml. of benzene and heated at reflux for 12 hr. The product was worked up in the same way as in the previous two experiments to give 0.52 g. (25% recovery) of 1,3,5-trinitrobenzene and 0.050 g. (2% yield based on converted 1,3,5-trinitrobenzene) of N-(3,5-dinitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine, m.p. 118–119°. Recrystallization from ether did not raise the melting point.

Anal. Calcd. for $C_{14}H_{15}N_5O_5$: C, 50.44; H, 4.54; N, 21.01. Found: C, 50.18; H, 4.63; N, 21.10.

Reaction of N-(*p*-Nitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine (II) with Hydrobromic Acid.—One gram (0.0035 mole) of II was added to 20 ml. of 48% hydrobromic acid and the mixture was boiled until all the solid had dissolved. All the liquid then was removed under reduced pressure. The residue was added to 25 ml. of water and extracted with three 25-ml. portions of ether. The aqueous phase was then neutralized with sodium bicarbonate and extracted again with three 25-ml. portions of ether. The ether extracts were combined and evaporated. The residue was dissolved in benzene and fractionated by elution chromatography on a 3 cm. by 13 cm. column of 4 to 1 silicic acid–Celite adsorbent. Using benzene and later ether and benzene as eluting solvents the components came off in the following order in the amounts shown: 2-bromo-4-nitroaniline, m.p. 100–102°, 0.086 g. (11% yield); *p*-nitroaniline, m.p. 146–148°, 0.22 g. (46% yield); 2,3-dihydro-2,2-dimethyl-7-nitro-1,4-benzoxazin-3-one (V), m.p. 206–210°, 0.063 g. (8% yield); α-hydroxyisobutyric acid, m.p. 76–78°, 0.050 g. (13% yield).

Recrystallization of the 2-bromo-4-nitroaniline from carbon tetrachloride raised the melting point to 104–105° (lit.[16] m.p. 104.5°).

The mixture melting point of *p*-nitroaniline with an authentic sample of *p*-nitroaniline (m.p. 147–148°) was not depressed.

Two recrystallizations of 2,3-dihydro-2,2-dimethyl-7-nitro-1,4-benzoxazin-3-one from benzene raised the melting point to 209–210°. This compound gave no depression of mixture melting point with V isolated from the treatment of III with boiling hydrobromic acid. The infrared spectra of 2,3-dihydro-2,2-dimethyl-7-nitro-1,4-benzoxazin-3-one and V isolated from II are identical. An analysis for V is given in the next experiment.

A mixture melting point of the α-hydroxyisobutyric acid with an authentic sample of α-hydroxyisobutyric acid (m.p. 78–79°) gave no depression.

Reaction of N-[2-(2-Cyano-2-propoxy)-4-nitrophenyl]-O,-N-bis-(2-cyano-2-propyl)-hydroxylamine (III) with Hydrobromic Acid.—One gram of phenol and 0.26 g. (0.00071 mole) of III were dissolved in 20 ml. of boiling 48% hydrobromic acid. The phenol was added to take up bromine produced in the reaction. After solution was complete the liquid, including the phenol, was removed under reduced pressure; 10 ml. of water was added to the residue and the mixture was extracted three times with 20-ml. portions of ether. The aqueous phase was neutralized with sodium bicarbonate and again extracted with ether. The ether solutions were all combined and evaporated. The residue was taken up in benzene and chromatographed on a 2.8 cm. by 12 cm. column of 4 to 1 silicic acid–Celite adsorbent. The eluting liquid was 20% ether and 80% benzene. The only material removed in significant quantity was 0.070 g. (45% yield) of 2,3-dihydro-2,2-dimethyl-7-nitro-1,4-benzoxazin-3-one (V), m.p. 205–210°. Two recrystallizations from benzene raised the melting point to 209–210°. The infrared spectrum of this compound showed N–H absorption at 3.15 μ and C=O absorption at 5.93 μ.

Anal. Calcd. for $C_{10}H_{10}N_2O_4$: C, 54.05; H, 4.54; N, 12.61. Found: C, 54.36; H, 4.72; N, 12.82.

Reaction of N-(*o*-Nitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine (I) with Hydrobromic Acid.—A suspension of 0.48 g. (0.0017 mole) of I in 20 ml. of 48% hydrobromic acid was boiled until all the solid was dissolved.

(16) J. Judd, *J. Chem. Soc.*, **105**, 1433 (1914).

TABLE I

INFRARED ABSORPTION BANDS OF Ar—N—O—C(CH$_3$)$_2$ IN THE 7.5–12 μ REGION OF THE SPECTRUM[a,b,c]

NC—C(CH$_3$)$_2$CN

Ar Wave lengths, μ, →	7.5–8.0	8.0–8.5	8.5–9.0	9.0–9.5	9.5–10.0	10.0–10.5	10.5–11.0	11.0–12.0
o-Nitrophenyl	7.72w	8.22m	8.62s	9.19w	9.58w	10.25w	10.6m	11.23w
	7.84w	8.33m	8.73m		9.82w	10.42w	10.96w	11.45m
		8.43m						11.74m
m-Nitrophenyl[14]	7.63w	8.16m	8.55s	9.23m	9.80w	10.42m	10.55w	11.14m
	7.85w	8.24m	8.63s		9.98w		10.74w	11.48w
		8.34m						11.72m
p-Nitrophenyl	7.63m	8.15m	8.58s	9.05s	9.82w	10.25w	10.70w	11.38s
	7.76w	8.20m	8.67s		9.95w	10.37m	11.00w	11.56m
		8.38m				10.42m		11.73s
								11.95w
2-[2-(Cyano-2-propoxy)-4-nitrophenyl]	7.68m	8.28s	8.67s	9.20m	9.82w	10.20m	10.72w	11.09w
	7.98s		8.92m			10.45m		11.32m
								11.46m
								11.95w
3,5-Dinitrophenyl	7.55m	8.04w	8.55s	9.04w	9.69w	10.08w	10.50w	11.10w
		8.12w	8.62s	9.25m		10.16m	10.58w	11.40w
		8.30w				10.45w	10.81m	11.80w
		8.42w					10.94s	

[a] w = weak absorption, m = moderate absorption, s = strong absorption. [b] The first four compounds were prepared for infrared scanning using the pressed KBr window technique. The last compound, Ar = 3,5-dinitrophenyl, was prepared as a Nujol mull. [c] The first four compounds showed an extremely weak C≡N absorption at 4.5 μ but the last compound showed none at all.

The products were isolated in the same manner as in the reaction of II with hydrobromic acid. The first material to come off the chromatographic column was 0.087 g. (24% yield) of 4-bromo-2-nitroaniline, m.p. 111–112° (lit.[17] m.p. 111.5°). Next came 0.074 g. (32% yield) of o-nitroaniline 68–70°. Recrystallization from hot water raised the melting point to 70–71°. A mixture melting point with an authentic sample of o-nitroaniline (m.p. 70–71°) did not show depression. There were additional small quantities of material on the column, but no attempt was made to isolate and identify these.

Reductive Acetylation of N-(p-Nitrophenyl)-O,N-bis-(2-cyano-2-propyl)-hydroxylamine (II).—Two grams of zinc dust and 0.27 g. (0.00093 mole) of II were added to 20 ml. of acetic anhydride. The mixture was heated to reflux for 10 min., and then filtered. The excess acetic anhydride was removed by distillation at 0.1 mm. pressure. The residue was washed with water and filtered. The solid residue

was recrystallized from ethanol to give about 5 mg. of diacetyl-p-phenylenediamine, m.p. 300–301°. A mixture melting point with an authentic sample of diacetyl-p-phenylenediamine (m.p. 303–304°) showed no depression.

Infrared Spectra.—Waters[6] published infrared absorption data on a number of di- and trisubstituted hydroxylamines. He was unable to assign any particular band as being diagnostic of the hydroxylamine group but noticed that there were four sharply defined bands in the 8–9 μ region and grouped bands in the 9.5–11.5 μ region. These are regions where the N–O bond of hydroxylamine might be expected to absorb. In Table I are listed infrared absorption bands in the 7.5 to 12 μ region of five additional trisubstituted hydroxylamines. There are certain similarities in the pattern of absorptions in Table I and Waters'[6] compilation. No speculations will be made here regarding assignments of bands to specific bonds.

The samples were prepared and the infrared absorption spectra determined by Dr. Allen L. Olsen of this Laboratory.

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(17) F. D. Chattaway, K. J. P. Orton and R. C. T. Evans, Ber., **33**, 3057 (1900).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELAWARE]

Oxidation of Vinyl Monomers[1]

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The rates of absorption of oxygen by acrylonitrile and by methacrylonitrile at 50° and atmospheric pressure in chlorobenzene and bromobenzene solutions are dependent on the first power of the monomer concentration and the one-half power of the concentration of the azo initiator, 2,2'-azobis-(2-methylpropionitrile). The initial rates of oxidation of several other α-alkylacrylonitriles have been determined. Relatively stable 1:1 copolymers of the α-alkylacrylonitriles with oxygen have been characterized.

Recently there have been extensive studies by Mayo and co-workers[2–5] on the action of oxygen on

various unsaturated compounds, from the point of view of both products and mechanisms. This paper reports a continuation of our work,[6] chiefly on the nitrile monomers. Studies have been made

(1) From the Ph.D. thesis of Stewart C. Brown, 1957, and the M.S. thesis of Robert W. Medeiros, 1957.

(2) A. A. Miller and F. R. Mayo, THIS JOURNAL, **78**, 1017 (1956).

(3) F. R. Mayo and A. A. Miller, ibid., **78**, 1023 (1956).

(4) G. A. Russell, ibid., **78**, 1035 (1956).

(5) F. R. Mayo and co-workers, ibid., **80**, (a) 2465, (b) 2480, (c) 2493, (d) 2497, (e) 2500 (1958).

(6) (a) K. C. Smeltz and E. Dyer, THIS JOURNAL, **74**, 623 (1952); (b) E. Dyer, O. A. Pickett, Jr., S. F. Strause and H. E. Worrell, Jr., ibid., **78**, 3384 (1956); (c) S. F. Strause and E. Dyer, ibid., **78**, 136 (1956).