[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Reactions of 1-Chloro-3-nitro-2-butene and Sodium 2-Propanenitronate; 3-Methyl-4-(2-nitro-2-propyl)-isoxazoline Oxide

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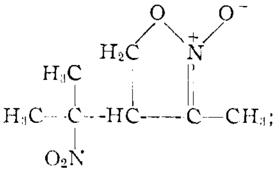
RECEIVED OCTOBER 28, 1953

Reaction of 1-chloro-3-nitro-2-butene and sodium 2-propanenitronate yields 3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide (I, 35–40%), 2,3-dimethyl-2,3-dinitrobutane (II, 10–12%) and 5-methyl-2-nitro-2,4-hexadiene (III, 3.5%, slightly impure). The structure of I was assigned on the basis of its (1) physical and chemical properties, (2) infrared absorption characteristics (>C=N— absorption at 6.05 μ; C–NO_2 absorption at 6.4, 7.4 and 11.5 μ), and (3) reaction with dilute sodium hydroxide to give 3-methyl-4-(2-isopropenyl)-isoxazole (VIII). Possible mechanisms for formation of I, II, III and VIII are discussed. 1-Chloro-3-nitro-2-butene was synthesized by (1) preparation of 1-chloro-3-nitro-2-butanol (56%) from chloroacetaldehyde and nitroethane in triethylamine, (2) formation of 1-chloro-3-nitro-2-butyl acetate (89%) from acetic anhydride and 1-chloro-3-nitro-2-butanol, and (3) conversion of the acetate to 1-chloro-3-nitro-2-butene (72%) by reaction with sodium carbonate.

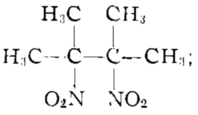
Salts of nitroalkanes undergo nucleophilic displacement with alkyl halides to give substituted nitro compounds (carbon-alkylation) or/and oximes and carbonyl compounds (possibly by decomposition of intermediate nitronic esters, oxygen-alkylation).[2,3] In general, benzyl halides which are substituted in the *ortho* or *para* positions with electronegative or electropositive groups react with alkanenitronates to yield substituted benzaldehydes and the oximes derived from the nitroalkanes[2b,3]; *o*- and *p*-nitrobenzyl halides[2b,3] are exceptions, however, in that they react with alkanenitronates to give carbon-alkylated products in good yields. In the present investigation, in order to determine the influence of a conjugated nitroölefinic group on the displacement properties of alkyl halides, a study has been made of the reactions of a substituted nitroallyl halide, *i.e.*, 1-chloro-3-nitro-2-butene,[4] with the sodium salt of 2-nitropropane.

1-Chloro-3-nitro-2-butene was synthesized by (1) condensation of chloroacetaldehyde and nitroethane in the presence of triethylamine to yield 1-chloro-3-nitro-2-butanol (56%), (2) reaction of the alcohol with acetic anhydride to give 1-chloro-3-nitro-2-butyl acetate (89%), and (3) conversion of the acetate to 1-chloro-3-nitro-2-butene (72%) by the action of sodium carbonate. 1-Chloro-3-nitro-2-butene gives a rapid chloride ion reaction with silver nitrate; it also exhibits "positive" halogen characteristics[5] in that iodine is liberated rapidly upon reaction with sodium iodide in acetone[6] (its homolog, 3-chloro-1-nitro-1-propene[1] does not give a rapid reaction with silver nitrate unless heated; it gives, however, an instantaneous oxidation reaction with iodide ion to yield iodine).

Reaction of equimolar amounts of 1-chloro-3-nitro-2-butene and sodium 2-propanenitronate in absolute ethanol at −20 to −15° occurs exothermically to yield 3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide (I, 35–40%)[7] and 2,3-dimethyl-2,3-dinitrobutane (II, 10–12%); evidence was also obtained for the formation of 5-methyl-2-nitro-2,4-hexadiene[8] (III, 3.5%, slightly impure, see Experimental).[9]

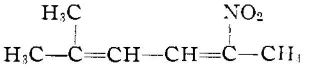


I



$$H_3C{-}\overset{\overset{H_3C}{|}}{\underset{\underset{O_2N}{|}}{C}}{-}\overset{\overset{CH_3}{|}}{\underset{\underset{NO_2}{|}}{C}}{-}CH_3;$$

II



$$H_3C{-}\overset{\overset{H_3C}{|}}{C}{=}CH{-}CH{=}\overset{\overset{NO_2}{|}}{C}{-}CH_3$$

III

The principal concern of the present communication is the establishment of structure of 3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide (I). The structural assignment of I is based on (1) the possible reactions which will allow its formation, (2) its quantitative, infrared and ultraviolet analyses, (3) its physical and chemical properties, and (4) its

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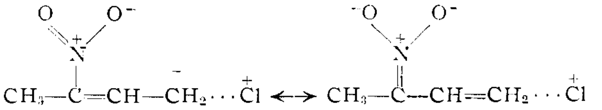
[1] Abstracted from a dissertation presented by F. Conrad to the Graduate School of The Ohio State University, April, 1952, in partial fufillment of the requirements for the Ph.D. degree. This research was sponsored by the Office of Naval Research.

[2] (a) J. T. Thurston and R. L. Shriner, *J. Org. Chem.*, **2**, 183 (1937); (b) L. Weisler and R. W. Helmkamp, THIS JOURNAL, **67**, 1167 (1945); (c) R. N. Boyd and R. J. Kelly, *ibid.*, **74**, 4600 (1952).

[3] H. B. Hass and M. L. Bender, *ibid.*, **71**, 1767, 3482 (1949); H. B. Hass, E. J. Berry and M. L. Bender, *ibid.*, **71**, 2290 (1949).

[4] 1-Chloro-3-nitro-2-butene is an olefinic analog of *o*- and *p*-nitrobenzyl halides.

[5] The positive characteristics of chlorine in 1-chloro-3-nitro-2-butene may be anticipated in view of the following electronic considerations

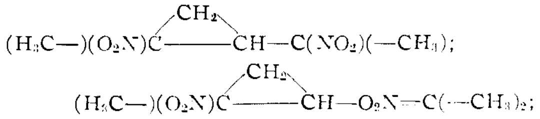


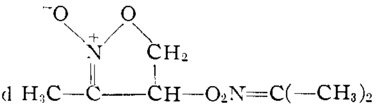
[6] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 140.

[7] Possible products which are isomeric with I such as:

$H_3C{-}C(NO_2){=}CH{-}CH_2{-}C(NO_2)({-}CH_3)_2;$

$H_3C{-}C(NO_2){=}CH{-}CH_2{-}O_2N{=}C({-}CH_3)_2;$



and 

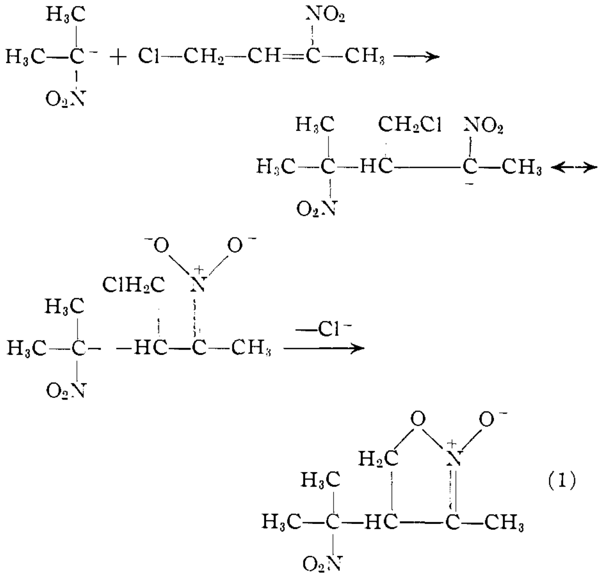
were not found; a complete discussion allowing differentiation of I from these products is contained in ref. 1.

[8] Formation of III may occur by carbon-alkylation of 2-nitropropane with 1-chloro-3-nitro-2-butene involving displacement of chloride ion to give 2,5-dinitro-5-methyl-2-hexene which then undergoes base-catalyzed elimination of nitrous acid.

[9] A complex low-boiling mixture and a tarry residue (20%) were also obtained which could not be separated and identified.

conversion by the action of bases to 3-methyl-4-(2-isopropenyl)-isoxazole (VIII).

The formation of I from 1-chloro-3-nitro-2-butene and sodium 2-propanenitronate may be explained by the following sequence (equations 1): (1) addition of the Michael type of the 2-propanenitronate anion by carbon-alkylation to 1-chloro-3-nitro-2-butene and (2) internal nucleophilic displacement of chlorine by the intermediate ion involving oxygen-alkylation to yield the isoxazoline oxide (I).



(1)

I

Addition of the Michael type of acidic nitroalkanes to conjugated nitroölefins to yield 1,3-dinitroalkanes is a general reaction[10]; formation of isoxazoline oxides or/and substituted nitrocyclopropyl ketones by intramolecular condensation of α-bromo, γ-nitroketones in the presence of bases has been reported by Kohler[11a] and by Smith,[11b] *et al.*

3-Methyl-4-(2-nitro-2-propyl)-isoxazoline oxide, $C_7H_{12}N_2O_4$ (I), is a stable white solid which crystallizes from acetone. Its polar characteristics are indicated by its insolubility in ethyl ether and in carbon tetrachloride; it is also only fairly soluble in ethanol[12] and insoluble in water. In contrast, dinitrocyclopropanes,[7] dinitroölefins[7] and dinitroalkanes whose molecular weights and structures might be compared with I are expected to be soluble in non-polar solvents. The isoxazoline oxide is oxidized rapidly by neutral permanganates.[12] It dissolves readily in dilute alkali with decomposition[12]; however, neither it nor its hydrolysis products give reactions of primary or secondary nitroalkanes upon acidification in the presence of nitrite ion.[13] The isoxazoline oxide, only slightly affected by dilute acids, dissolves in concentrated sulfuric acid with evolution of heat to give mixtures which on dilution evolve oxides of nitrogen; these properties are characteristic of nitronic esters[14a] and of isoxazoline oxides.[14b]

The structure proposed for I is in excellent agreement with its infrared (Fig. 1A) spectra. The presence of a nitro group attached to a saturated carbon atom in I (Fig. 1A) is indicated by absorption at 6.4 (asymmetric stretching), 7.4 (symmetrical stretching) and 11.75 μ[15] (deformation of C–N bond). A sharp intense absorption band occurs at 6.05 μ; this absorption is of major importance in the structure assignment since it is believed to indicate the presence of the —C=N— linkage of an isoxazoline oxide. In general, —C=N— groups absorb at 6.0–6.3 μ[15a]; absorption by the —C=N— group in Schiff bases occurs at 6.1 μ.[16b] The Raman absorption frequencies of the —C=N— group of imides, oximes and their esters and salts, and benzalanilides also range from 6.0 to 6.5 μ.[17] Further confirmation for the >C=N— absorption frequency of I was obtained upon determining the infrared characteristics of the methyl ester of dimethyl nitromalonate[18] ($H_3C{-}O_2N{=}C({-}CO_2CH_3)_2$, a nitronic ester; Fig. 1B, >C=N— at 6.2 μ), dimethyl nitromalonate (Fig. 1–C, C–NO_2 at 6.4 μ), acetone oxime (>C=N— at 5.94 μ), and trimethylisoxazole[19] (Fig. 1D, >C=N— at 6.1 μ); in converting dimethyl nitromalonate into its methyl nitronic ester, the absorption for a nitro group at 6.4 μ has been replaced by >C=N— absorption at 6.2 μ.[20]

Aliphatic nitronic esters are usually very sensitive to heat (and possibly to bases) and decompose into oximes and aldehydes.[2b,3,14a] Kohler[21] has reported that 5-benzoyl-3,4-diphenylisoxazoline oxide (IV, equations 2) is converted to its isoxazole (VI) by the action of heat; the ketoöximino intermediate (V) also was obtained. 3,4,5-Triphenylisoxazoline oxide[14b] also is converted into triphenylisoxazole by bases; however, its ketoöximino intermediate could not be isolated. It may be concluded therefore that the action of bases on isoxazoline oxides is analogous to their action on nitronic esters; however, at elevated temperatures or under alkaline conditions the intermediate ketoöximes may

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[10] A. Lambert and H. A. Piggott, *J. Chem. Soc.*, 1489 (1947); C. T. Bahner and H. T. Kite, THIS JOURNAL, **71**, 3597 (1949).

[11] (a) E. P. Kohler and A. R. Davis, *ibid.*, **52**, 4520 (1930), and the many previous papers by Kohler and associates concerning isoxazoline oxides and nitrocyclopropanes; (b) L. I. Smith and J. S. Showell, *J. Org. Chem.*, **17**, 836 (1952), and the many previous papers of Smith and associates concerning nitrocyclopropanes.

[12] These properties of I are similar to those of isoxazoline oxides which are substituted by aryl groups, ref. 11a.

[13] H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 373 (1943).

[14] (a) F. Arndt and J. D. Rose, *J. Chem. Soc.*, 1 (1935); (b) E. P. Kohler and G. R. Barrett, THIS JOURNAL, **46**, 2105 (1924).

[15] (a) D. C. Smith, C. Y. Fan and J. R. Nielsen, *J. Chem. Phys.*, **18**, 707 (1950); (b) a nitro group attached to a carbon-carbon double bond exhibits its principal absorption at 6.5–6.6 μ and thus can be readily differentiated from a nitro group attached to a saturated center, J. W. Shepherd, Master's thesis, The Ohio State University, 1951.

[16] (a) R. B. Barnes, R. C. Gore, V. Liddel and V. Z. Williams, "Infrared Spectroscopy," Reinhold Publ. Corp., New York, N. Y., 1944, pp. 19–25; (b) L. W. Daasch and V. E. Hanninen, THIS JOURNAL, **72**, 3673 (1950); L. W. Daasch, *ibid.*, **73**, 4523 (1951).

[17] K. W. Kohlrausch and R. Seka, *Z. physik. Chem.*, **38B**, 72 (1937).

[18] Prepared by the method of ref. 14a.

[19] Prepared by the method of W. R. Dunstan and T. S. Dymond, *J. Chem. Soc.*, 410 (1891).

[20] (a) The ultraviolet absorption of I in 50% ethanol is simple and is consistent with the proposed structure.[20b] The absorption characteristics of I are summarized as: strong extended absorption over the region 220–230 mμ (absorption maximum at 220 mμ, log ϵ 3.95), continuous decreased absorption over the range 230–270 mμ (log ϵ range of 3.87–2.64), and weak absorption over the range 270–200 mμ. (b) E. A. Braude, *Ann. Rep.*, **42**, 105 (1945); E. A. Braude, E. R. H. Jones and G. G. Rose, *J. Chem. Soc.*, 1104 (1947).

[21] E. P. Kohler, THIS JOURNAL, **46**, 1737 (1924).

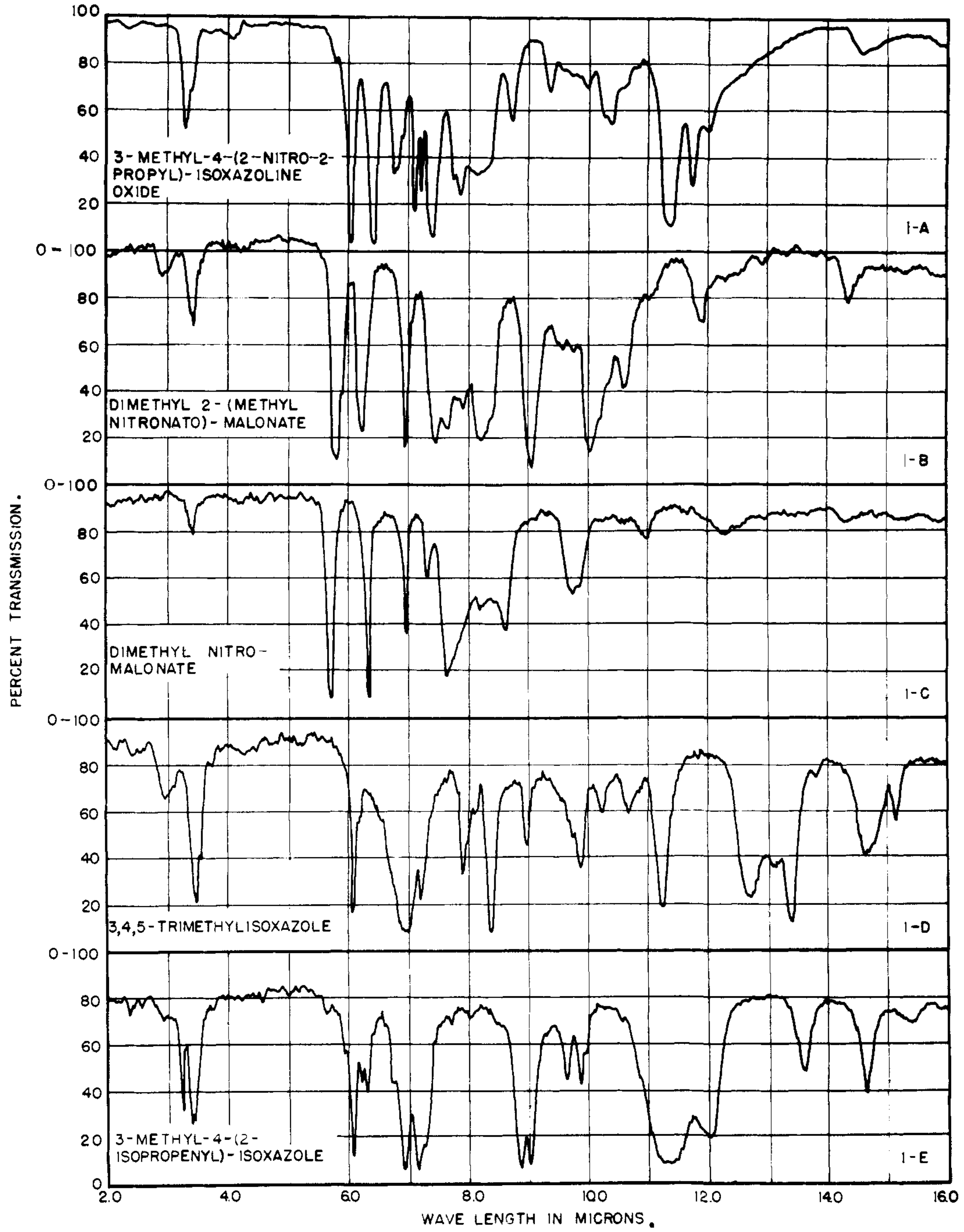
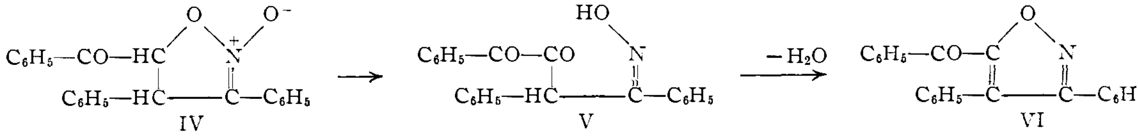


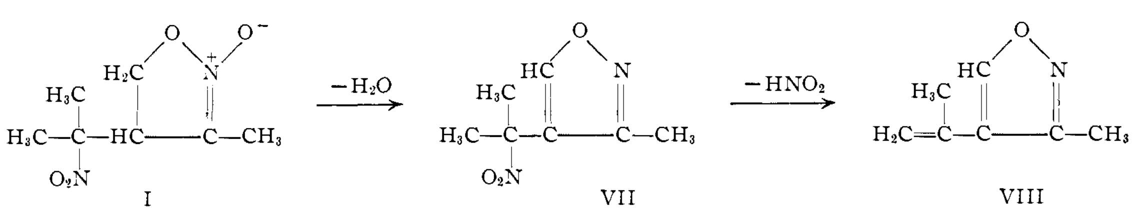
Fig. 1.—Infrared absorption spectra (Baird spectrophotometer, model B): 1-A (0.10-mm. cell; 10% by weight in $Cl_2CH-CHCl_2$); 1-B and 1-C, (0.10-mm. cell; 0.4 *M* in $Cl_2CH-CHCl_2$); and 1-D and 1-E (sandwich cell).

be converted readily into their isoxazoles with elimination of water.



(2)

In an attempt to develop a chemical proof of structure for I, its decomposition reactions with dilute aqueous sodium hydroxide (1–2%) at 55° were investigated. Decomposition of I occurred readily (equations 3) under these conditions; the products isolated were 3-methyl-4-(2-isopropenyl)-isoxazole (VIII, 8% yield), and nitrite ion. Attempts to obtain a sample of intermediate VII, presumably 3-methyl-4-(2-nitro-2-propyl)-isoxazole,[1] of analytical purity were unsuccessful because



I VII VIII (3)

it decomposed rapidly evolving oxides of nitrogen[22]; the decomposition and elimination reactions of I were thus conducted under conditions to favor formation of VIII. The identification of VIII was based on (1) its quantitative analysis, C_7H_9NO, (2) its physical properties, (3) its formation of a solid addition product with mercuric chloride[23] and (4) the natures of its infrared (Fig. 1E) and ultraviolet spectra (see Experimental) and their similarities to those of trimethylisoxazole (Fig. 1D), see Experimental.

The identity of 2,3-dimethyl-2,3-dinitrobutane (II) was established from its chemical and physical properties and by comparison with an authentic sample.[24] Although 2-chloro-2-nitropropane and 3-nitro-1(or -2-)-butene have not been isolated from the reaction mixture[9] (see Experimental), the formation of II (10–12%) may be related to exchange of "positive" chlorine of 1-chloro-3-nitro-2-butene with sodium 2-propanenitronate to give 2-chloro-2-nitropropane (equation 4) and subsequent reaction of 2-chloro-2-nitropropane with sodium 2-propanenitronate (equation 5). This reaction sequence might be predicted on the basis of the "positive"

$$H_3C—C(NO_2){=}CH—CH_2Cl + Na^{+-}O_2N{=}C(—CH_3)_2 \longrightarrow H_3C—C(NO_2){=}CH—CH_2^-Na^{-+} + H_3C—ClC(NO_2)—CH_3 \quad (4)$$

$$H_3C—ClC(NO_2)—CH_3 + Na^{+-}O_2N{=}C(—CH_3)_2 \longrightarrow (H_3C—)_2C(NO_2)—C(NO_2)(—CH_3)_2 + NaCl \quad (5)$$

characteristics of the halogen of 1-chloro-3-nitro-2-butene and that salts of secondary nitroalkanes undergo displacement with the corresponding *gem*-halonitroalkanes to give tertiary *vicinal* dinitroalkanes in good yields.[24] Other evidence that indicates that halogen interchange may occur in systems of this type is that II is formed by reaction of sodium 2-butanenitronate or sodium ethanenitronate with 2-bromo-2-nitropropane[24] or by reaction of sodium 2-propanenitronate with 1-bromo-1-nitroethane,[24] 1,1-dichloro-1-nitroethane,[24] iodoform[25] or ethyl bromomalonate.[25] Similarly van Tamelen and Van Zyl[26] have postulated halogen interchange and subsequent displacement to account for the formation of II, sodium 2-propanenitronate, diethyl bromoethylmalonate and sodium bromide by reaction of 2-bromo-2-nitropropane and sodium diethyl ethylmalonate.

Experimental

1-Chloro-3-nitro-2-butanol.—A stirred solution of nitroethane (75 g., 1.0 mole), chloroacetaldehyde (98 g., 0.5 mole of 40% aqueous solution) and 95% ethanol (75 ml.) was heated to 65-70°. Triethylamine (3 ml.) was then added; additional portions (1 ml.) were added at hourly intervals. After 4 hours, water (300 ml.) and concentrated hydrochloric acid (5 ml.) were added to the reaction mixture; the solution then separated into two layers. The aqueous layer was extracted with ethyl ether; the ether extract was then concentrated at reduced pressure. The residue was distilled under nitrogen to give **1-chloro-3-nitro-2-butanol**, b.p. 80–86° (1.2 mm.), 42.9 g., 56% yield. The physical constants of an analytical sample are: b.p. 74–76° (0.8 mm.), n^{20}_D 1.4778, d^{20}_{20} 1.3424, MR_D (calcd.) 32.58, MR_D (found) 32.39.

Anal. Calcd. for $C_4H_8O_3NCl$: C, 31.37; H, 5.15; N, 9.12. Found: C, 31.29; H, 4.71; N, 9.38.

Commercial nitroethane (Commercial Solvents Corporation) which has been washed with aqueous sodium bicarbonate and dried by extraction with saturated sodium chloride is sufficiently pure for this synthesis. If the chloroacetaldehyde is acidic, it should be neutralized in order to obtain satisfactory results. Ethanol may be added to effect complete solution of the starting materials; it may be omitted, however, without resulting in serious lowering of yields. Yields obtained from larger runs (2–3 mole quantities) ranged consistently from 40–45%.

1-Chloro-3-nitro-2-butyl Acetate.—Acetic anhydride (53 g., 0.575 mole) was added slowly to a stirred solution of 1-chloro-3-nitro-2-butanol (76.8 g., 0.5 mole) and concd. sulfuric acid (1 ml.). The rate of addition was controlled such that the temperature of reaction did not rise above 45°. After addition was completed, the mixture was distilled at reduced pressures to yield acetic acid, acetic anhydride, and **1-chloro-3-nitro-2-butyl acetate**, b.p. 84–92° (1.2 mm.), 86.6 g., 89% yield. The physical constants of an analytical sample are: b.p. 76–77° (0.8 mm.), n^{20}_D 1.4553, d^{20}_{20} 1.2702, MR_D (calcd.) 42.05, MR_D (found) 41.53.

Anal. Calcd. for $C_6H_{10}O_4NCl$: C, 36.83; H, 5.16; N, 7.16. Found: C, 37.05; H, 4.97; N, 6.88.

1-Chloro-3-nitro-2-butene.—A stirred mixture of 1-chloro-3-nitro-2-butyl acetate (78.4 g., 0.4 mole), anhydrous sodium carbonate (21.2 g., 0.2 mole), and C.P. benzene (200 ml., dried over calcium hydride) was refluxed for 5–6 hours and then cooled. The solid was filtered and washed with benzene and ethyl ether; the filtrates were combined and then concentrated at reduced pressure. The residue was distilled at reduced pressure to give **1-chloro-3-nitro-2-butene**, b.p. 75–90° (3.0-4.0 mm.), 39.4 g., 72% yield. The physical constants of a redistilled sample are: b.p. 64–65° (2.5 mm.), n^{20}_D 1.4997, d^{20}_{20} 1.2719, MR_D (calcd.) 31.37; MR_D (found) 31.55; infrared absorption for conjugated C–NO₂ at 6.5 μ.

Anal. Calcd. for $C_4H_6O_2NCl$: C, 35.16; H, 4.40; N, 10.25. Found: C, 35.10; H, 4.17; N, 10.25.

It is essential that the benzene be dried and that the sodium carbonate be anhydrous to obtain good yields consistently. Substitution of potassium carbonate or sodium acetate for sodium carbonate is not recommended; the product is often converted to lower boiling liquids (unidentified). The time factor should be increased several hours for larger runs.

Reaction of 1-Chloro-3-nitro-2-butene and Sodium 2-Propanenitronate.—2-Nitropropane (62 g., 0.70 mole) was slowly added to a cooled solution of sodium (15.0 g., 0.65 mole) in absolute ethanol (700 ml.). The mixture was cooled to −20°, and 1-chloro-3-nitro-2-butene (88.7 g., 0.65 mole) was added rapidly; the mixture was then stirred for 24 hours. The cold reaction mixture then contained a white solid and was filtered; the precipitate was washed with ether (100 ml.). The ether washings and the alcoholic filtrate (I) were combined. The white solid, a mixture of sodium chloride, organic salts, and insoluble organic products, was triturated with water (100 ml.) and refiltered. Titration of the aqueous filtrate with silver nitrate indicated

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[22] The intermediate ketoöximino compounds of VII and of VIII or its dioximes or 2,4-dinitrophenylhydrazones could not be isolated.

[23] This reaction is characteristic of trimethylisoxazole, ref. 18.

[24] L. W. Seigle and H. B. Hass, *J. Org. Chem.*, **5**, 100 (1940).

[25] D. E. Hudgin, Master's Thesis, Purdue University, 1941.

[26] E. E. van Tamelen and G. Van Zyl, THIS JOURNAL, **71**, 835 (1949); E. E. van Tamelen and G. Van Zyl, *ibid.*, **72**, 2979 (1950).

that 95–98% of the theoretical chloride ion had formed. The white solid was recrystallized from C.P. acetone to yield **3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide**, 37.8 g., m.p. 77–78°.

Anal. Calcd. for $C_7H_{12}N_2O_4$: C, 44.67; H, 6.43; N, 14.89. Found: C, 44.71; H, 6.24; N, 14.28.

The alcoholic filtrate I was evaporated at reduced pressure to a volume of approximately 150 ml. Ethyl ether (100 ml.) was added and the mixture was kept in a refrigerator for 24 hours. The yellow solid which formed was filtered; the filtrate II was saved. The yellow solid was washed with water (100 ml.) and filtered to yield additional 3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide, 4.4 g. The total yield of isoxazoline oxide was 42.2 g., 36% of theoretical. (The reaction temperatures were varied from −20° to 30°; at the higher temperatures the yields of isoxazoline oxide ranged from 10–15% and the amounts of tarry residues were much greater). The aqueous filtrate, after acidification, gave a carbonyl group reaction with 2,4-dinitrophenylhydrazine; this reaction arises from conversion of sodium 2-propanenitronate by the Nef[27] reaction to acetone.

Filtrate II was evaporated at reduced pressure; the resulting thick sirup was cooled for 2 days in a refrigerator. A solid precipitated and was filtered (5.2 g.); the filtrate III was saved. The white solid, after recrystallization from ether, was identified as 2,3-dimethyl-2,3-dinitrobutane, m.p. 205–207°, lit.[24] 209°; no depression by an authentic[24] sample (m.p. 208–210°).

The filtrate III was distilled to give a yellow liquid, b.p. 50–75° at 2 mm. Ether (10 ml.) was added and the solution was cooled to −78°. A yellow solid precipitated which was filtered from the cold solution; the filtrate IV was saved. The yellow solid, **5-methyl-2-nitro-2,4-hexadiene** (3.2 g., 3.5% yield) melted at 25–28° after several recrystallizations from cold ether. Its infrared spectrum contains well-defined bands at 6.15 (conjugated diene system), 6.65 (nitro group conjugated with diene system) and 7.65 μ (nitro group); absorption in the ultraviolet region (95% ethanol) occurs at 230 mμ ($\epsilon_{\max}$ 7,700) and 335 mμ ($\epsilon_{\max}$ 11,700), respectively.[1,28]

Anal. Calcd. for $C_7H_{11}NO_2$: C, 58.57; H, 7.80; N, 9.93. Found: C, 58.11; H, 7.06; N, 9.15.

The filtrate IV was distilled to yield a yellow liquid[9] (33 g.): b.p. 50–58.5° (0.8 mm.), n^{20}_{D} 1.4812–1.5042. Repeated distillations[1] failed to result in effective purification of this mixture. The combined residues[9] (20.3 g.) from all distillations were steam distilled to give additional 2,3-dimethyl-2,3-dinitrobutane (1.2 g.); the total yield of 2,3-dimethyl-2,3-dinitrobutane (6.4 g.) was 11%.

3-Methyl-4-(2-isopropenyl)-isoxazole.—3-Methyl-4-(2-nitro-2-propyl)-isoxazoline oxide (25 g., 0.14 mole) was stirred vigorously with 2% aqueous sodium hydroxide (200 ml.) at 55–60°. Within several minutes, the isoxazoline oxide had dissolved to give a clear yellow solution. After 5 minutes, cloudiness developed and an oil separated at the bottom of the reaction mixture. The mixture was heated for one hour at 55–60°, cooled, and then extracted with ethyl ether; the aqueous layer, upon acidification, evolved oxides of nitrogen. The ether extract was dried over sodium sulfate, concentrated and then distilled at 60° (1 mm.) to give a volatile product (condensed at −80°) and a high boiling residue (12.4 g., extensively decomposed). Redistillation of the volatile product gave **3-methyl-4-(2-isopropenyl)-isoxazole** (1.4 g., 8.1% yield), a colorless liquid of powerful, fragrant odor, insoluble in water and soluble in usual organic solvents, b.p. 70–71° (17 mm.), n^{20}_{D} 1.4863, infrared spectra Fig. 1E. The isoxazole reacted with saturated mercuric chloride to give a white solid which softens and then dissociates at 124–126°.

Anal. Calcd. for C_7H_9NO: C, 68.29; H, 7.32; N, 11.38. Found: C, 68.27; H, 7.17; N, 11.31.

The high boiling residue was distilled in a Hickman-type still (0.08 mm., considerable decomposition) to give a viscous yellow oil (3.2 g.); redistillation of this product (0.02 mm., b.p. ~ 50°) gave a colorless oily liquid (2.8 g.), n^{20}_{D} 1.5335 which turned dark-red quickly on storage. Consistent analyses for this material could not be obtained because of its rapid decomposition; the analyses fell within the ranges expected for mixtures of 3-methyl-4-(2-nitro-2-propyl)-isoxazole (VII) and 3-methyl-4-(2-isopropenyl)-isoxazole (VIII) (similar agreement was obtained from the infrared and ultraviolet spectra of the product). The freshly-distilled liquid dissolves slowly in dilute aqueous alkali to give a product having the characteristic odor and many of the properties of 3-methyl-4-(2-isopropenyl)-isoxazole; it is thus believed to consist mainly of unstable 3-methyl-4-(2-nitro-2-propyl)-isoxazole (VII).

Ultraviolet Spectra of VIII and of Trimethylisoxazole.—The ultraviolet spectra of VIII and of trimethylisoxazole in 50% ethanol (1×10^{-4} M, resp.) are simple and almost identical; each spectrum exhibited only very little fine structure. The absorption spectrum for VIII is described as: extended absorption at 220 mμ (log ϵ 4.13), continuous decreased absorption over the range 220–270 mμ (log ϵ range of 4.13–2.71), and weak absorption at 270–400 mμ. The spectrum of trimethylisoxazole indicates maximum absorption at 223 mμ (log ϵ 3.92) with continuous decreased absorption over the range 223–250 mμ (log ϵ range of 3.92–2.78) and weak absorption over the range 250–400 mμ.

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[27] J. U. Nef, *Ann.*, **280**, 263 (1894).

[28] E. A. Braude, E. R. H. Jones and G. G. Rose, *J. Chem. Soc.*, 1104 (1947), report that the ultraviolet spectra of conjugated nitroolefins contain from one to three bands of similar intensities (6–10μ apart) in the region of 225–260 mμ; $\epsilon_{\max}$ 3300–9700. 1-Nitro-1,3-pentadiene absorbs at 225 mμ ($\epsilon_{\max}$ 5500) and 298 mμ ($\epsilon_{\max}$ 12,000); β-nitrostyrene absorbs at 227 mμ ($\epsilon_{\max}$ 9500) and 309 mμ ($\epsilon_{\max}$ 16,500).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND]

An Improved Procedure for Preparing Primary Nitroalkanes by the Victor Meyer Reaction

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RECEIVED NOVEMBER 10, 1953

An improved procedure is described for preparing six primary nitroalkanes of high purity in much better yields than those formerly obtained.

A search of the literature has revealed the need of a good laboratory procedure for preparing the higher homologs of primary nitroalkanes. These have been prepared almost exclusively by two methods: (1) the well-known reaction between an alkyl halide and silver nitrite,[1] and (2) the reaction of an α-halocarboxylic acid with sodium nitrite.[2] Of these, the first gives considerably better yields, although they are low. More recently, a few primary nitroalkanes have been prepared by the 1,4-addition of an alkylmagnesium bromide to an α,β-unsaturated nitroölefin.[3] In general, the yields are comparable to those obtained from the Victor Meyer reaction.

The review and extension of the Victor Meyer re-

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[1] V. Meyer and O. Stuber, *Ber.*, **5**, 203 (1872).

[2] H. Kolbe, *J. prakt. Chem.*, **5**, 427 (1872).

[3] G. D. Buckley and E. Ellery, *J. Chem. Soc.*, 1494 (1947).