4-methoxybenzoic acid[14] from compound 10, m.p. 186–187°. 5-Nitro-2,3-dimethoxybenzoic acid[15] had m.p. 178°. The n.m.r. spectrum showed a 2.85-c.p.s. splitting of the aromatic protons which is further evidence for the assumed structure.

Anal. Calcd. for $C_9H_9NO_6$: N, 6.17. Found: N, 6.28.

3-Nitro-4-methylbenzoic acid[16] had m.p. 190°. 4-Nitro-2,5-dimethoxybenzoic acid had m.p. 198°, lit.[10] m.p. 192–193°.

Anal. Calcd. for $C_9H_9NO_6$: N, 6.17. Found: N, 6.18.

Hydrogenation gave α-(4-amino-2,5-dimethoxybenzyl)-γ-butyrolactone, m.p. 108°. The infrared spectrum showed absorption peaks corresponding to a primary amino group (2.98 and 3.08 μ) and a carbonyl group (5.67 μ). The n.m.r. spectrum is in agreement with aromatic protons occupying the positions *para* to each other.

Anal. Calcd. for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57. Found: C, 63.65; H, 6.98; N, 5.59.

6-Nitro-3,4-dimethoxybenzoic acid[17] had m.p. 187° and 6-nitro-3,4-diethoxybenzoic acid[18] had m.p. 143–144°. 3,4-Diethoxybenzoic acid was nitrated at 0° with nitric acid (*d* 1.42); after purification it showed m.p. 144–145°. Mixture melting point with acid obtained by degradation showed no depression. 6-Nitro-3,4-dichlorobenzoic acid[19] had m.p. 164°.

Reduction of α-(Nitrobenzylidene)-γ-butyrolactones to α-(Aminobenzylidene)-γ-butyrolactones.—The general procedure has been published elsewhere.[5] It was altered so that only 180 ml. of hydrochloric acid was used and instead of chloroform in the Soxhlet extraction dry acetone was used. The advantage was that no tars occurred. All amines possessed a yellow color.

Schiff's Bases.—One-half gram of the appropriate amine was dissolved in 1 ml. of benzaldehyde and heated on the water bath for 30 min. Addition of 5 ml. of methanol and cooling in an ice bath caused precipitation of yellow needles. Recrystallization was performed from methanol.

Acknowledgment.—This work was supported financially through Grant RG-08797 by the National Institutes of Health, Bethesda, Maryland. R. W. received for 1961–1962 a stipend by "Honnefer Model" of the Federal Republic of Germany.

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(14) (a) H. Salkowski, *Ann.*, **163**, 8 (1872); (b) V. Froelicher and F. B. Cohen, *J. Chem. Soc.*, **121**, 1656 (1922).

(15) (a) F. C. Cannell and J. L. Simonsen, *ibid.*, **105**, 159 (1913); (b) L. Rubenstein, *ibid.*, 649 (1926).

(16) See under *i*, Table II.

(17) (a) Th. Zincke and B. Francke, *Ann.*, **293**, 192 (1897); (b) J. L. Simonsen and M. G. Rau, *J. Chem. Soc.*, **113**, 24 (1921).

(18) (a) A. G. Perkin and E. R. Watson, *ibid.*, **107**, 206 (1915); (b) O. L. Galmarini, *Anales asoc. quim. arg.*, **39**, 92 (1951); (c) T. Szabo and E. Vinkler, *Acta Chim. Sci. Hung.*, **17**, 201 (1958).

(19) (a) A. Claus and A. W. Bücher, *Ber.*, **20**, 1624 (1887); (b) P. Ruggli and H. Zaeslin, *Helv. Chim. Acta*, **19**, 439 (1936).

A Novel Synthesis of Nitroalkyl Ethers and Their Cleavage to Nitro Alcohols

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The reaction of 2-nitroalkyl acetates with alkali alkoxides and alkyl thiolates has been found to constitute a convenient route for the synthesis of 1-alkoxy-2-nitro alkanes and alkyl 2-nitroalkyl sulfides, respectively. Michael-type additions of 1-alkoxy-2-alkane nitronates to 2-nitro alkenes (prepared *in situ* from 2-nitroalkyl acetates) afford 1-alkoxy-2-alkyl-2,4-dinitro alkanes in satisfactory yields. Reaction of these nitro ethers with boron trichloride results in cleavage with the formation of 2-alkyl-2,4-dinitro 1-alkanols in good yield.

It has been well-established that the Michael-type addition of primary nitro alkanes to α-nitro alkenes gives the desired adducts only in poor yield.[2–6] On the other hand, the reaction affords high yields with secondary nitro alkanes. It seems, therefore, that in order to obtain good yields in the Michael-type addition with primary nitro alkanes, the latter should first be converted to secondary ones. Such a conversion is available readily in the methylolation reaction which converts primary nitro alkanes into secondary nitro alcohols.[7] However, at the basic conditions of the Michael-type addition, these nitro alcohols undergo demethylolation and cannot be employed satisfactorily. It was, therefore, the purpose of this investigation to convert the hydroxyl group in nitro alcohols into a group which would be stable under the conditions of the Michael-type addition, then to regenerate the hydroxyl group, and finally to convert by demethylolation the resulting polynitro alkanol into the polynitro alkane. While the first two goals of this research could be realized, the demethylolation step which required basic catalysis did not lead to the desired polynitro alkanes; instead, a rearrangement took place leading to isoxazoles.[8]

At the outset of this investigation it was hoped that acetals would be good protecting groups and would subsequently be removed readily. These expectations were, however, not fulfilled when tested on model compounds. For instance, 2-(2-nitro-2-methyl-1-propoxy)-tetrahydropyran which was prepared from dihydropyran and 2-nitro-2-methyl-1-propanol according to the procedure of Parham[9] could not be cleaved to the alcohol with dilute hydrochloric acid. Stronger acids such as concentrated hydrochloric acid or boron trichloride caused extensive tar formation. The acetal, bis(2-nitrobutoxy)methane[10] (I), was quantitatively converted to 2-nitro-1-butanol (II) by cleavage with boron trichloride but was found to be unstable at the conditions of the Michael-type reaction. I was readily hydrolyzed in basic medium to the alcohol (II) and formaldehyde.

$$\underset{\text{I}}{(H_3CCH_2CH(NO_2)CH_2O)_2CH_2} \xrightarrow{OH^-} \underset{\text{II}}{2H_3CCH_2CH(NO_2)CH_2OH} + CH_2O$$

Preparation of 1-Alkoxy-2-nitro Alkanes.—Because of the instability of nitroalkyl acetals at the conditions at which Michael-type additions are usually carried out, our investigation turned to 2-nitroalkyl ethers in which

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(1) From the Ph.D. thesis of S. Markofsky, Purdue University, 1962.

(2) A. Lambert and H. A. Piggott, *J. Chem. Soc.*, 1489 (1947).

(3) C. T. Bahner and H. T. Kite, *J. Am. Chem. Soc.*, **71**, 3597 (1949).

(4) H. R. Snyder and W. E. Hamlin, *ibid.*, **72**, 5082 (1950).

(5) G. L. Shoemaker and R. W. Keown, *ibid.*, **76**, 6374 (1954).

(6) H. Feuer and R. Miller, *J. Org. Chem.*, **26**, 1348 (1961).

(7) H. B. Hass and E. F. Riley, *Chem. Rev.*, **39**, 373 (1943).

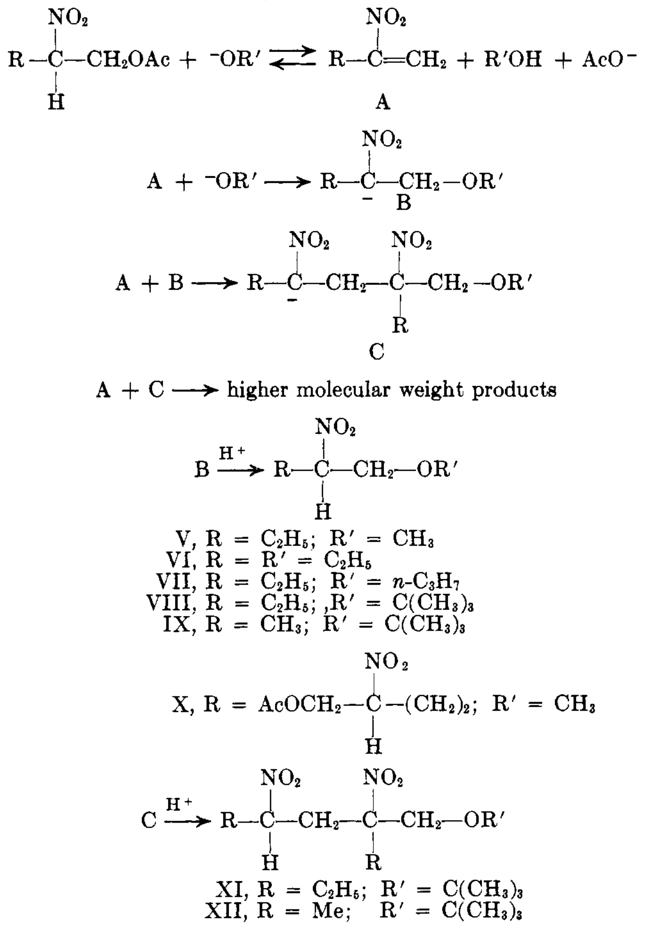
(8) This transformation is discussed in a subsequent paper. H. Feuer and S. Markofsky, *J. Org. Chem.*, **29**, 935 (1964).

(9) W. E. Parham and E. L. Anderson, *J. Am. Chem. Soc.*, **70**, 4187 (1948).

(10) M. Senkus, *ibid.*, **69**, 1380 (1947).

SCHEME I

FORMATION OF 1-ALKOXY-2-NITRO ALKANES AND 1-ALKOXY-2-ALKYL-2,4-DINITRO ALKANES



$$R{-}CH(NO_2){-}CH_2OAc + {}^-OR' \rightleftharpoons R{-}C(NO_2){=}CH_2 + R'OH + AcO^- \quad (A)$$

$$A + {}^-OR' \longrightarrow R{-}\overset{-}{C}(NO_2){-}CH_2{-}OR' \quad (B)$$

$$A + B \longrightarrow R{-}\overset{-}{C}(NO_2){-}CH_2{-}C(NO_2)(R){-}CH_2{-}OR' \quad (C)$$

A + C ⟶ higher molecular weight products

$$B \xrightarrow{H^+} R{-}CH(NO_2){-}CH_2{-}OR'$$

V, R = C_2H_5; R′ = CH_3
VI, R = R′ = C_2H_5
VII, R = C_2H_5; R′ = n-C_3H_7
VIII, R = C_2H_5; ,R′ = $C(CH_3)_3$
IX, R = CH_3; R′ = $C(CH_3)_3$
X, R = $AcOCH_2{-}CH(NO_2){-}(CH_2)_2$; R′ = CH_3

$$C \xrightarrow{H^+} R{-}CH(NO_2){-}CH_2{-}C(NO_2)(R){-}CH_2{-}OR'$$

XI, R = C_2H_5; R′ = $C(CH_3)_3$
XII, R = Me; R′ = $C(CH_3)_3$

the hydroxyl group is substituted by an alkoxy group. It was established that such groups are not affected by dilute base and that such ethers conveniently could be employed in Michael-type additions (see Scheme I).

2-Nitroalkyl ethers usually have been prepared by treating α-nitro alkenes with sodium alkoxides.[11-13] The disadvantage of this method is that α-nitro alkenes are difficult to work with because they (a) tend to decompose during purification which usually requires distillation, (b) are strong lachrymators, and (c) have a tendency to polymerize on standing.[14] Lambert, *et al.*,[12] recognized these difficulties and prepared 1-alkoxy-2-nitro alkanes from α-nitro alkenes which were generated *in situ* from 1,2-dinitro alkanes (III) or 2-nitroalkyl nitrates (IV) However, compounds of structure III or IV are not obtained in good yields, are difficult to purify and to store, and are explosive in nature.[15,16]

Recently, a more convenient way of synthesizing 2-nitroalkyl ethers presented itself due to the work of Feuer and Miller,[6] who showed that 2-nitro alkenes could be generated readily *in situ* from 2-nitroalkyl acetates in the presence of a base. We have now found that 1-alkoxy-2-nitro alkanes can be prepared much more conveniently by adding 2-nitroalkyl acetates slowly to a large excess of an alkali alkoxide (see Table I). An excess was employed in order to minimize the formation of high molecular weight products, formed by the addition of anions such as B and C to the nitro olefin. The nature of the higher molecular weight compounds was established for two cases. 1-*t*-Butoxy-2-ethyl-2,4-dinitrohexane (XI) and 1-*t*-butoxy-2-methyl-2,4-dinitropentane (XII) were obtained directly on treatment of 2-nitrobutyl acetate and 2-nitropropyl acetate, respectively, with potassium *t*-butoxide (see Table II).

A diether, 1,6-dimethoxy-2,5-dinitrohexane (X), was prepared also from the reaction between 1,6-diacetoxy-2,5-dinitrohexane[6] and sodium methoxide. Compound X was separated into its diastereomers by fractionated crystallization. It is of interest to note that the lower melting isomer did not isomerize to the higher melting one on treatment with acid. This is in contrast to the behavior of the 2,5-dinitro-1,6-hexanediols in which the lower melting isomer was found to undergo acid-catalyzed isomerization into the higher melting one.[17]

The convenient synthesis of 2-nitroalkyl ethers was extended to 2-nitroalkyl thioethers (see Table I). These thioethers were obtained in higher yield than the corresponding nitroalkyl ethers and the formation of higher molecular weight by-products was not observed. These findings are in agreement with those of Heath and Lambert, who had prepared a number of alkyl 2-nitroalkyl thioethers from nitro alkenes and sodium alkane thiolates.[18]

Preparation of 1-Alkoxy-2-alkyl-2,4-dinitro Alkanes.—The stability of 1-alkoxy-2-nitro alkanes in basic medium made it possible to employ them in Michael-type additions with α-nitro olefins which were generated *in situ* from 2-nitroalkyl acetates.

In order to obtain optimum yields of these Michael adducts, different solvent systems had to be used. For example, 1-*t*-butoxy-2-ethyl-2,4-dinitrohexane (XI) and 1-methoxy-2-ethyl-2,4-dinitrohexane (XIII) were prepared in high yield when the solvent was aqueous methanol. This same solvent system afforded 1-*t*-butoxy-2-ethyl-2,4-dinitropentane (XIV) only in small amounts. The major products consisted of black high molecular weight material which probably formed by the anionic polymerization of 2-nitro-1-propene. When the reaction was carried out heterogeneously in water as the solvent, the polymerization was minimized and XIV was obtained in 49% yield.

The reaction between sodium 1-*t*-butoxy-2-propanenitronate and 2-nitropropyl acetate gave the highest yield (44%) of 1-*t*-butoxy-2-methyl-2,4-dinitropentane (XII) when a mixture of tetrahydrofuran and water was employed as the solvent. Compound XII also was obtained directly from the reaction between 3 equivalents of 2-nitropropyl acetate and 4 equivalents of potassium *t*-butoxide. Under these conditions, the anion, 1-butoxy-2-propanenitronate, which formed *in situ*, added to 2-nitropropene which also was generated *in situ* to give XII in 36% yield. A summary of examples studied is presented in Table II.

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[11] M. Senkus, U. S. 2,391,815 (Jan. 29, 1946); *Chem. Abstr.*, **40**, 4391 (1946).

[12] A. Lambert, C. W. Scaife, and A. E. Wilder-Smith, *J. Chem. Soc.*, 1474 (1947).

[13] W. Seagers and P. Elving, *J. Am. Chem. Soc.*, **71**, 2947 (1949).

[14] N. Levy and J. D. Rose, *Quart. Rev.* (London), **1**, 358 (1947).

[15] N. Levy, C. W. Scaife, and A. E. Wilder-Smith, *J. Chem. Soc.*, 1096 (1946).

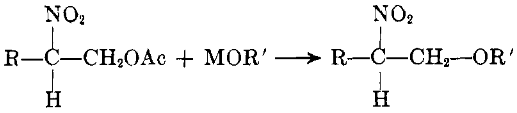
[16] N. Levy and C. W. Scaife, *ibid.*, 1100 (1946).

[17] H. Feuer and A. T. Nielsen, *Tetrahedron*, **19**, 65 (1963).

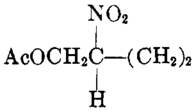
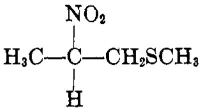
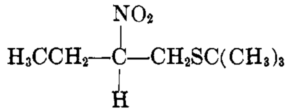
[18] R. L. Heath and A. Lambert, *J. Chem. Soc.*, 1477 (1947).

Table I

Preparation of 2-Nitroalkyl Ethers and Thioethers



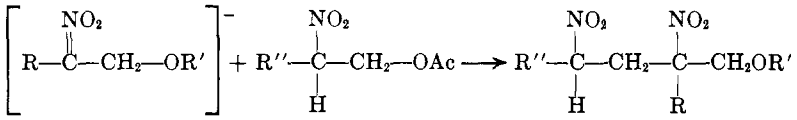
$$R-\underset{H}{\overset{NO_2}{C}}-CH_2OAc + MOR' \longrightarrow R-\underset{H}{\overset{NO_2}{C}}-CH_2-OR'$$

Nitro compound R	MOR' M; R'	Solvent	Product	Yield, %	B.p., °C. (mm.)
C_2H_5	Na; CH_3	CH_3OH	V	66[a]	69 (7)
C_2H_5	Na; C_2H_5	C_2H_5OH	VI	59[a]	80 (10)
C_2H_5	Na; n-C_3H_7	n-C_3H_7OH	VII	55[a]	89 (9)
C_2H_5	K; $C(CH_3)_3$	$(CH_3)_3COH$, THF[c]	VIII	40,[b] 52[a]	80 (5)
CH_3	K; $C(CH_3)_3$	$(CH_3)_3COH$, THF[c]	IX	38,[b] 57[a]	103 (35)
 $AcOCH_2\underset{H}{\overset{NO_2}{C}}-(CH_2)_2$	Na; CH_3	CH_3OH	X	78[a,d]	
CH_3	$NaSCH_3$	CH_3OH	 $H_3C-\underset{H}{\overset{NO_2}{C}}-CH_2SCH_3$	76[a]	100 (16)
C_2H_5	$NaSC(CH_3)_3$	CH_3OH	 $H_3CCH_2-\underset{H}{\overset{NO_2}{C}}-CH_2SC(CH_3)_3$	93[a]	87 (3)

[a] The reaction was carried out at 0–5°. [b] The reaction was carried out at room temperature. [c] Tetrahydrofuran (THF) was added to increase the solubility of potassium t-butoxide. [d] A mixture of diastereomers was obtained, m.p. 56–70°.

Table II

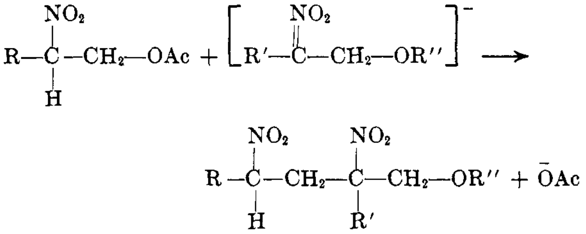
Michael Reactions of 2-Nitroalkyl Ethers



$$\left[R-\overset{NO_2}{\overset{\|}{C}}-CH_2-OR'\right]^- + R''-\underset{H}{\overset{NO_2}{C}}-CH_2-OAc \longrightarrow R''-\underset{H}{\overset{NO_2}{C}}-CH_2-\underset{R}{\overset{NO_2}{C}}-CH_2OR'$$

Nitro ethers R; R'	Nitro acetate R''	Product	Yield, %	B.p., °C. (μ)	M.p., °C.	$n^{20}D$	Formula	Calcd., %			Found, %		
								C	H	N	C	H	N
C_2H_5; $C(CH_3)_3$	C_2H_5	XI	74[a]	70 (4)		1.4521	$C_{12}H_{24}N_2O_5$	52.16	8.75	10.14	52.25	9.00	10.17
CH_3; $C(CH_3)_3$	CH_3	XII	24[b]; 44[c]	85 (35)	52.4–59[d]		$C_{10}H_{20}N_2O_5$	48.37	8.12	11.28	48.61	8.31	11.08
C_2H_5; CH_3	C_2H_5	XIII	74[a]	69 (8)		1.4580	$C_9H_{18}N_2O_5$	46.14	7.75	11.96	46.19	7.60	11.98
C_2H_5; $C(CH_3)_3$	CH_3	XIV	49[b]	75 (10)		1.4516	$C_{11}H_{22}N_2O_5$	50.37	8.45	10.68	50.77	8.49	10.96
CH_3; $C(CH_3)_3$	C_2H_5	XV	66[b]	85 (1)	57–65[d]		$C_{11}H_{22}N_2O_5$	50.37	8.45	10.68	50.86	8.49	10.71

[a] The solvent was H_2O–CH_3OH. [b] The solvent was H_2O. [c] The solvent was H_2O–THF. [d] Constituted a mixture of diastereomers.



$$R-\underset{H}{\overset{NO_2}{C}}-CH_2-OAc + \left[R'-\overset{NO_2}{C}-CH_2-OR''\right]^- \longrightarrow R-\underset{H}{\overset{NO_2}{C}}-CH_2-\underset{R'}{\overset{NO_2}{C}}-CH_2-OR'' + \bar{O}Ac$$

XIII, R = R' = C_2H_5; R'' = CH_3
XIV, R = CH_3; R' = CH_3CH_2; R'' = $C(CH_3)_3$
XV, R = C_2H_5; R' = CH_3; R'' = $C(CH_3)_3$

Cleavage of 2-Nitroalkyl Ethers.—The successful synthesis of 1-alkoxy-2-alkyl-2,4-dinitro alkanes (*vide supra*) indicated a route to the preparation of polynitro monoalcohols, provided that suitable conditions for ether cleavage could be achieved. In a preliminary investigation, a number of cleavage experiments were carried out with 1-alkoxy-2-nitro alkanes. It was found that 1-t-butoxy-2-nitrobutane (VIII) was cleaved in 59% yield with concentrated hydrochloric acid and in 65% yield with gaseous hydrogen chloride. Both cleavage reactions were accompanied by the formation of black tarry decomposition products. This decomposition was not unexpected since strong acids are known to affect primary and secondary nitro alkanes.[7,19] When 4 N hydrochloric acid was used only unchanged VIII was recovered.

In order to eliminate the decomposition of 1-alkoxy-2-nitro alkanes in the cleavage reaction with a strong acid such as hydrogen chloride, it was decided to investigate the applicability of an aprotic acid such as boron trichloride. Gerrard and Lappert[20] have reported that this reagent readily cleaved ethers in high yields and at low temperatures.

It was established that the simple nitro ethers (V, VI, and VIII) were readily cleaved by boron trichloride to the 2-nitrobutyl dichloroboronite which, on subsequent warming with methanol, was converted to 2-nitro-1-butanol (XVI) in high yield. In accordance with the proposed mechanism of ether cleavage with boron trichloride,[20] it would be expected that the ether in which the leaving group would form the most stable carbonium ion would cleave most readily.

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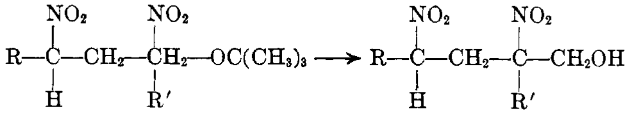
(19) Henry Feuer and Arnold T. Nielsen, *J. Am. Chem. Soc.*, **84**, 688 (1962).

(20) W. Gerrard and M. F. Lappert, *Chem. Rev.*, **58**, 1081 (1958).

TABLE III

CLEAVAGE OF NITRO ETHERS WITH BORON TRICHLORIDE TO NITRO ALCOHOLS



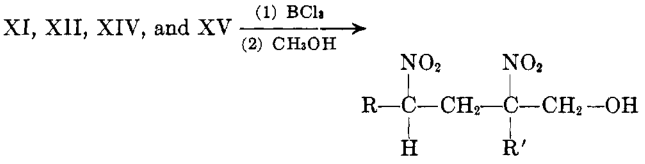
$$\mathrm{R{-}\underset{H}{\overset{NO_2}{C}}{-}CH_2{-}\underset{R'}{\overset{NO_2}{CH_2}}{-}OC(CH_3)_3 \longrightarrow R{-}\underset{H}{\overset{NO_2}{C}}{-}CH_2{-}\underset{R'}{\overset{NO_2}{C}}{-}CH_2OH}$$

Nitro ethers R; R'	Product	Yield, %	B.p., °C. (μ)	M.p., °C.	$n^{20}\text{D}$	Formula	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
C_2H_5; C_2H_5	XVII	64	90 (1)		1.4740	$C_8H_{16}N_2O_5$	43.63	7.32	12.72	43.86	7.31	12.76
CH_3; CH_3	XVIII[a]	53		54.5–55.5		$C_6H_{12}N_2O_5$	37.50	6.29	14.58	37.50	6.37	14.31
CH_3; C_2H_5	XIX	56		30–32		$C_7H_{14}N_2O_5$	40.77	6.84	13.59	41.38	7.09	13.09
C_2H_5; CH_3	XX	67	90 (10)		1.4735	$C_7H_{14}N_2O_5$	40.77	6.84	13.59	40.74	6.83	13.89

[a] The nitro ether was dissolved in dichloromethane prior to treatment with boron trichloride.

Our experiments bear this out, since ether VIII containing a *t*-butoxy group was readily cleaved at ice-bath temperatures to XVI in 80% yield. On the other hand, temperatures of 25 and 38° were required with ethers V and VI carrying an ethoxy and methoxy group, respectively.

The importance of the formation of a stable carbonium ion in the ether cleavage with boron trichloride was further evidenced with 1-alkoxy-2-alkyl-2,4-dinitro alkanes. A number of attempts to cleave 1-methoxy-2-ethyl-2,4-dinitrohexane (XIII) resulted in only partial cleavage, and pure 2-ethyl-2,4-dinitrohexanol (XVII) could not be obtained. In contrast, when the reaction was carried out with 1-*t*-butoxy-2-alkyl-2,4-dinitro alkanes, cleavage occurred readily and 2-alkyl-2,4-dinitro 1-alkanols were obtained in reasonably good yield (see Table III).

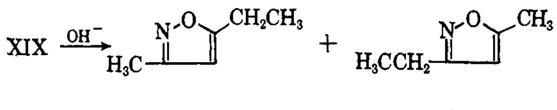


$$\text{XI, XII, XIV, and XV} \xrightarrow[\text{(2) } \mathrm{CH_3OH}]{\text{(1) } \mathrm{BCl_3}} \mathrm{R{-}\underset{H}{\overset{NO_2}{C}}{-}CH_2{-}\underset{R'}{\overset{NO_2}{C}}{-}CH_2{-}OH}$$

XVII, R = R' = C_2H_5
XVIII, R = R' = CH_3
XIX, R = CH_3; R' = C_2H_5
XV, R = C_2H_5; R' = CH_3

The cleavage of the *t*-butoxy ethers usually occurred at the reflux temperature of boron trichloride and a homogeneous solution was obtained. In the case of ether XII, however, the reaction was incomplete because of heterogeneity of the reaction mixture. Complete cleavage resulted by the addition of dichloromethane which rendered the reaction mixture homogeneous.

The cleavage of ether XIV gave the expected alcohol (XIX), but its purification proved to be quite difficult. It was characterized by conversion into an isomeric mixture of 3-methyl-5-ethylisoxazole (XXI) and 3-ethyl-5-methylisoxazole (XXII) on treatment with aqueous base.[8]



XXI XXII

Experimental

2-(2-Nitro-2-methyl-1-propoxy)tetrahydropyran.—To a well-stirred mixture of 9.75 g. (0.08 mole) of 2-nitro-2-methyl-1-propanol and an excess amount of dihydropyran (45 ml.) was added 2 drops of concentrated hydrochloric acid and the temperature was maintained at 35–40° for 21 hr. At the end of this time, 20 ml. of ether was added, the resulting solution was washed with a saturated aqueous solution of sodium bicarbonate, the aqueous solution was extracted with ether, and the ethereal solution evaporated on a rotating evaporator to remove the ether and unchanged dihydropyran. Distillation at 68° and 2 mm. afforded an 88% yield of the pyran ether which had $n^{20}\text{D}$ 1.4521.

Anal. Calcd. for $C_9H_{17}NO_4$: C, 53.19; H, 8.43; N, 6.89. Found: C, 53.26; H, 8.44; N, 6.91.

Cleavage of Bis(2-nitrobutoxy)methane (I). A. With Boron Trichloride.—At a temperature of −80°, 14.6 g. of bis(2-nitrobutoxy)methane[10] was added to an excess (40 ml.) of boron trichloride. After stirring the reaction mixture for 2 hr., it was brought to room temperature and the volatile boron trichloride was removed under vacuum. The crude 2-nitro-1-butyl dichloroboronite was then cooled to 0°, and excess methyl alcohol slowly was added. Evaporating the reaction mixture at room temperature and 20 mm. to remove methyl borate and excess methyl alcohol gave a quantitative yield of 2-nitro-1-butanol, $n^{20}\text{D}$ 1.4394, lit.[21] $n^{20}\text{D}$ 1.4390.

B. **With Aqueous Sodium Hydroxide.**—A 100-ml. three-necked flask equipped with an electric stirrer and thermometer, was charged with 14.5 g. (57 mmoles) of bis(2-nitrobutoxy)-methane and 6.0 g. (150 mmoles) of sodium hydroxide in 30 ml. of water. The contents were stirred for 8 hr. at 38° and then neutralized with glacial acetic acid. After the mixture was extracted with six 75-ml. portions of ether, the extract was evaporated on a rotating evaporator. Distillation of the residue at 93° and 5 mm. afforded a 65% yield of 2-nitro-1-butanol. The infrared spectrum of this material was superimposable on that of an authentic sample of 2-nitro-1-butanol.

1-Methoxy-2-nitrobutane (V).—A solution of sodium methoxide, prepared by dissolving 55.1 g. (2.4 g.-atoms) of sodium in 1740 ml. of methanol, was placed in a three-necked flask equipped with an electric stirrer. Then, 100 g. (0.62 mole) of 2-nitrobutyl acetate, dissolved in 500 ml. of methanol, was added dropwise at 0–5°, over a period of 6 hr. After stirring for 9 hr. more at room temperature, the solution was evaporated in an air stream to remove the solvent. When all of the methanol had been removed, 400 ml. of water was added to dissolve the salts and the solution was neutralized at 0° with 160 ml. of glacial acetic acid. The aqueous solution was extracted with four 750-ml. portions of ether; the extract was dried over anhydrous magnesium sulfate and evaporated on a rotating evaporator. Distillation at 69° and 7 mm. afforded a 66% yield of 1-methoxy-2-nitrobutane, $n^{20}\text{D}$ 1.4200, lit.[6] $n^{20}\text{D}$ 1.4217.

1-Ethoxy-2-nitrobutane (VI).—The experimental procedure was the same as for the corresponding methoxy derivative except that 48.8 g. (2.12 g.-atoms) of sodium was dissolved in 1100 ml. of ethanol prior to the addition of 44.1 g. (0.27 mole) of 2-nitrobutyl acetate. Distillation at 80° and 10 mm. afforded a 59% yield of 1-ethoxy-2-nitrobutane, $n^{20}\text{D}$ 1.4212, lit.[13] $n^{20}\text{D}$ 1.4212.

1-Propoxy-2-nitrobutane (VII).—The experimental procedure was the same as for the corresponding methoxy derivative except that 41.3 g. (1.8 g.-atoms) of sodium was dissolved in 1100 ml. of 1-propanol prior to the addition of 43.5 g. (0.27 mole) of 2-nitrobutyl acetate. Distillation at 89° and 9 mm. afforded a 55% yield of 1-propoxy-2-nitrobutane, $n^{20}\text{D}$ 1.4240, lit.[13] $n^{20}\text{D}$ 1.4238.

1-*t*-Butoxy-2-nitrobutane (VIII).—The experimental procedure was exactly the same as for the preparation of the other 2-nitro-

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(21) B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).

alkyl ethers except that 90 g. (2.3 g.-atoms) of potassium was dissolved in a mixture of 1500 ml. of *t*-butyl alcohol and 350 ml. of tetrahydrofuran prior to the addition of 60 g. (0.37 mole) of 2-nitrobutyl acetate. Distillation at 80° and 5 mm. afforded a 52% yield of 1-*t*-butoxy-2-nitrobutane, n^{20}D 1.4249.

Anal. Calcd. for $C_8H_{17}NO_3$: C, 54.83; H, 9.78; N, 7.99. Found: C, 55.01; H, 9.82; N, 8.04.

1-*t*-Butoxy-2-nitropropane (IX).—The experimental procedure was exactly the same as for the preparation of the other 2-nitroalkyl ethers except that 62 g. (1.59 g.-atoms) of potassium was dissolved in a mixture of 800 ml. of *t*-butyl alcohol and 200 ml. of tetrahydrofuran prior to the addition of 43.5 g. (0.31 mole) of 2-nitropropyl acetate, dissolved in 150 ml. of *t*-butyl alcohol. Distillation at 103° and 35 mm. afforded a 57% yield of 1-*t*-butoxy-2-nitropropane, n^{20}D 1.4219. The nitro ether was injected into a G.E.–S.F. 96 on Chromosorb W gas chromatographic column and analytically pure 1-*t*-butoxy-2-nitropropane was collected and had n^{20}D 1.4209.

Anal. Calcd. for $C_7H_{15}NO_3$: C, 52.15; H, 9.38; N, 8.69. Found: C, 52.42; H, 9.59; N, 8.78.

Further distillation at 125° and 1 mm. afforded a 9% yield of 1-*t*-butoxy-2-methyl-2,4-dinitropentane (XII). The infrared spectrum and retention time (on the gas chromatogram) of this dinitro ether were the same as those of an authentic sample of XII (*vide infra*).

1,6-Dimethoxy-2,5-dinitrohexane (X).—The experimental procedure was essentially the same as for the preparation of 1-methoxy-2-nitrobutane except that 6.2 g. (270 mg.-atoms) of sodium was dissolved in 200 ml. of methanol prior to the addition of 13.1 g. (45 mmoles) of 1,6-diacetoxy-2,5-dinitrohexane.[6] The crude reaction product was sublimed at 50° and 1 μ to afford a 78% crude yield of the diastereomers of 1,6-dimethoxy-2,5-dinitrohexane, m.p. 56–70°. A portion of the mixture of isomers was repeatedly recrystallized from a minimum amount of hot (85°) dibutyl ether until a solid was obtained which had constant m.p. 90°. Sublimation of this material at 65° and 1 μ afforded a pure sample of the high-melting isomer of **1,6-dimethoxy-2,5-dinitrohexane**, m.p. 90°.

Anal. Calcd. for $C_8H_{16}N_2O_6$: C, 40.67; H, 6.83; N, 11.86. Found: C, 40.71; H, 6.73; N, 11.62.

In order to obtain the low-melting isomer, the mixture of diastereomers was dissolved in a minimum amount of ether at room temperature and pentane slowly was added to precipitate the high-melting isomer. The solution was boiled to coagulate the solids, filtered at room temperature, and the filtrate was cooled in Dry Ice to precipitate the 1,6-dimethoxy-2,5-dinitrohexane, enriched in the low-melting isomer. The entire process was repeated to concentrate further the low-melting material. The low-melting isomer was distilled several times at 25° and 1 μ until a constant melting point range of 22.5–23.5° was obtained. (The distillation was carried out in a sublimator, and the distillate was collected as a solid on the cold finger.)

Anal. Calcd. for $C_8H_{16}N_2O_6$: C, 40.67; H, 6.83; N, 11.86. Found: C, 40.65; H, 6.74; N, 11.99.

2-Nitropropyl Acetate.—Into a three-necked flask equipped with a stirrer were placed 195.2 g. (1.85 moles) of 2-nitro-1-propanol and an excess of acetic anhydride (600 ml.). Then, 1 ml. of concentrated sulfuric acid was added dropwise, and the reaction mixture was kept at 60° for 3.5 hr. Distillation at 80° and 5 mm. afforded an 83% yield of 2-nitropropyl acetate, n^{20}D 1.4267.

Anal. Calcd. for $C_5H_9NO_4$: C, 40.81; H, 6.16; N, 9.52. Found: C, 40.90; H, 6.25; N, 9.45.

Methyl 2-Nitropropyl Sulfide.—A sodium methoxide solution was prepared by dissolving 17.3 g. (0.75 g.-atom) of sodium in 400 ml. of methanol. Then, 31 g. (0.65 mole) of methyl mercaptan was added to the methoxide solution at 0°. To the alkaline reaction mixture, containing sodium methylthiolate, was added dropwise with stirring at 0° 39.89 g. (0.27 mole) of 2-nitropropyl acetate. The mixture was kept at ice-bath temperatures for 3 hr. and acidified with a slight excess (50 ml.) of glacial acetic acid. The solution then was evaporated on a rotating evaporator to remove the solvent, 200 ml. of water was added to dissolve the inorganic salts, the aqueous solution was extracted with four 300-ml. portions of ether, and the extract was evaporated on a rotating evaporator. Distillation at 100° and 16 mm. afforded a 76% yield of methyl 2-nitropropyl sulfide, n^{20}D 1.4790, lit.[18] b.p. 105° (20 mm.). The sulfide was characterized by its conversion to methyl 2-nitropropyl sulfone, m.p. 71.5°, lit.[18] m.p. 69–70°.

2-Nitrobutyl *t*-Butyl Sulfide.—The experimental procedure was the same as for the preparation of methyl 2-nitropropyl sulfide except that 13.4 g. (0.54 g.-atom) of sodium, dissolved in 250 ml. of methanol, was treated with 42.6 g. (0.47 mole) of *t*-butanethiol prior to the addition of 35 g. (0.215 mole) of 2-nitrobutyl acetate. Distillation at 87° and 3 mm. afforded a 93% crude yield of 2-nitrobutyl *t*-butyl sulfide. Three distillations were necessary to obtain a pure product with n^{20}D 1.4710, lit.[22] n^{25}D 1.469.

Cleavage of 1-*t*-Butoxy-2-nitrobutane (VIII). A. With Concentrated Hydrochloric Acid.—Into a three-necked flask equipped with an electric stirrer, were placed 9.44 g. (55 mmoles) of VIII and an excess (30 ml.) of concentrated hydrochloric acid. The reaction mixture was stirred at 0° for 30 min. and then at room temperature for 12 hr. The organic material was removed from the acid solution by continuous extraction with ether, and the ethereal solution was dried over anhydrous magnesium sulfate and then evaporated on a rotating evaporator. Distillation at 83° and 4 mm. afforded a 59% yield of 2-nitro-1-butanol, n^{20}D 1.4396, lit.[21] n^{20}D 1.4390.

B. With Gaseous Hydrogen Chloride.—An excess of dry hydrogen chloride was bubbled into 8.27 g. (46 mmoles) of VIII for 2 hr. at 0°. Distillation of the product at 83° and 4 mm. afforded at 65% yield of 2-nitro-1-butanol, n^{20}D 1.4398.

C. With Boron Trichloride.—At a temperature of −80°, 14.9 g. (84.5 mmoles) of VIII was added to an excess (19.5 ml.) of boron trichloride. After 15 min., the flask was placed in an ice bath, and the reaction mixture was kept at 0° for 1 hr. Then, excess boron trichloride was removed under vacuum, the remaining 2-nitro-1-butyl dichloroboronite was cooled to 0°, and excess methanol was added very slowly. The reaction mixture was evaporated at room temperature and 20 mm. to remove methyl borate and excess methanol. Distillation of the residue at 66° and 1 mm. afforded an 80% yield of 2-nitro-1-butanol, n^{20}D 1.4390. The infrared spectrum of this compound was superimposable on that of an authentic sample of 2-nitro-1-butanol.

Cleavage of 1-Methoxy-2-nitrobutane (V) with Boron Trichloride.—The experimental procedure was essentially the same as for the cleavage of VIII by procedure C except that 11.1 g. (83 mmoles) of V and 40 ml. of boron trichloride were employed. After the boron trichloride was removed *in vacuo*, the residue was kept at 38° for 6 hr. in order to decompose the boron trichloride–etherate complex. Work-up as described in procedure C afforded a 72% yield of 2-nitro-1-butanol, n^{20}D 1.4400.

Cleavage of 1-Ethoxy-2-nitrobutane (VI) with Boron Trichloride.—The experimental procedure was essentially the same as above, except that 10 g. (68 mmoles) of VI and 25 ml. of boron trichloride were employed. The reaction mixture was maintained at room temperature for 2 hr. and boron trichloride and ethyl chloride were collected as condensates at −80°. Work-up of the residue afforded a 73% yield of 2-nitro-1-butanol, n^{20}D 1.4380.

On addition of water to the condensate of ethyl chloride and boron trichloride at −80°, boric acid was formed. The ethyl chloride was then removed under vacuum as a gas. The infrared spectrum of this gas was essentially superimposable on that of a known sample of ethyl chloride.

1-Methoxy-2-ethyl-2,4-dinitrohexane (XIII).—A 500-ml. three-necked flask equipped with a mechanical stirrer was charged with 11.24 g. (0.284 mole) of sodium hydroxide dissolved in a mixture of 80 ml. of water and 120 ml. of methanol. The solution was cooled to 0–5°, and 37.8 g. (0.284 mole) of 1-methoxy-2-nitrobutane was added. The reaction mixture then was allowed to come to room temperature, and, after salt formation was complete, 23 g. (0.142 mole) of 2-nitrobutyl acetate was added dropwise at 0° over a 75-min. period. After the addition was complete, the reaction mixture was kept at 0° for 1 hr. and then at room temperature for 3 hr. At the end of this time, the methanol was removed under vacuum, water was added to dissolve the salts, and the aqueous solution was acidified with a slight excess (13 ml.) of glacial acetic acid. The solution was extracted with four 200-ml. portions of ether; the extract was dried over anhydrous magnesium sulfate and evaporated on a rotating evaporator. Distillation of the product at 85° and 10 μ gave a 74% yield of **1-methoxy-2-ethyl-2,4-dinitrohexane**. Repeated distillations of this material at 69° and 8 μ gave fractions with a n^{20}D range of 1.4571–1.4582, due to the presence of two *dl* pairs. The fraction, n^{20}D 1.4580, was analyzed.

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[22] Carl T. Bahner, U. S. Patent 2,511,961; *Chem. Abstr.*, **44**, 8942 (1950).

1-*t*-Butoxy-2-ethyl-2,4-dinitrohexane (XI).—The experimental procedure was essentially the same as for the preparation of XIII except that 16.7 g. (95 mmoles) of 1-*t*-butoxy-2-nitrobutane was added to a solution of 3.74 g. (95 mmoles) of sodium hydroxide in a mixture of 47 ml. of water and 40 ml. of methanol prior to the addition of 7.75 g. (48 mmoles) of 2-nitrobutyl acetate. Distillation of the products at 65° and 2 mm. gave 8.21 g. of recovered 1-*t*-butoxy-2-nitrobutane. Further distillation at 84° and 10 μ afforded a 74% yield of **1-*t*-butoxy-2-ethyl-2,4-dinitrohexane (XI)**. The compound was redistilled at 70° and 4 μ into several portions (n^{20}_D 1.4512–1.4522). The fraction, n^{20}_D 1.4521, was analyzed.

1-*t*-Butoxy-2-ethyl-2,4-dinitropentane (XIV).—Sodium 1-*t*-butoxy-2-butanenitronate was prepared by the addition of 17.6 g. (0.1 mole) of 1-*t*-butoxy-2-nitrobutane to a stirred solution of 4 g. (0.1 mole) of sodium hydroxide in 100 ml. of methanol. After the mixture had been stirred for 4 hr., the solvent was removed in an air stream and the solid salt residue was dissolved in a minimum amount (30 ml.) of water. After 7.35 g. (0.05 mole) of 2-nitropropyl acetate was added, the procedure followed was essentially the same as for the preparation of XIII. Distillation at 75° and 10 μ afforded a 49% yield of XIV. Chromatographing with a G.E.–S.F. 96 on Chromosorb W column gave analytically pure 1-*t*-butoxy-2-ethyl-2,4-dinitropentane.

1-*t*-Butoxy-2-methyl-2,4-dinitrohexane (XV).—The experimental procedure was essentially the same as for the preparation of XIV except that sodium 1-*t*-butoxy-2-propanenitronate was dissolved in 30 ml. of water prior to the addition of 8.05 g. (0.05 mole) of 2-nitrobutyl acetate. Distillation at 85° and 1 μ afforded a 66% yield of XV. The nitro ether was recrystallized by dissolving it in hexane at room temperature and cooling the solution to Dry Ice temperatures. Nine recrystallizations followed by three sublimations at room temperature and 1 μ produced a pure sample of **1-*t*-butoxy-2-methyl-2,4-dinitrohexane**.

1-*t*-Butoxy-2-methyl-2,4-dinitropentane (XII) A. From Sodium 1-*t*-Butoxy-2-propanenitronate and 2-Nitropropyl Acetate.—The experimental procedure was essentially the same as for the preparation of XIV except that sodium 1-*t*-butoxy-2-propanenitronate was dissolved in a mixture of 30 ml. of water and 100 ml. of tetrahydrofuran (THF) prior to the addition of 9.1 g. (0.062 mole) of 2-nitropropyl acetate. The work-up procedure was the same as in the preparation of the other dinitro ethers, except that the THF was evaporated on a steam bath before the reaction mixture was neutralized with acetic acid. Distillation at 85° and 35 μ afforded a 44% yield of 1-*t*-butoxy-2-methyl-2,4-dinitropentane. The nitro ether was injected into a G.E.–S.F. 96 on Chromosorb W gas chromatographic column, and the sample collected was sublimed five times at 40° and 1 μ and had m.p. 52.5–59°.

B. **From Potassium *t*-Butoxide and 2-Nitropropyl Acetate.**—A solution of potassium *t*-butoxide, prepared by the dissolution of 25 g. (0.644 g.-atom) of potassium in a mixture of 370 ml. of *t*-butyl alcohol and 165 ml. of tetrahydrofuran, was placed in a three-necked flask equipped with a thermometer, addition funnel, and electric stirrer. The solution was cooled to 0–5°, and 71 g. (0.482 mole) of 2-nitropropyl acetate, dissolved in 150 ml. of *t*-butyl alcohol, was added dropwise over a period of 2.5 hr. After stirring for 8 hr. more, excess (36 g., 0.644 mole) potassium hydroxide, dissolved in 100 ml. of water, was added at 0° in order to convert any free nitro compounds to their potassium salts. After the solution was stirred at 0–5° for 2 hr. more, the reaction flask was placed in a water bath maintained at 56°, and the organic solvents were removed in an air stream. The aqueous solution was cooled to 0–5° and neutralized with 60 g. of glacial acetic acid dissolved in 100 ml. of water. The mixture was extracted with six 500-ml. portions of chloroform; the extract was dried over anhydrous magnesium sulfate and evaporated on a steam bath. Distillation of the residue at 84° and 10 mm. afforded 16.5 g. of 1-*t*-butoxy-2-nitropropane. When this compound was analyzed by gas chromatography, a peak was obtained which had the same retention time as a known sample of 1-*t*-butoxy-2-nitropropane.

Further distillation at 109° and 1 mm. afforded 14.5 g. (36% yield) of XII. XII gave a peak on a G.E.–S.F. 96 on Chromosorb W gas chromatographic column which had the same retention time as an authentic sample of XII.

2-Ethyl-2,4-dinitro-1-hexanol (XVII).—An excess (12 ml.) of boron trichloride was added at −70° to a 100-ml. flask equipped with a magnetic stirrer, Dry Ice condenser, and drying tube. Then 5 g. (0.018 mole) of 1-*t*-butoxy-2-ethyl-2,4-dinitrohexane was added to the reaction flask. The cold bath was replaced with a water bath, and the mixture stirred rapidly for 6 min. at the reflux temperature of boron trichloride (13°). Immediately, after excess boron trichloride and other volatile substances were removed under vacuum, the residue was cooled to −70°. Excess methanol was added slowly down the sides of the flask (owing to exothermic nature of the reaction), and the reaction mixture very slowly was allowed to come to room temperature. Removing all volatile components at room temperature and 20 mm. left a dark liquid which gave off hydrogen chloride fumes. Therefore, the liquid was dissolved in 500 ml. of chloroform, and the resulting solution was extracted with water until the aqueous phase no longer gave a test for chloride ion with silver nitrate. After the chloroform was evaporated on a steam bath, the residue was distilled at 88° and 1 μ to afford a 64% yield of **2-ethyl-2,4-dinitro-1-hexanol**. Two redistillations at 90° and 1 μ gave an analytically pure sample of the nitro alcohol.

2-Ethyl-2,4-dinitro-1-pentanol (XIX).—The experimental procedure was the same as for the preparation of XVII except that 5 g. (19 mmoles) of 1-*t*-butoxy-2-ethyl-2,4-dinitropentane and 20 ml. of boron trichloride were employed. Distillation at 115° and 4 μ afforded a 56% yield of **2-ethyl-2,4-dinitro-1-pentanol**. Repeated distillations at 85° and 1 μ followed by several recrystallizations from hexane produced a fairly pure sample of the nitro alcohol, m.p. 30–32°.

2-Methyl-2,4-dinitro-1-hexanol (XX).—The experimental procedure was the same as for the preparation of XVII except that 5.3 g. (20.2 mmoles) of 1-*t*-butoxy-2-methyl-2,4-dinitrohexane and 20 ml. of boron trichloride were employed. Distillation at 105° and 4 μ afforded a 67% yield of XX. Several distillations at 90° and 10 μ gave an analytically pure sample of 2-methyl-2,4-dinitro-1-hexanol.

2-Methyl-2,4-dinitro-1-pentanol (XVIII).—The experimental procedure was the same as for the preparation of XVII except that 5 g. of 1-*t*-butoxy-2-methyl-2,4-dinitropentane was first dissolved in 30 ml. of dichloromethane prior to its addition to 10 ml. of boron trichloride. Distillation at 85° and 1 μ afforded a 53% yield of 2-methyl-2,4-dinitro-1-pentanol. The compound was purified for analysis by three recrystallizations from hexane, followed by four distillations at 70° and 1 μ. The nitro alcohol was distilled in a sublimator; the solid was collected on the cold finger and had m.p. 54.5–55.5°.

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