methyl group. The uv spectrum of IX (MeOH) showed maximum absorptions at 227 and 378 nm.

Thermal Decomposition of VI in Benzene.—When a suspension of VI (1.0 g) in benzene (200 ml) was refluxed for 48 hr, a clear yellow solution resulted. Concentration of this solution to 25 ml resulted in a white crystalline precipitate (0.25 g), which when recrystallized three times from a benzene–cyclohexane mixture yielded white needles of VII, mp 186°, lit.[27] mp 180–186°. The uv and pmr spectra of VII are identical with those previously reported.[29,30]

Thermal Decomposition of VI in Dioxane.—When a suspension of VI was refluxed in dioxane, a clear yellow solution was obtained. When this solution was distilled, the first 10-ml fraction had a uv spectrum identical with that of benzene in dioxane. When the reaction solution was further concentrated, VII was obtained.

Thermal Decomposition of IX in Benzene.—When a suspension of IX (1.4 g) in benzene (350 ml) was refluxed for 48 hr, a clear yellow solution resulted. Concentration of this solution to 25 ml resulted in a white powder which when recrystallized three times from a benzene–cyclohexane mixture yielded white needles, mp 211–212°, which analyzed correctly for X. *Anal.* Calcd for $C_{14}H_{10}N_6O_9$: C, 41.38; H, 2.47; N, 20.67. Found: C, 41.31; H, 2.41; N, 20.41.

The uv spectrum of X is almost identical with that of VII.[29] The former exhibits maxima (MeOH) at 243, 248, 254, 260, and 326 nm. The pmr spectrum ($CDCl_3$) showed absorptions at δ 8.8 (2 H, s), δ 8.7 (2 H, s), δ 2.65 (3 H, s), and δ 2.60 (3 H, s). The ir spectrum (KBr) showed absorptions at 1620, 1550, 1490, 1355, 908, 811, 725 cm^{-1}.

Registry No.—V, 35211-98-4; VI, 35211-99-5; IX, 35212-00-1; X, 35212-01-2; TNB, 99-35-4; TNT, 118-96-7; phenylhydrazine, 100-63-0.

Acknowledgments. This research was supported by the Army Research Office at Durham, Grant No. DAHCO4 69 C 0064, and the Research Corporation.

[29] P. H. Gore and O. H. Wheeler, *J. Amer. Chem. Soc.*, **78**, 2160 (1956).

[30] V. I. Steinberg and D. J. Holter, *J. Org. Chem.*, **29**, 3420 (1964).

Thermal Rearrangement of β-Nitro Nitrates to Dinitro Alcohols

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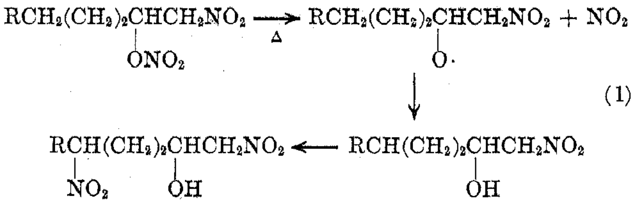
The decomposition of β-nitroalkyl nitrates in dilute hydrocarbon or halocarbon solution follows first-order kinetics ($\Delta H_a = 38$–40 kcal mol^{-1}) to give dinitro or bromonitro alcohols derived from a 1,5 intramolecular hydrogen shift. For instance, 1-nitro-2-methyl-2-pentyl nitrate (**5**) rearranges at 130° in chlorobenzene to 1,5-dinitro-2-methyl-2-pentanol (**13**) in 86% yield; in refluxing $CBrCl_3$, **5** is converted to 1-nitro-5-bromo-2-methyl-2-pentanol (**13a**) in 72% yield. Products from a cyclohexyl β-nitro nitrate **19** indicate partial decay of the intermediate alkoxyl radical by β scission. The β-nitro nitrates are less thermally stable than are simple alkyl nitrates. Product structures were established by alternate syntheses or by base-catalyzed cleavage of β-nitro alcohols to the expected nitroalkane and carbonyl compound; *e.g.*, treatment of **13** with base yields 5-nitro-2-pentanone (**25**) and nitromethane. In addition to cleaving, bromonitro alcohols cyclized when treated with base; *e.g.*, **13a** gave a mixture of 5-bromo-2-pentanone (**32**), nitromethane, and the tetrahydrofuran **30**.

The low-pressure gas phase pyrolyses of ethyl,[1,2] *n*-propyl,[3,4] and *tert*-butyl[4] nitrates proceed by homolytic decomposition to give NO_2 and an alkoxyl radical intermediate. It has been established in these cases that the nitrate decomposition follows at least initial first-order kinetics, and, if the cleavage is made irreversible, first-order kinetics are obeyed over the entire decomposition range. These decompositions are difficult to study, however, because the intermediates undergo subsequent reactions to give a wide range of products. For instance, *tert*-butyl nitrate gives, besides nitrogen dioxide, *tert*-butyl nitrite, acetone, nitromethane, methyl nitrite, and nitric oxide.[4,5]

Our studies have shown that the complexity of nitrate decompositions may be markedly reduced if one chooses a vicinal nitro nitrate with a carbon chain of sufficient length to accommodate intramolecular hydrogen abstraction by the intermediate alkoxyl radical; molecules of this structure decompose at lower temperatures than do simple nitrates. Moreover, intramolecular abstraction by a 1,5 hydrogen shift appears to be the preferred reaction of the alkoxyl radicals so generated. Such a rearrangement (eq 1) appears to be a general reaction of alkoxyl radicals having a hydrogen atom at the correct distance in the molecule.[6] In addition, such substituted nitrates, readily prepared from the reaction of nitrogen dioxide and oxygen with olefins,[7] allow the effect of the vicinal nitro group on homolytic cleavage to be evaluated.



$$\underset{\text{ONO}_2}{\text{RCH}_2(\text{CH}_2)_2\text{CHCH}_2\text{NO}_2} \xrightarrow[\Delta]{} \underset{\text{O}\cdot}{\text{RCH}_2(\text{CH}_2)_2\text{CHCH}_2\text{NO}_2} + \text{NO}_2 \quad (1)$$

$$\underset{\text{NO}_2\qquad\quad \text{OH}}{\text{RCH}(\text{CH}_2)_2\text{CHCH}_2\text{NO}_2} \longleftarrow \underset{\text{OH}}{\text{RCH}(\text{CH}_2)_2\text{CHCH}_2\text{NO}_2}$$

Decomposition of β-Nitro Nitrates in Inert Solvents.—When β-nitro nitrates are heated neat or in concentrated solution, nitro olefins are major products.[8] Nitro olefin formation became insignificant, however, when dilute solutions of nitro nitrates were heated in inert solvents. Suitable inert solvents were chlorobenzene, *o*-dichlorobenzene, or Fluorolube.[10] Intra-

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[1] J. B. Levy, *J. Amer. Chem. Soc.*, **76**, 3790 (1954); J. B. Levy, Navy Ordnance Report 2897, (1953).

[2] L. Phillips, *Nature (London)*, **160**, 753 (1947); **165**, 564 (1950).

[3] L. Phillips, Thesis, University of London, 1949.

[4] J. B. Levy and F. J. Adrian, Navy Ordnance Report 2608, Dec 22, 1952.

[5] R. Boschan, R. T. Merrow, and R. W. Van Dolah, *Chem. Rev.*, **55**, 485 (1955).

[6] R. S. Davidson, *Quart. Rev. Chem. Soc.*, **21**, 249 (1967); O. L. Chapman, *Advan. Photochem.*, **1**, 399 (1963); D. H. R. Barton, G. C. Ramsay, and D. Wege, *J. Chem. Soc. C*, 1915 (1967); K. Heusler and J. Kalvoda, *Angew. Chem., Int. Ed. Engl.*, **3**, 525 (1964).

[7] (a) D. R. Lachowicz and K. L. Kreuz, *J. Org. Chem.*, **32**, 3885 (1967). (b) D. R. Lachowicz, J. M. Larkin, and K. L. Kreuz, paper in preparation; D. R. Lachowicz and K. L. Kreuz, U. S. Patent 3,282,983 (Nov 1, 1966).

[8] *E.g.*, 1-nitro-2,4,4-trimethyl-2-pentyl nitrate (**1**), when heated neat at 138° for 1.5 hr, gives 1-nitro-2,4,4-trimethyl-1-pentene as the major product.[9]

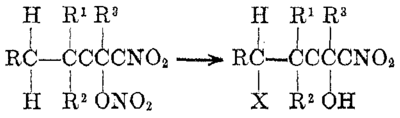
[9] W. S. Pelton, Texaco Research Center, private communication.

[10] Fluorolube, grade S-30, Hooker Chemical Corp., is a perhalogenated alkane (with repeating –CF_2CFCl– units) of 775 average mol wt.

molecular hydrogen abstraction occurred according to eq 1 above; nitrogen dioxide produced in the homolysis step apparently combined with the resultant alkyl radical to give the dinitro alcohol as the final product. 1-Nitro-2,4,4-trimethyl-2-pentyl nitrate (**1**), 1-nitro-2-pentyl nitrate (**2**), 1-nitro-2-hexyl nitrate (**3**), 1-nitro-4-methyl-2-pentyl nitrate (**4**), 1-nitro-2-methyl-2-pentyl nitrate (**5**), 1-nitro-4-acetoxy-2-hexyl nitrate (**6**), and 1-nitro-2-methyl-2-hexyl nitrate (**7**) all underwent smooth rearrangement to give the corresponding dinitro alcohols in moderate to good yields (see Table I).

TABLE I

CONVERSION OF NITRO NITRATES TO DINITRO AND BROMONITRO ALCOHOLS



$$\mathrm{R}\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}—\underset{R^2}{\overset{R^1}{\mathrm{C}}}\underset{\mathrm{ONO_2}}{\overset{R^3}{\mathrm{C}}}\mathrm{CNO_2} \longrightarrow \mathrm{R}\underset{\mathrm{X}}{\overset{\mathrm{H}}{\mathrm{C}}}—\underset{R^2}{\overset{R^1}{\mathrm{C}}}\underset{\mathrm{OH}}{\overset{R^3}{\mathrm{C}}}\mathrm{CNO_2}$$

I II

Nitro nitrate (I)	R	R^1	R^2	R^3	X	Product II	Yield, %
2	H	H	H	H	NO_2	**10**	80
3	CH_3	H	H	H	NO_2	**11**	72
4	H	CH_3	H	H	NO_2	**12**	83
5	H	H	H	CH_3	NO_2	**13**	86
5	H	H	H	CH_3	Br	**13a**	72
6	CH_3	OA_c	H	H	NO_2	**14**	58
7	CH_3	H	H	CH_3	NO_2	**15**	75
1	H	CH_3	CH_3	CH_3	NO_2	**16**	*a*
1	H	CH_3	CH_3	CH_3	Br	**16a**	74

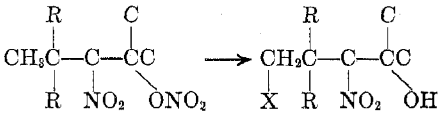
[a] Yield could not be calculated because of a large amount of impurities.

It was necessary to heat the β-nitro *tert*-nitrates to above 100° and the β-nitro *sec*-nitrates to above 140° to effect rearrangement. Improved yields of dinitro alcohols could be realized from the β-nitro *sec*-nitrates by conducting the rearrangement at high temperatures for short periods of time (above 170° for less than 30 min). When heated for extended periods, even at lower temperatures, the dinitro alcohols themselves decomposed to give black resinous solids.

The rearrangement also occurred with the nitrate esters **8** and **9** (*cf.* Table II) where the vicinal nitro substituent was on an internal carbon atom. In no instance were nitro nitrito alcohols isolated. On the basis of products isolated and identified, there is an exclusive preference for the six-membered ring transition state (*i.e.*, a 1,5 hydrogen shift) in the intramolecular hydrogen abstraction.

TABLE II

PRODUCTS FROM INTERNAL NITRO NITRATES

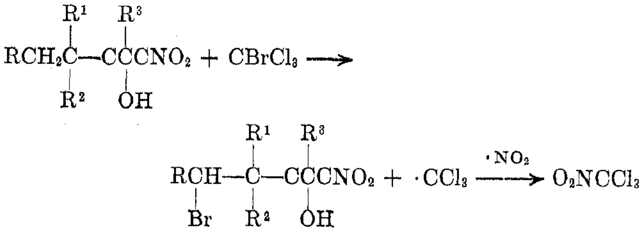


$$\mathrm{CH_3}\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{C}}}—\underset{\mathrm{NO_2}}{\mathrm{C}}—\overset{\mathrm{C}}{\mathrm{C}}\mathrm{C}\ \mathrm{ONO_2} \longrightarrow \underset{\mathrm{X}}{\mathrm{CH_2}}\underset{\mathrm{R}}{\overset{\mathrm{R}}{\mathrm{C}}}—\underset{\mathrm{NO_2}}{\mathrm{C}}—\overset{\mathrm{C}}{\mathrm{C}}\mathrm{C}\ \mathrm{OH}$$

III IV

Nitro nitrate (III)	R	X	Product IV	Yield, %
8	H	NO_2	**17**	64
9	CH_3	NO_2	**18**	77
9	CH_3	Br	**18a**	75

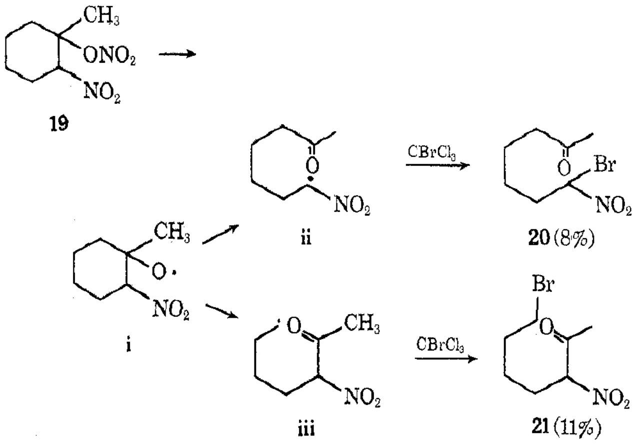
Decomposition of β-Nitrates in the Presence of Radical Trapping Agents.—By conducting the decomposition of **1**, **5**, or 3-nitro-2,4,4-trimethyl-2-pentyl nitrate (**9**) in refluxing bromotrichloromethane, it was possible to trap the intermediate alkyl radical to give the corresponding bromonitro alcohols **16a**, **13a**, and **22a**, respectively (*cf.* Tables I and II).[11] During the reactions conducted in bromotrichloromethane, an infrared peak at 6.19 μ attributable to chloropicrin (CCl_3NO_2) increases as the nitrate peaks decrease. Although their proximate boiling points precluded separation, a synthetic mixture of $CBrCl_3$ and CCl_3NO_2 give an ir spectrum identical to that of the solvent from the reaction mixtures.



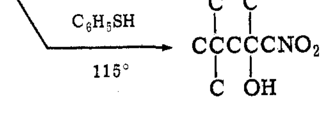
$$\mathrm{RCH_2}\underset{R^2}{\overset{R^1}{\mathrm{C}}}—\mathrm{C}\underset{\mathrm{OH}}{\overset{R^3}{\mathrm{C}}}\mathrm{CNO_2} + \mathrm{CBrCl_3} \longrightarrow$$

$$\underset{\mathrm{Br}}{\mathrm{RCH}}—\underset{R^2}{\overset{R^1}{\mathrm{C}}}—\mathrm{C}\underset{\mathrm{OH}}{\overset{R^3}{\mathrm{C}}}\mathrm{CNO_2} + \cdot\mathrm{CCl_3} \xrightarrow{\cdot\mathrm{NO_2}} \mathrm{O_2NCCl_3}$$

1-Methyl-2-nitrocyclohexyl nitrate (**24**) should decompose to give an alkoxy radical (i) incapable of abstracting hydrogen by a 1,5 shift. The radical should decay (at least partially) by β scission to give either of the ring-opened radicals (ii or iii) which, on interception by Br, would give the bromonitroheptanones **20** and **21**. These compounds were produced in *isolated* yields of 8 and 11% when **19** was heated in $CBrCl_3$ at reflux. The remainder of the products were unidentified.



When the decomposition of 1-nitro-2-pentyl nitrate (**2**) or of 1-nitro-2,4,4-trimethyl-2-pentyl nitrate (**1**) was conducted in an atmosphere of nitric oxide, only dinitro alcohols (**10** and **16**, respectively) were found.



$$\mathbf{1} \xrightarrow[115^\circ]{\mathrm{NO}} \mathbf{16} \qquad \mathbf{1} \xrightarrow[115^\circ]{\mathrm{C_6H_5SH}} \mathrm{C}\underset{\mathrm{C}}{\overset{\mathrm{C}}{\mathrm{C}}}\mathrm{C}\underset{\mathrm{OH}}{\overset{\mathrm{C}}{\mathrm{C}}}\mathrm{CNO_2}$$

22

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[11] For similar trapping of alkyl radicals (after intramolecular hydrogen abstraction by alkoxy radicals from nitrite photolyses) by bromotrichloromethane, see M. Akhtar, D. H. R. Barton, and P. G. Sammes, *J. Amer. Chem. Soc.*, **87**, 4601 (1965).

This result is somewhat surprising because nitric oxide is ordinarily an efficacious radical-trapping agent.[12] In the presence of thiophenol, nitro nitrate **1** was converted to 1-nitro-2,4,4-trimethyl-2-pentanol (**22**). This observation parallels those of Barton, *et al.*,[13] who used thiophenol as a hydrogen source to trap alkyl radicals derived from alkoxyl radical intramolecular abstraction.[11,12]

While this work was in progress, Mills reported the thermal rearrangement of a steroidal β-chloro nitrate to a chloronitro alcohol in 15% yield,[14] and a corresponding photochemical rearrangement in somewhat lower yield.[15] These rearrangements were also shown to occur by cleavage to an alkoxyl radical followed by intramolecular hydrogen abstraction in a six-membered ring transition state.[14,15] Mills also found no nitrite products, indicating that under rearrangement conditions NO_2 combines with the alkyl radical through nitrogen rather than oxygen.

Kinetics of Nitro Nitrate Decompositions.—The rate of decomposition (See Experimental Section) was measured for several nitro nitrates in dilute (1.0–3.7%) solutions of Fluorolube,[10] *n*-alkanes, or bromotrichloromethane, as listed in Table III. In addition, observed rates of decomposition for 2-octyl nitrate (**24**) and the reported rate for ethyl nitrate[1] are included for comparison.

First-order kinetics are obeyed for all decompositions listed in Table III over a range of at least two half-lives. Previous workers have reported the energies of activation for the homolysis of ethyl nitrate in the range of 36 to 41.3 kcal/mol, with the latter figure obtained by Levy[1] probably being the most nearly accurate.[5] An Arrhenius treatment of the rate data for 1-nitro-2,4,4-trimethyl-2-pentyl nitrate (**1**) in Fluorolube gives an energy of activation of 40.0 kcal mol^{-1}, a value which is in reasonable agreement with the reported values for homolysis of ethyl nitrate.[5] The activation energies for **1** and 1-nitro-2-octyl nitrate (**23**) in saturated hydrocarbons, 38.0 and 39.7 kcal mol^{-1}, respectively, are also indicative of homolytic cleavage. The kinetic data then is in accord with the mechanism postulated for production of dinitro alcohols *via* an alkoxyl radical intermediate.

There is an important difference concerning the relative thermal stability of the β-nitro nitrates and simple alkyl nitrates toward homolytic cleavage. The simple nitrates, as exemplified by ethyl nitrate and 2-octyl nitrate, require temperatures in excess of 170° to achieve reasonably rapid (half-lives of less than 35 min) homolytic decomposition, whereas the β-nitro *sec*-nitrate **23** is noticeably unstable above 150° and it was qualitatively observed (*cf.* Table I) that other β-nitro *sec*-nitrates decomposed at about the same rate as nitro nitrate **23**. The β-nitro *tert*-nitrate **1** undergoes rapid decomposition above 120°, and the other β-nitro *tert*-nitrates listed in Table III (**5** and **19**) are also unstable to prolonged heating at relatively low temperatures (105°). Because the measured activation energies are about equivalent for all three types of nitrates, the entropies of activation must decrease in the order β-nitro *tert*-nitrates > β-nitro *sec*-nitrates > unsubstituted alkyl nitrates. The Arrhenius parameters for the decomposition of **1** in Fluorolube are given by $k = 10^{18.5} \times e^{-40,000/RT}$ sec^{-1}. The very high frequency factor indicates that the transition from reactant to transition state (in this case, emerging alkoxy radical) requires little molecular reorientation. It is not clear whether this could be due to an electronic or steric interaction between the nitrate function and the adjacent nitro group. It may be significant that the radical decomposition temperatures for a vicinal dinitrate (60–90°)[16] and of a vicinal chloro nitrate (130°)[14] (two other types of β-substituted nitrates) lie below the decomposition temperature of simple alkyl nitrates.

TABLE III

RATES OF VICINAL NITRO NITRATE DECOMPOSITION IN DILUTE SOLUTIONS

Nitro nitrates	Solvent	Concentration, vol. %	Av temp, °C	$k \times 10^{3}$[a] (min^{-1})	Method[b]
1	Fluorolube[c]	2.5	100	1.5	A
	Fluorolube	2.5	110	6.5	A
	Fluorolube	2.5	114.5	11	A
	Fluorolube	2.5	120	21	A
	Fluorolube	2.5	130	84	A
	n-Dodecane	1.0	110	12	A
	n-Dodecane	2.5	120	34	A
	n-Octane	2.5	123.5	70	B
	n-Dodecane	2.5	130	120	A
	n-Dodecane[d]	2.4	128	160	B
23	*n*-Dodecane	2.5	142	4.3	B
	n-Dodecane	2.5	151	14	B
	n-Dodecane	2.5	160.5	37	B
	n-Dodecane[f]	2.0	139.4	3.4	B
5	$CBrCl_3$	1.8	105.3[g]	1.0	B[h]
19	$CBrCl_3$	3.7	*ca.* 105[g]	1.3	B[h]
Alkyl nitrate					
24	*n*-Dodecane	2.5	171.5[i]	13[i]	B
	n-Dodecane	2.5	178.5[i]	32[i]	B
Ethyl nitrate[j] (gas phase)					
20-mm initial pressure			171	21.8	Ref 1

[a] First-order rate constant. [b] Method A: decomposition conducted in AgCl infrared cell. Method B: decomposition conducted in Pyrex glassware, and $CHCl_3$ added to aliquots prior to ir determination. [c] Fluorolube is described in ref 10. [d] 1% of 1-nitro-2-octanone[7a] added.[e] [e] These compounds were added to assess the effects of these possible reaction products on the reaction rate. [f] 2% of 1-nitro-2-octanol added.[e] [g] Temperature of refluxing solution. [h] $CHCl_3$ not added to aliquots prior to ir determination. [i] Temperature control was poor above 170° (±1.5°) and these data are considered less accurate. [j] NO and CH_3CHO added.[1]

Characterization and Reactions of Homolysis Products.—Structural assignments of products were made on the basis of alternate methods of synthesis, degradation to known compounds, or in some instances spectral analysis only.[17] All dinitro alcohols had ir peaks (singlets) at about 2.8 (–OH), 6.4, and 7.3 μ ($-NO_2$).

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(12) See M. Akhtar, *Advan. Photochem.*, **2**, 263 (1964).

(13) Barton[11] has established, by use of deuterium labeling, that the alkyl radical and not the alkoxyl radical is trapped by thiophenol.

(14) J. S. Mills, *J. Chem. Soc. C*, 2261 (1966).

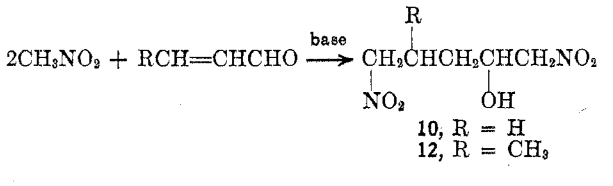
(15) B. W. Finucane, J. B. Thomson, and J. S. Mills, *Chem. Ind.* (*London*), 1747 (1967).

(16) J. A. Hicks, *Trans. Faraday Soc.*, **52**, 1526 (1956).

(17) Because the products were all high-boiling liquids, unstable at high temperatures, no method of separation and purification other than elution chromatography was found. Consequently, elemental analyses were often not in strict agreement with calculated molecular formulae, and heavy reliance was placed on ir and nmr spectra for identification.

The 60-MHz nmr spectra of the dinitro *sec*-alcohols (**10**, **11**, **12**, and **14**) showed a multiplet (sometimes poorly resolved) at τ 5.4–5.78 attributable to the protons on both the carbon atoms bearing the nitro groups and to the proton adjacent to the hydroxy group. In simple β-nitro alcohols, there is a near coincidence of the position of the proton signals from the hydrogens on the carbon atoms bearing the nitro and hydroxy groups.[18] In the dinitro alcohols, the second nitro group apparently causes a downfield shift of the proton adjacent to the hydroxy group, so that overlap is complete.

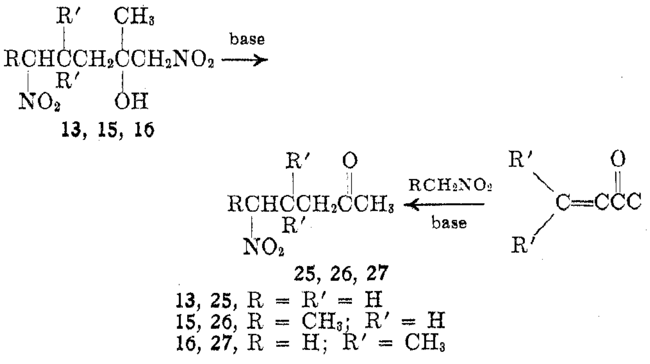
Alternate syntheses of 1,5-dinitro-2-pentanol (**10**) and 1,5-dinitro-4-methyl-2-pentanol (**12**) were achieved by the reaction of acrolein and crotonaldehyde, respectively, with excess nitromethane according to published procedures.[19]



$$2\mathrm{CH_3NO_2} + \mathrm{RCH{=}CHCHO} \xrightarrow{\text{base}} \underset{\mathrm{NO_2}}{\mathrm{CH_2}}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{HCH_2}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{HCH_2NO_2}$$

10, R = H
12, R = CH_3

1,5-Dinitro-2-methyl-2-pentanol (**13**), 1,5-dinitro-2-methyl-2-hexanol (**15**), and 1,5-dinitro-2,4,4-trimethyl-2-pentanol (**16**) reacted with weak bases (Al_2O_3, Na_2CO_3, or NaOAc) to give the 5-nitro-2-pentanones, **25**, **26** and **27**, respectively, by loss of nitromethane (a reverse Henry[20] reaction). 3,5-Dinitro-2-methyl-2-pentanol (**17**) and 3,5-dinitro-2,4,4-trimethyl-2-pentanol (**18**), when treated with benzyltrimethylammonium hydroxide in refluxing methanol, reacted similarly to give acetone and 1,3-dinitropropanes (**28** and **29**, respectively). Authentic nitro ketones (**25**, **26**, and **27**) and 1,3-dinitro-2,2-dimethylpropane (**29**) were prepared for comparison purposes. Positive identification of 1,3-dinitropropane (**28**) was made on the basis of its ir and nmr spectra, and acetone was characterized as its 2,4-dinitrophenylhydrazone.



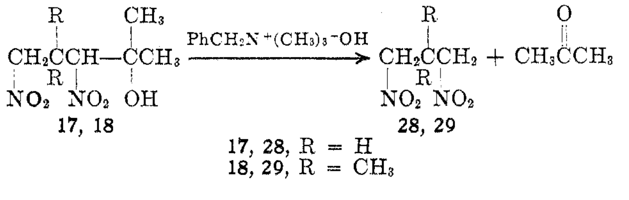
$$\underset{\mathrm{NO_2}}{\mathrm{RC}}\mathrm{H}\overset{\mathrm{R'}}{\underset{\mathrm{R'}}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{OH}}{\mathrm{C}}}\mathrm{CH_2NO_2} \xrightarrow{\text{base}}$$

13, 15, 16

$$\underset{\mathrm{NO_2}}{\mathrm{RC}}\mathrm{H}\overset{\mathrm{R'}}{\underset{\mathrm{R'}}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3} \xleftarrow[\text{base}]{\mathrm{RCH_2NO_2}} \overset{\mathrm{R'}}{\underset{\mathrm{R'}}{\vphantom{C}}}\mathrm{C{=}CC}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}$$

25, 26, 27

13, 25, R = R′ = H
15, 26, R = CH_3; R′ = H
16, 27, R = H; R′ = CH_3



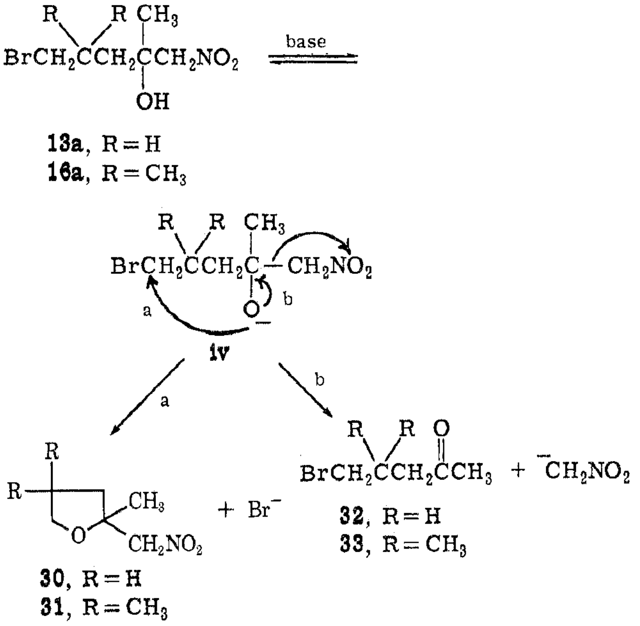
$$\underset{\mathrm{NO_2}}{\mathrm{CH_2}}\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{C}}}\underset{\mathrm{NO_2}}{\mathrm{CH}}\text{—}\overset{\mathrm{CH_3}}{\underset{\mathrm{OH}}{\mathrm{C}}}\mathrm{CH_3} \xrightarrow{\mathrm{PhCH_2N^+(CH_3)_3\,^-OH}} \underset{\mathrm{NO_2}}{\mathrm{CH_2}}\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{C}}}\underset{\mathrm{NO_2}}{\mathrm{CH_2}} + \mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3}$$

17, 18 **28, 29**

17, 28, R = H
18, 29, R = CH_3

7-Bromo-7-nitro-2-heptanone (**20**) was analyzed as its semicarbazone, and reliance on the ir and nmr spectra was made for the structure elucidation of 3-nitro-7-bromo-2-heptanone (**21**). The latter compound (**21**) has an infrared carbonyl peak at 5.75 μ (a hypsochromic shift of 0.05 μ from a normal carbonyl) as do other α-nitro ketones.[21] The nmr shows two triplets [τ 4.75 (1 proton) and 6.56 (2 protons)] for the hydrogens adjacent to the nitro and bromine, a singlet [τ 7.70 (3 protons)] for the methyl ketone, and a six-proton multiplet centered at τ 8.03 for the normal alkyl protons. 7-Bromo-7-nitro-2-heptanone (**20**), on the other hand, showed normal ir carbonyl absorption at 5.80 μ. The nmr showed the three-proton singlet for the methyl ketone at τ 7.90, poorly resolved multiplets (4 protons each) at about τ 7.6 and 8.5 attributable to the alkyl hydrogens, and a triplet at τ 4.11 (1 proton) for the proton adjacent to both the nitro and bromo groups. 1,3-Dinitropropane (**28**) had ir absorption at 6.4 μ; its nmr spectrum consisted of a triplet at τ 5.41 and a quintet at τ 7.32 in a respective ratio of 2:1.

The bromonitro alcohols **13a** and **16a** were characterized by their reaction with weak bases (Al_2O_3 or NaOAc). The possibility arises that the alkoxide intermediate **iv**, once formed, may give stable products in either of two ways. It may eliminate nitromethyl anion (reverse Henry[20] reaction) to give a bromo ketone, or it may displace bromide ion to give a cyclic ether.[22]



13a, R = H
16a, R = CH_3

iv

32, R = H
33, R = CH_3

30, R = H
31, R = CH_3

Actually, both reactions occur. Treatment of 1-nitro-2-methyl-5-bromo-2-pentanol (**13a**) with alumina in benzene for 28 hr results in formation in high yield of a mixture of 2-methyl-2-(nitromethyl)tetrahydrofuran (**30**) and 5-bromo-2-pentanone (**32**) in respective ratios of between 4:1 and 7:1. 1-Nitro-2,4,4-trimethyl-5-bromo-2-pentanol (**16a**) under similar conditions gives 2,4,4-trimethyl-2-(nitromethyl)tetrahydrofuran (**31**) and 4,4-dimethyl-5-bromo-2-pentanone (**33**) in a 3:2 ratio. When methanolic sodium acetate is used, bromonitro alcohol **16a** gives **31** and **33** in a respective ratio of 1:3. The product ratios were determined by nmr integration.

The 7:1 mixture of 2-methyl-2-(nitromethyl)tetrahydrofuran (**30**) and 5-bromo-2-pentanone (**32**) was

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[18] A. I. Meyers and J. C. Sicar, *J. Org. Chem.*, **32**, 4134 (1967).

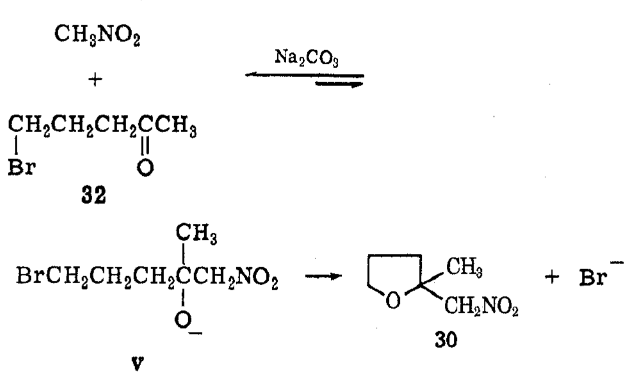
[19] O. Wulff, German Patent 860,795 (Dec 22, 1952).

[20] L. Henry, *C. R. Acad. Sci.*, **120**, 1265 (1895).

[21] T. Simmons, R. F. Love, and K. L. Kreuz, *J. Org. Chem.*, **31**, 2400 (1966).

[22] C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, **85**, 1597 (1963).

converted entirely to the cyclic ether **30** by treatment with excess nitromethane and sodium carbonate. In this case, the unfavorable thermodynamic equilibrium in the Henry reaction[20] of **32** with nitromethane was apparently overcome by providing an irreversible step for the alkoxide ion intermediate **v**, namely cyclic ether formation.[23]



It has been shown that the presence of a β-nitro substituent fosters the controlled decomposition of the alkyl nitrate function along a relatively clean reaction path. Furthermore, such reactions provide ready access to a variety of interesting trifunctional compounds. It is likely that nitrate ester pyrolysis will assume an increasingly important role in functionalization of unactivated alkyl groups. The nature of the effect of the vicinal nitro substituent, which markedly changes the kinetics of nitrate decomposition, is presently being investigated in these laboratories.

Experimental Section

The vicinal nitro nitrates were prepared and purified as previously described.[7] 2-Octyl nitrate (**24**) was prepared (91% yield) by the reaction at −5° of 2-octanol with acetyl nitrate.[24,25] The reaction solvents were the best quality commercially available and generally were used without further purification. Alumina was Fisher adsorption alumina, 80–200 mesh. Chromatographic grade silica gel (28–200 mesh) was from W. R. Grace and Co. Chromatography solvents were dried and distilled prior to use. Infrared spectra were obtained with a Beckman IR-4 or a Perkin-Elmer Model 137 spectrophotometer. Nmr spectra were obtained in $CDCl_3$ with a Varian Associates Model V-4311 spectrometer operated at 60 MHz using tetramethylsilane as an internal standard. Gas–liquid chromatography was performed on an Aerograph A-90-P2 instrument using a 10 ft × $^1/_4$ in. column of 12% XF-1150 Cyanosilicon oil on 44/60 mesh Embosel. Melting points, determined on a Fisher–Johns apparatus, are uncorrected. Elemental analyses were performed by the Analytical Research Section of Texaco Inc., Beacon, N. Y.

Unless otherwise stated, products obtained were high-boiling liquids.

Kinetic Procedure.—Nitrate ester decomposition was followed by measuring the decrease of the infrared absorption at 6.05–6.10 or 7.8 μ by one of two methods. In method A, a solution of the nitro nitrate was heated in a variable temperature infrared cell (Limit Model V-LTJ) in the optical beam of a Beckman IR-4 or a Perkin-Elmer 21 recording spectrophotometer. A variable thickness cell containing the same solvent as the sample cell was placed in the reference beam, and the thickness was adjusted for optimum optical balance. The electrically heated cell was controlled with a variable resistor, and temperature was monitored with an iron–constantan thermocouple. The temperature was maintained constant to within ±5–9°, and spectra were scanned at timed intervals.

In method B, a solution of the nitro nitrate was heated in Pyrex glassware. The solution temperatures were maintained constant to ±1° by use of a thermostated oil bath or by refluxing the solution at its boiling point. In some instances, dry nitrogen was slowly conducted through the hot solutions. Measured aliquots were withdrawn at timed intervals and were rapidly cooled by contact with cool vessels. Each aliquot was diluted with a given amount of chloroform (to effect homogeneity in the cold samples), and the spectra were recorded differentially on a Perkin-Elmer Model 137 Infracord. Chloroform was not added to bromotrichloromethane solutions prior to infrared determinations.

The absorbances at 6.05–6.10 or 7.8 μ were obtained by determining the difference between maximum deflection and base line absorption. (Similar techniques are described by Morgan, *et al.*[26]) The rate constants were obtained from straight-line plots of log absorbance *vs.* time. Beer's law was found to hold for nitro nitrates **1** and **23** over the concentration range studied.

1,5-Dinitro-2-pentanol (10).—A solution of 8.00 g of 1-nitro-2-pentyl nitrate (**2**) in 80 ml of *o*-dichlorobenzene was heated at reflux (175°) in a nitrogen atmosphere for 19 min. The solvent was removed by vacuum distillation [67° (15 mm)]. The yellow oil **10** remaining (6.41 g) is identical spectrally to authentic[19] **10**: ir (neat) 2.8 (OH), 6.4, 7.25 μ ($-NO_2$); nmr ($CDCl_3$) δ 1.7, 2.2 (m, 4), 4.5 (m, 5), 5.94 (s, 1, exchanges with D_2O).

1,5-Dinitro-2-hexanol (11).—A solution of 6.00 g of 1-nitro-2-hexyl nitrate (**3**) in 100 ml of *o*-dichlorobenzene was refluxed under nitrogen for 18 min. The solvent was distilled [108–117° (80–85 mm)] and the brown liquid remaining was chromatographed on 100 g of silica gel. There was eluted (80:20 CH_2Cl_2–hexane) 0.22 g of starting material (**14**) and (92–80:8–20 CH_2Cl_2–Et_2O) 4.17 g (72%) of dinitro alcohol **11**: ir (neat) 2.8 (−OH), 6.4, 7.25 μ ($-NO_2$); nmr (acetone-d_6–$CDCl_3$) δ 1.56 [d, J = 7 Hz, $CH_3CH(NO_2)$] superimposed on 1.3–2.9 [m, 7 total, $CH_3CH(NO_2)CH_2CH_2-$], 4.3–4.9 (m, 4), 6.34 (s, 1 -OH).

1,5,-Dinitro-4-methyl-2-pentanol (12).—A solution of 2.00 g of 1-nitro-4-methyl-2-pentyl nitrate (**4**) in 90 ml of *o*-dichlorobenzene was refluxed (179–180°) in a nitrogen atmosphere for 10 min. The solvent was concentrated by vacuum distillation [67° (15 mm)] to about 4 ml. This liquid was washed with pentane (3 × 10 ml) and air dried. The product (1.53 g) is dinitro alcohol **12**. From the pentane extract there was obtained an additional 0.03 g of **12** and 0.10 g of starting material **4**. Total yield of **12** (based on unrecovered **4**) is 83%. It is spectrally identical with **12** prepared according to Wulff:[19] ir (neat) 2.8 (−OH), 6.4, 7.25 μ ($-NO_2$); nmr ($CDCl_3$) δ 1.11 (dd, 3, J = 7 Hz, $-CHCH_3$), 1.6 (m, 2, $-CHCH_2CH(OH)-$], 2.5 [m, 1, $O_2NCH_2CH(CH_3)-$], 3.86 (s, 1, -OH), 4.48 [m, 5, $O_2NCH_2CH(OH)CH$, $(CH_3)CH_2NO_2$].

1,5-Dinitro-2-methyl-2-pentanol (13).—A solution of 7.34 g of 1-nitro-2-methyl-2-pentyl nitrate (**5**) in 150 ml of chlorobenzene was refluxed (130–132°) in a nitrogen atmosphere for 25 min. After cooling, the solvent was removed by distillation [38° (20 mm)]. There remained 6.28 g (86%) of **13**: ir (neat) 2.8 (−OH), 6.4, 7.25 μ ($-NO_2$); nmr ($CDCl_3$) δ 1.35 (s, 3, CH_3-), 1.7, 2.1 (m, 4, $-CH_2CH_2-$), 3.69 (s, 1, -OH), 4.50 (m, 4, O_2NCH_2-).

1-Nitro-2-methyl-5-bromo-2-pentanol (13a).—A solution of 1.35 g of 1-nitro-2-methyl-2-pentyl nitrate (**5**) in 75 ml of $CBrCl_3$ was heated at reflux (105.3°) for 31 hr. During heating, the infrared nitrate absorbances (6.1, 7.8 μ) decreased, and a band at 6.19 μ (CCl_3NO_2) appeared. The solvent from 73 ml of the solution was removed *in vacuo* at 35°. (The recovered solvent contained CCl_3NO_2.) A yellow-brown liquid (1.23 g) remained. It was chromatographed on silica gel. There was eluted (70:30 CH_2Cl_2–hexane) 0.26 g of nitro nitrate **5** and (80:20 CH_2Cl_2–Et_2O) 0.88 g of 1-nitro-2-methyl-5-bromo-2-pentanol (**13a**). The yield of **13a** is 72%, based on unrecovered starting material: ir (neat) 2.8 (−OH), 6.43, 7.27 μ ($-NO_2$); nmr ($CDCl_3$–D_2O) δ 1.34 (s, 3), 1.96 (m, 4), 3.47 (t, 2), 4.45 (s, 2).

1,5-Dinitro-4-acetoxy-2-hexanol (14).—A solution of 2.00 g of 1-nitro-2-nitrato-4-acetoxyhexane (**6**) in 75 ml of *o*-dichlorobenzene was heated at reflux (179–180°) in a nitrogen atmosphere for 22 min. The solvent was removed by distillation at reduced pressure, and the residue was chromatographed on 28 g of silica

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[23] *Cf.* H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, pp 234–242, for examples of other types of condensation reactions made irreversible by internal cyclizations.

[24] F. G. Bordwell and E. W. Garbisch, Jr., *J. Amer. Chem. Soc.*, **82**, 3588 (1960).

[25] F. Hodosan, I. Jude, N. Serban, and A. Balogh, *Chem. Ber.*, **95**, 1094 (1962).

[26] H. Morgan, R. M. Sherwood, and T. A. Washall, *Anal. Chem.*, **38**, 1009 (1966).

gel. There was eluted (5–50:95–50 ether–CH_2Cl_2) 1.17 g (58%) 1,5-dinitro-4-acetoxy-2-hexanol (**14**): ir (neat) 2.8 (–OH), 5.72, 8.1 [$OC(=O)CH_3$], 6.41, 7.30 μ (–NO_2); nmr ($CDCl_3$) δ 1.58 (d, 3, 8 Hz), 1.86 (m, 2), 2.12 (s, 3), 3.50 (s, 1, exchanges with D_2O), 4.44 [m, 3, –$\mathbf{CH}(OH)\mathbf{CH_2}NO_2$], 4.78 (m, 1), 5.58 (m, 1).

Anal. Calcd for $C_8H_{14}N_2O_7$: C, 38.4; H, 5.6; N, 11.2. Found: C, 39.2; H, 6.1; N, 10.5.

1,5-Dinitro-2-methyl-2-hexanol (**15**).—A solution of 2.75 g of 1-nitro-2-methyl-2-hexyl nitrate (**7**) in 80 ml of Fluorolube[10] was heated at 128 ± 3° for 2.5 hr. When cool, the mixture was extracted with methanol (3 × 25 ml). The solvent from the methanol extract was evaporated *in vacuo*. The two-phase liquid which remained was chromatographed on 50 g of silica gel. There was obtained 0.48 g of starting material (**7**) and 1.70 g (75%) of 1,5-dinitro-2-methyl-2-hexanol (**15**): ir (neat) 2.8 (–OH), 6.42, 7.25, 7.35 μ (–NO_2); nmr ($CDCl_3$) δ 1.34 (s, 3), 1.55 [d, 3, J = 6 Hz, $\mathbf{CH_3}CH(NO_2)$], 1.68–2.3 (m, 4), 3.85 (s, 1, exchanges with D_2O), 4.47 (s, 2), 4.67 [m, 1, $CH_3\mathbf{CH}(NO_2)CH_2$–].

1,5-Dinitro-2,4,4-trimethyl-2-pentanol (**16**).—A solution of 2.00 g of 1-nitro-2,4,4-trimethyl-2-pentyl nitrate (**1**) in 50 ml of Fluorolube[10] was heated at 112° for 17 hr. The solution was cooled and extracted with methanol (45, 25 ml). The methanol was evaporated from the extract, and the two-phase liquid was chromatographed on 16 g of silica gel. Excess Fluorolube[10] was eluted with 25:75 CH_2Cl_2–hexane. With 100% CH_2Cl_2 there was eluted 0.467 g of a yellow liquid which showed ir –NO_2, –OH, and –$C{=}CNO_2$ bands. With 20:80 ether–CH_2Cl_2 there was eluted 0.977 g of crude 1,5-dinitro-2,4,4-trimethyl-2-pentanol (**16**). This material contained some carbonyl impurity, tentatively identified as 2,2,4-trimethyl-4-hydroxy-5-nitropentanoic acid lactone.[27] When vacuum distilled [110° (0.05 mm)], the carbonyl impurity codistilled. When rechromatographed on silica gel, there was obtained relatively uncontaminated dinitro alcohol **16**: ir (neat) 2.8 (–OH), 6.4, 7.3 μ (–NO_2); nmr ($CDCl_3$) δ 1.22, 1.25 [2 s, 6, –$C(CH_3)_2$–], 1.47 [s, 3, –$C(\mathbf{CH_3})(OH)CH_2NO_2$], 1.73 (s, 2 –$CH_2$–), 3.30 (s, 1, exchanges with D_2O), 4.42, 4.44 (2 s, 2, –CH_2NO_2), 4.57, 4.60 (2 s, 2, –CH_2NO_2).

Anal. Calcd for $C_8H_{16}N_2O_5$: N, 12.7 (mol wt 220). Found: N, 12.3 [mol wt (osmometry) 229].

1-Nitro-5-bromo-2,4,4-trimethyl-2-pentanol (**16a**).—A solution of 2.80 g of 1-nitro-2,4,4-trimethyl-2-pentyl nitrate (**1**) in 50 ml of $CBrCl_3$ was heated at reflux for 17 hr. The solvent was stripped at reduced pressure at 45°. The yellow oil which remained was chromatographed on 20 g of silica gel. There was eluted (with CH_2Cl_2 and 80:20 CH_2Cl_2–Et_2O) 2.39 g (74%) of 1-nitro-5-bromo-2,4,4-trimethyl-2-pentanol: ir (neat) 2.8 (–OH), 6.40, 7.25 μ (–NO_2); nmr ($CDCl_3$) δ 1.08, 1.16 [2 s, 6, –$C(CH_3)_2$–], 1.43 [s, 3, –$C(\mathbf{CH_3})OHCH_2NO_2$], 1.70 (s, 2), 3.42 (s, 1, exchanges with D_2O), 3.52 (s, 2, –CH_2Br), 4.55, 4.57 (2 s, 2, –CH_2NO_2).

Anal. Calcd for $C_8H_{16}NO_3Br$: C, 37.8; H, 6.3; N, 5.5; Br, 31.5. Found: C, 38.7; H, 6.9; N, 5.5; Br, 31.9.

3,5-Dinitro-2-methyl-2-pentanol (**17**).—A solution of 4.55 g of 2-methyl-3-nitro-2-pentyl nitrate (**8**) in 175 ml of chlorobenzene was heated at reflux (130°) in a nitrogen atmosphere for 3 hr. The solvent was distilled at reduced pressure [31–34°, (15 mm)]. The residue remaining (2.89 g, 64%) was 3,5-dinitro-2-methyl-2-pentanol (**17**): ir (neat) 2.85 (–OH), 6.4, 7.25 μ (–NO_2); nmr ($CDCl_3$) δ 1.32, 1.36 [2 s, 6, –$C(CH_3)_2$–], 2.7, (m, 2), 3.78 (s, 1, exchanges with D_2O), 4.53 (m, 3, O_2NCH_2–, –$CHNO_2$–).

3,5-Dinitro-2,4,4-trimethyl-2-pentanol (**18**).—A solution of 6.00 g of crude 3-nitro-2,4,4-trimethyl-2-pentyl nitrate[7b] (**9**) in 125 ml of chlorobenzene was heated at 120–123° for 1 hr and at 113–120° for 0.5 hr. The solvent was removed at 13 mm. The liquid which remained (4.65 g) was 3,5-dinitro-2,4,4-trimethyl-2-pentanol (**18**): ir (neat) 2.8 (–OH), 6.42, 7.25 μ (–NO_2).

3-Nitro-5-bromo-2,4,4-trimethyl-2-pentanol (**18a**).—A solution of 2.20 g of 3-nitro-2,4,4-trimethyl-2-pentyl nitrate (**9**) in 75 ml of $CBrCl_3$ was heated at reflux (103–104°) for 10 hr. The solution was cooled and decanted from some black residue (0.2 g), and the solvent was distilled under reduced pressure at 38°. The residual yellow oil was chromatographed on silica gel. By elution with 80:20 CH_2Cl_2–hexane, 100% CH_2Cl_2, 20:80 Et_2O–CH_2CH_2, and 100% Et_2O, there was obtained 1.91 g of liquid 3-nitro-2,4,4-trimethyl-2-pentanol (**18a**): ir (neat) 2.8 (–OH), 6.4, 7.25 μ (–NO_2); nmr ($CDCl_3$) δ 1.25 (s, 3), 1.40 (s, 6), 1.48 (s, 3), 2.87 (s, 1, exchanges with D_2O), 3.24, 3.84 (dd, 2, J = 10 Hz), 4.73 (s, 1).

7-Bromo-7-nitro-2-heptanone (**20**) **and 7-Bromo-3-nitro-2-heptanone** (**21**).—A solution of 1.85 g of 1-methyl-2-nitrocyclohexyl nitrate (**19**) in 50 ml of $CBrCl_3$ was heated at reflux for 28 hr. (During heating, a total of 1.5 ml of solution was removed for kinetic measurements.) The solvent was removed under reduced pressure at 40–45°. The residual yellow liquid (1.76 g) was chromatographed on 32 g of silica gel. From 80:20 CH_2Cl_2–hexane eluent there was obtained a yellow liquid which was rechromatographed on silica gel. There was obtained 222 mg (11%) of liquid 7-bromo-3-nitro-2-heptanone (**21**): ir (neat) 5.75 (C=O), 6.4, 7.3 μ (–NO_2); nmr ($CDCl_3$) δ 1.97 (m, 6), 2.30 (s, 3), 3.44 (t, 2, J = 6 Hz), 5.25 (t, 1, J = 7 Hz).

From 90:10 CH_2Cl_2–hexane eluent there was obtained a yellow liquid which, after rechromatography on silica gel, yielded (with 100% CH_2Cl_2 eluent) 162 mg (8%) of 7-bromo-7-nitro-2-heptanone (**20**): ir (neat) 5.8 (C=O), 6.4, 7.3 μ (–NO_2); nmr ($CDCl_3$) δ 1.50 (m, 4), 2.10 (s, 3), 2.32 (m, 4), 5.89 (t, 1, J = 7 Hz).

From **20** there was prepared a semicarbazone, mp 124–126°.

Anal. Calcd for $C_8H_{15}N_4O_3Br$: C, 32.6; H, 5.1; N, 19.0. Found: C, 33.2; H, 5.3; N, 19.1, 19.2.

5-Nitro-2-pentanone (**25**).—A mixture of 2.29 g of 1,5-dinitro-2-methyl-2-pentanol (**13**), 50 ml of methanol, and 4 g of Na_2CO_3 was allowed to stand overnight. Insolubles were removed by filtration, and the solvent was evaporated *in vacuo*. The pasty residue was dissolved in 50 ml of water and extracted with 50 ml of ether. Evaporation of the ether left 0.94 g of liquid 5-nitro-2-pentanone (**25**). From the H_2O, there was obtained an additional 0.50 g of **25** (by acidification with 1.2 *N* HCl and extraction into ether, followed by drying and evaporation of the ether). Total yield of **25** was 1.44 g (92%); it is identical to **25** (by ir and nmr) prepared by reaction of nitromethane with methylvinyl ketone, and forms a 2,4-dinitrophenylhydrazine (mp 130–132°) which has an undepressed melting point when mixed with the 2,4-dinitrophenylhydrazone of authentic **25**.[29]

5-Nitro-2-hexanone (**26**).—Alumina (4.2 g) was added to a solution of 0.91 g of 1,5-dinitro-2-methyl-2-hexanol (**15**) in 25 ml of benzene. The slurry was stirred at room temperature for 24 hr. The alumina was filtered off and washed with benzene, and the filtrate was evaporated. 5-Nitro-2-hexanone (*26*) (0.29 g) remained. It has ir and nmr spectra identical to **26** prepared from methylvinyl ketone and nitroethane:[29] nmr ($CDCl_3$) δ 1.56 (d, 3, J = 7 Hz, $\mathbf{CH_3}CHNO_2$–), 2.17 (s, 3 superimposed on m, 2), 2.57 (m, 2), 4.63 [m, 1, $CH_3\mathbf{CH}(NO_2)CH_2$–].

Degradation of 3,5-Dinitro-2-alkanols. I. 3,5-Dinitro-2-methyl-2-pentanol. A solution of 2.85 g of 3,5-dinitro-2-methyl-2-pentanol (**17**), 1 ml of 40% methanolic benzyltrimethylammonium hydroxide, and 225 ml of methanol was slowly distilled for 6 hr. The distillate was delivered into a receiver containing 2.0 g of 2,4-dinitrophenylhydrazone, 10 ml of concentrated H_2SO_4, and 15 ml of H_2O. A total of 0.81 g of orange crystals was recovered (by filtration) from the distillate. A portion was recrystallized from 95% ethanol to give acetone 2,4-dinitrophenylhydrazone, mp 123–125°, undepressed when mixed with authentic acetone 2,4-dinitrophenylhydrazone.

The pot residue was concentrated by vacuum evaporation at 40°. Water (100 ml) was added, and the heterogeneous mixture was extracted with 150 ml of ether. The extract was washed (saturated NaCl solution), dried ($MgSO_4$), and evaporated. The residue (0.99 g) was crude 1,3-dinitropropane (**28**). It was chromatographed on silica gel and was eluted with CH_2Cl_2. There was obtained 0.24 g of (**28**): $n^{20}{}_D$ 1.4669; ir (neat) 6.4, 7.2, 7.35 μ (–NO_2); nmr ($CDCl_3$) δ 2.68 (p, 2, J = 6 Hz), 4.59 (t, 4, J = 7 Hz).

II. 3,5-Dinitro-2,4,4-trimethyl-2-pentanol.—A solution of 2.50 g of 3,5-dinitro-2,4,4-trimethyl-2-pentanol (**18**), 1 ml of 40% methanolic benzyltrimethylammonium hydroxide, and 75 ml of methanol was slowly distilled, and the distillate was delivered to a receiver containing 2,4-dinitrophenylhydrazine solution as in the preceding experiment. Total yield of acetone 2,4-dinitrophenylhydrazone from the distillate was 0.90 g (33%). The melting point (127–129°) is undepressed when mixed with authentic acetone 2,4-dinitrophenylhydrazone.

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(27) 2,2,4-Trimethyl-4-hydroxy-5-nitropentanoic acid lactone has been synthesized by an alternate route.[28]

(28) D. R. Lachowicz and K. L. Kreuz, unpublished results.

(29) H. Schechter, D. E. Ley, and L. Zeldin, *J. Amer. Chem. Soc.*, **74**, 3664 (1952).

The pot residue was concentrated by vacuum evaporation at 35°. Water (50 ml) was added and the mixture was extracted with ether (2 × 50 ml). The extract was dried ($MgSO_4$) and evaporated. The orange liquid residue (1.59 g) was chromatographed on silica gel. With CH_2Cl_2 there was eluted 0.19 g of 1,3-dinitro-2,2-dimethylpropane (**29**). Its ir and nmr spectra are identical to those of **29** prepared by the procedure of Lambert and Lowe:[30] nmr ($CDCl_3$) δ 1.20 (s, 6), 4.58 (s, 4).

5-Nitro-4,4-dimethyl-2-pentanone (**27**).—A solution of 1.00 g of crude 1,5-dinitro-2,4,4-trimethyl-2-pentanol (**16**) in 20 ml of benzene was allowed to stand at room temperature for 20 hr over 3.0 g of alumina. After filtration and evaporation of the filtrate, 0.56 g (72%) of 5-nitro-4,4-dimethyl-2-pentanone (**27**) remained. It is identical spectrally (ir and nmr) to authentic[31] **27** and forms a semicarbazone (mp 163.5–165.5°), the melting point of which is undepressed when mixed with the semicarbazone of authentic **27** (lit.[31] mp 164–165°).

1-Nitro-2,4,4-trimethyl-2-pentanol (**22**).—A solution of 2.63 g of 1-nitro-2,4,4-trimethyl-2-pentyl nitrate (**1**) in 150 ml of benzenethiol was heated in a nitrogen atmosphere at 115–118° for 3.5 hr. Then most of the benzenethiol was removed by vacuum distillation. The residue was dissolved in 10 ml of 20:80 CH_2Cl_2–hexane and chromatographed on silica gel. Unidentified material was eluted with mixtures of hexane and CH_2Cl_2 and with 100% CH_2Cl_2. With 95:5 CH_2Cl_2–ether there was eluted 0.38 g of 1-nitro-2,4,4-trimethyl-2-pentanol (**22**):[32] ir (neat) 2.8 (–OH), 6.41, 7.25 μ ($-NO_2$); nmr ($CDCl_3$) δ 1.05 [s, 9, $-C(CH_3)_3$], 1.39 (s, 3, CH_3COH), 1.57 (s, 2, $\geqslant CCH_2C \leqslant$), 3.10 (s, 1, exchanges with D_2O), 4.43 (s, 2, $-CH_2NO_2$).

2-Methyl-2-(nitromethyl)tetrahydrofuran (**30**) **and 5-Bromo-2-pentanone** (**32**).—A solution of 0.80 g of 1-nitro-2-methyl-5-bromo-2-pentanol (**15a**) in 50 ml of benzene was allowed to stand over 3.6 g of alumina for 27 hr. The solution was filtered and the filtrate was evaporated. A yellow oil (0.48 g) composed of **30** and **32** remained: ir (neat) 5.80 (C═O), 6.42, 7.22 ($-NO_2$), 9.55 μ (five-membered cyclic ether); nmr ($CDCl_3$) δ 1.36 (s, CH_3- of **30**), 2.00 (m, $-CH_2-$ of **30** and **32**), 2.15 (s, $-COCH_3-$ of **32**), 3.39 (m, $-CH_2Br$ of **32**), 3.88 (m, $-CH_2O-$ of **30**), 4.41 (s, $-CH_2NO_2$ of **32**). The ratio of peak areas δ 1.36:2.15 is 4:1.

In a repeat experiment with 4.00 g of **13a**, 18 g of alumina, and 200 ml of benzene, and with a reaction time of 28 hr, there was obtained 2.61 g of the mixture of **30** and **32**. The ratio of peak areas of δ 1.34:2.19 is 7:1.

A solution composed of 1.83 g of 7:1 mixture of **30** and **32** (from the preceding experiment), 50 ml of 95% ethanol, 5.0 ml of nitromethane, and 0.5 g of sodium carbonate was allowed to stand for 66 hr. The filtrate was concentrated to about 3 ml by vacuum evaporation at 45–50°. The pasty residue was dissolved in 25 ml of H_2O, and the solution was extracted with ether (2 × 50 ml). The extract was dried ($MgSO_4$) and evaporated. The residue consisting of 2-methyl-2-(nitromethyl)-tetrahydrofuran (**30**) only weighed 0.96 g. A portion was chromatographed on silica gel: nmr ($CDCl_3$) δ 1.34 (s, 3), 1.99 (m, 4, $-CH_2\mathbf{CH_2}-$), 3.88 (m, 2, $-CH_2O-$), 4.40 (s, 2).

Anal. Calcd for $C_6H_{11}NO_3$: C, 49.7; H, 7.7; N, 9.7. Found: C, 50.5; H, 7.6; N, 9.0.

2,4,4-Trimethyl-2-(nitromethyl)tetrahydrofuran (**31**) **and 5-Bromo-4,4-dimethyl-2-pentanone** (**36**). **A. From Bromonitro Alcohol 16a and Alumina.**—A solution of 0.30 g of 1-nitro-5-bromo-2,4,4-trimethyl-2-pentanol (**16a**) and 15 ml of benzene was allowed to stand over alumina (2.3 g) for 25 hr. After filtration and evaporation of the solvent there was obtained 152 mg of a clear liquid composed of **31** and **33**: ir (neat) 5.80 (C═O), 6.43, 7.23 ($-NO_2$), 9.58 μ (five-membered cyclic ether); nmr ($CDCl_3$) δ 1.11, 1.17 [s, $-C(CH_3)_2-$], 1.46 [s, $-C(\mathbf{CH_3})CH_2NO_2-$ of **31**], 1.77, 1.90 (s, $\geqslant CCH_2C \leqslant$ of **31**), 2.14 (s, CH_3CO- of **33**), 2.54 (s, $-CH_2CO-$ of **33**), 3.52 (s, $-CH_2Br$ of **33**), 3.58 (s, $-CH_2O$ of **31**), 4.44 (s, CH_2NO_2 of **31**). There is a 3:2 ratio of the following peak areas: δ 1.46:2.14; 1.77, 1.90:2.54; 3.58:3.52; 4.44:3.52.

The reaction was repeated with a reaction time of 92 hr. The same ratio of **31** and **33** was obtained. Glpc of the mixture on a preparative scale (175°, He flow = 120 $cm^3\ min^{-1}$) resulted in isolation of 2,4,4-trimethyl-2-(nitromethyl)tetrahydrofuran (**31**) (retention time, 6 min); 5-bromo-4,4-dimethyl-2-pentanone (**33**) was not recovered from the column.

B. From Bromonitro Alcohol 16a and Sodium Acetate.—A solution of 1.05 g of 1-nitro-5-bromo-2,4,4-trimethyl-2-pentanol (**16a**) and 0.75 g of $NaOAc \cdot 3H_2O$ in 25 ml of methanol stood at room temperature for 22 hr. The solvent was removed *in vacuo*, and the wet solid residue was stirred with ether. The solids were removed by filtration. (An aqueous solution of the solids gives precipitate with $AgNO_3$.) The solvent was evaporated from the filtrate, and a brown liquid (0.51 g) remained. It is composed of **31** and **33** in a 1:3 ratio, as determined by nmr peak ratios.

Registry No.—**1**, 32778-22-6; **5**, 35223-51-9; **10**, 35223-52-0; **11**, 35223-53-1; **12**, 35223-54-2; **13**, 35223-55-3; **13a**, 32774-58-6; **14**, 35223-57-5; **15**, 35223-58-6; **16**, 31710-59-5; **16a**, 32774-56-4; **17**, 35223-61-1; **18**, 35223-62-2; **18a**, 32774-57-5; **19**, 35262-02-3; **20**, 35223-64-4; **20** semicarbazone, 35223-65-5; **21**, 35223-66-6; **22**, 35223-67-7; **23**, 13434-64-5; **24**, 7214-64-4; **25**, 22020-87-7; **26**, 35223-72-4; **27**, 35223-73-5; **28**, 6125-21-9; **29**, 762-98-1; **30**, 35223-76-8; **31**, 35262-01-2.

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[30] A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947).

[31] M. C. Kloetzel, *J. Amer. Chem. Soc.*, **69**, 2271 (1947).

[32] Compound **22** has an ir spectrum identical to that prepared by the method of Bordwell and Garbisch[24,33] (addition of acetyl nitrate to 2,4,4-trimethyl-1-pentene followed by hydrolysis).

[33] Private communication, R. F. Love.