π and σ Interactions of Electron-Deficient Aromatics with Amines. Addition to the Ring and to a Ring Substituent

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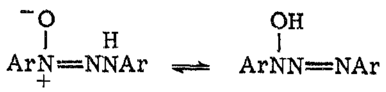
The addition of phenylhydrazine to the ring and to a nitro group in 1,3,5-trinitrobenzene has been observed. Only addition to the nitro group occurs with 2,4,6-trinitrotoluene. This is the first confirmed observation of concurrent substituent and ring addition, and confirms earlier proposals. The nature of the interactions is discussed.

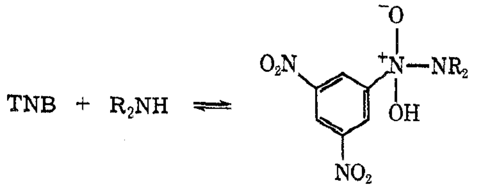
Reactions of electron-deficient aromatics with amines have been of interest for a number of years, and a variety of different types of interactions have been identified.[1–12] With aromatic amines, the most commonly observed product is a donor–acceptor or π complex.[1,2] There is some evidence in one instance for formation of an aromatic amine σ complex, but it was not isolated.[13] Tertiary aliphatic amines also form donor acceptor complexes with electron-deficient aromatics if the solvent in which the precursors are mixed is aprotic.[4,7] With primary and secondary amines, there is substantial evidence for addition to the aromatic ring, resulting in stable covalently bonded σ complexes.[7,13] In addition to these more commonly observed interactions, anion radicals and aromatic anions have been proposed to arise from the reaction of amines and 1,3,5-trinitrobenzene.[11,12] A proposal of amine addition to a nitro group in this latter aromatic has recently been published.[6]

We report here a study of the reaction of 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrotoluene (TNT) with phenylhydrazine. This latter amine is of interest for several reasons. It possesses both aromatic and aliphatic amine character, and was expected to easily form both π and σ complexes. In addition, attack of phenylhydrazine on a nitro group in TNB or TNT could lead to isolable triazene oxides or diazohydroxyamino compounds. Similar reactions occur upon addition of phenylhydrazine to nitrosobenzenes,[14] and the reducing action of phenylhydrazines on aromatic nitro compounds to yield anilines[15] suggests that a similar addition might occur to the nitro group. In fact, an oxyhydroxylamine intermediate was recently proposed to result from the interaction of TNB and amines, but the product was quite unstable and could not be isolated.[6]

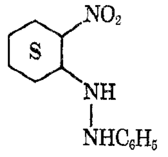
$ArNO + ArNHNH_2 \longrightarrow$



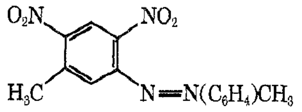
$$Ar\overset{\overset{-}{O}}{\underset{+}{N}}{=}\overset{H}{N}NAr \rightleftharpoons Ar\overset{OH}{N}N{=}NAr$$



It has been reported that phenylhydrazine adds to 1-nitrocyclohexene to give the adduct I,[16] and that p-methylphenylhydrazine displaces a nitro group in 2,4,6-trinitrotoluene to give the rearranged substitution product II.[17] A mixture of trinitrobenzene and phenylhydrazine was reported to yield a 1:1 adduct,[18] but the nature of this interaction is unclear as the authors did not state which isomer of trinitrobenzene was used.



I



II

It is well known that ortho dinitro substituted benzenes are prone to lose NO_2^- when attacked by nucleophiles[19–21] whereas polynitrobenzenes without ortho nitro groups can form reasonably stable charge transfer or σ complexes under similar conditions.[5]

Addition of 0.02 equiv (2.2 g) of phenylhydrazine in 50 ml of benzene to 0.01 equiv (2.1 g) of TNB in 100 ml of benzene produces a yellow solution which absorbs strongly below 400 mμ. This absorption develops instantaneously and probably results from a charge transfer interaction as depicted in III.[22] It is difficult to determine λ_{max} as absorptions from uncomplexed phenylhydrazine and *sym*-trinitrobenzene overlap the charge transfer band.[23] Upon standing 3 days

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(1) R. Foster, "Organic Charge Transfer Complexes," Academic Press, New York, N. Y., 1969.

(2) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964.

(3) E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev. Chem. Soc.*, **22**, 123 (1968).

(4) M. J. Strauss, *Chem. Rev.*, **667**, 70 (1970).

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(8) K. L. Servis, *J. Amer. Chem. Soc.*, **89**, 1508 (1967).

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(10) G. N. Lewis and G. T. Seaburg, *J. Amer. Chem. Soc.*, **62**, 2122 (1940).

(11) R. E. Miller and W. F. K. Wynne Jones, *Nature (London)*, **186**, 149 (1960).

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(13) E. Buncel and J. Webb, *Can. J. Chem.*, **50**, 129 (1972).

(14) Bamberger and Billeter, *Helv. Chim. Acta*, **14**, 219 (1931).

(15) L. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967.

(16) A. V. Topchiev and E. L. Fantalova, *Dokl. Akad. Nauk SSSR*, **132**, 628 (1960).

(17) M. Giva and A. Angeletti, *Gazz. Chim. Ital.*, **51**, 318 (1921).

(18) K. A. Hoffmann and H. Kirmrenther, *Ber.*, **43**, 1746 (1910).

(19) A. Holleman and F. v. Haeften, *Recl. Trav. Chim. Pays-Bas*, **40**, 67–98 (1921).

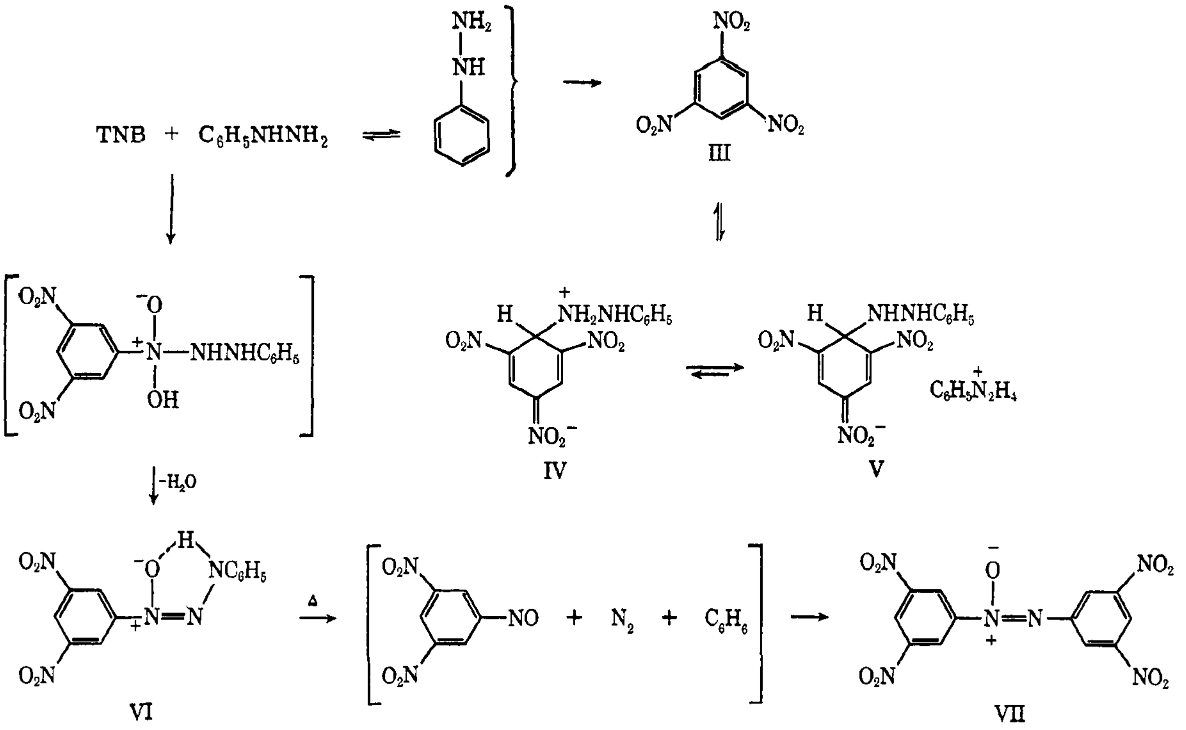
(20) R. E. Parker and T. O. Read, *J. Chem. Soc.*, 3149 (1962).

(21) D. C. Morrison, *J. Org. Chem.*, **27**, 296 (1962).

(22) The type of coordination (n donation or π donation) is not specified.

(23) Charge transfer bands arising from solvent interaction with both *sym*-trinitrobenzene and phenylhydrazine may also obscure the absorption of interest. Since alkoxide forms to some extent in alcoholic solutions of phenylhydrazine and since halogenated hydrocarbons react with amines, these other solvents were excluded. Hydrocarbons and ethers did not dissolve sufficient *sym*-trinitrobenzene for the subsequent reactions to occur.

Scheme I



the solution turns red and a small quantity of purple crystals (<0.2 g) forms on the bottom of the reaction flask. These melt at 109-111° and observation of this material with a Bausch and Lomb stereomicroscope for 6 hr showed decomposition occurring at room temperature. The nmr spectrum in DMSO-d_6 (Figure 1) and the two absorption maxima in methanol at 462 and 561 mμ are consistent with a σ complex salt like V. A σ complex in which nitrogen adjacent to the ring in the phenylhydrazine moiety is bonded to the cyclohexadienide ring is not precluded by the data presented here. However, aniline forms a π complex with *sym*-trinitrobenzene,[24] presumably because the nonbonding pair on nitrogen is delocalized into the aromatic ring and is not available for covalent bond formation. Similar considerations in the system under investigation here lead us to conclude that the σ complex between *sym*-trinitrobenzene and phenylhydrazine is best represented as V (Scheme I).

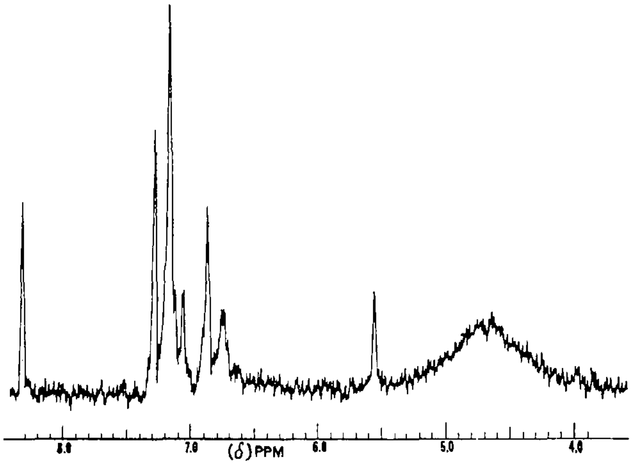


Figure 1.

The nmr spectrum (Figure 1) deserves comment. The cyclohexadienide protons appear as a singlet at δ 8.3 (2 H) and the tertiary ring proton as a singlet at δ 5.5 (1 H). This latter absorption is not split as the adjacent NH proton is rapidly exchanged. The aromatic protons of both phenyl rings (in the cation and anion) appear as a multiplet from δ 7.4 to δ 6.4 and the NH protons as a broad absorption centered at δ 4.7. Both these absorptions integrate to slightly more than the expected relative area (10 H and 6 H, respectively) owing to slow decomposition to starting materials and other products (*vide infra*).

Formation of V might proceed through a preliminary equilibrium between the charge transfer complex III and the zwitterionic structure IV (Scheme I). Abstraction of an NH$^+$ proton in IV by phenylhydrazine would yield V. Similar processes, in which zwitterionic σ complexes of primary or secondary amines and *sym*-trinitrobenzene are converted to σ complex salts, are known to occur.[13]

When the reaction solution is allowed to stand for extended periods of time (about 2 weeks), yellow needles of another product precipitate. This material violently decomposes at 139.5° with extensive gaseous evolution, and analyzes correctly for $C_{12}H_9N_5O_5$ (see Experimental Section). The infrared spectrum (KBr) shows N—O (N=O) absorptions at 1530, 1505, and 1337 cm^{-1}. The nmr spectrum (DMSO-d_6) was poorly resolved and consisted of two aromatic absorptions and a broad absorption for NH (see Experimental Section). The compound is extremely unstable in a variety of common nmr solvents (DMSO, DMF, pyridine-d_5, etc). It reacts violently with DMSO on warming and explodes when rapidly heated. It is insoluble in, and unreactive toward, sulfuric acid (6 *N*), but is very sensitive to base, yielding red solutions which turn black upon standing. We initially supposed that the yellow product might have arisen by cyclization–

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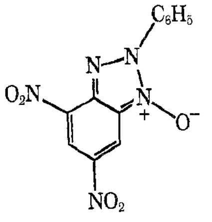
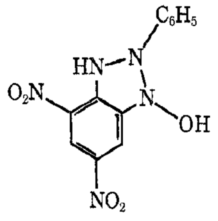
[24] S. D. Ross and M. M. Labes, *J. Amer. Chem. Soc.*, **79**, 76 (1957).

dehydration of V to yield a 5,7-dinitrobenzotriazole derivative, VIII, but such benzotriazoles, including VIIIa which we prepared by a published method,[25] are not temperature sensitive and do not decompose in solution. In addition, their infrared spectra are markedly different from that of the yellow product formed from phenylhydrazine and TNB. The thermal instability of this latter material is similar to that of triazene oxides,[26] and suggests that the structure could be VI. Aromatic triazenes readily liberate nitrogen on heating.[26] In the case of VI, benzene and 3,5-dinitronitrosobenzene might then be formed. This latter aromatic has never been isolated, as its readily formed dimer is rapidly converted to 3,3′,5,5′-tetranitroazoxybenzene,[27] VII. In fact, boiling a benzene solution of TNB–phenylhydrazine condensation product for 12 hr gives a high yield of VII (see Experimental Section). In addition, when the decomposition is carried out in dioxane, benzene can be distilled from the reaction solution. These results, coupled with the elemental analysis, chemical properties, and infrared and pmr spectra, are substantial evidence for structure VI.

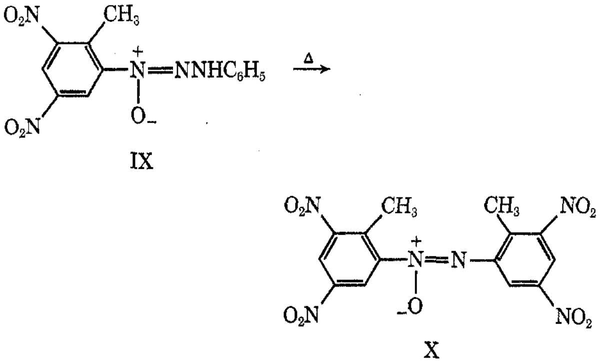


VIIIa



VIIIb

The reaction of TNT with phenylhydrazine results in a compound analogous to IX, which analyzes correctly for $C_{13}H_{12}N_5O_5$ and explodes at 143.5°. In this case, there is no evidence at all for σ complex formation. The visible spectrum of the reaction solution immediately after mixing, and during the reaction, shows no double maximum characteristic of the 2,4,6-trinitrocyclohexadienate function. Instead, a spectrum similar to that of VI is observed. Although anionic σ complexes are formed from TNT and a variety of organic bases, they are considerably less stable than those formed from TNB.[4] The product of phenylhydrazine addition to TNT is thus IX. Addition to the nitro group ortho to methyl is confirmed by the pmr spectrum of IX. This compound is more soluble and stable in common nmr solvents than VI (see Experimental Section). Thermal decomposition of IX gives good yields of X.



IX

X

The formation of V and VI by attack of phenylhydrazine on TNB is the first confirmed observation of concurrent nitro group and ring attack on this electron deficient aromatic, and supports Bernasconi's earlier proposals.[6] It is clear that ring substitution strongly affects the mode of reaction, since only addition to a nitro group is observed with TNT and phenylhydrazine. With other organic bases, ring addition to TNT becomes predominant however.[4,28]

Addition to the nitro group is a further type of interaction, besides charge transfer and σ complexation, radical ion formation, and proton transfers, which is likely to occur when electron-deficient aromatics are treated with base. Many such addition products probably revert rapidly back to starting materials,[6] and thus are difficult to detect. Phenylhydrazine may be unique in that stable nitro group addition products cannot be isolated by treating alkyl hydrazines or alkyl amines with TNB.[4,28]

Experimental Section

All melting points are uncorrected. Ir and uv spectra were recorded with Perkin-Elmer Model 21 and Model 402 spectrophotometers, respectively. Pmr spectra were recorded with JEOL C-60HL and MH-100 spectrometers, and chemical shifts are reported with respect to internal tetramethylsilane.

Reaction of TNB and Phenylhydrazine.—Addition of phenylhydrazine (2.16 g, 0.02 mol) to a benzene solution of TNB (2.13 g, 0.01 mol, in 100 ml of solvent) resulted in a bright yellow solution. After 72 hr purple crystals of V (~0.2 g) were deposited on the bottom of the flask. After filtering and washing with ether, these melted at 109–111°. Slow decomposition at room temperature precluded a satisfactory elemental analysis. Spectra were taken on freshly washed and dried crystals: visible λ_{max} 452, 561 nm; nmr shown in Figure 1.

If V was not filtered from the initial reaction mixture, and the solution was allowed to stand for 10 days, a yellow precipitate formed. After filtration, a methanol wash, and recrystallization from benzene, yellow needles were obtained (~1.0 g) which exploded at 139.5° and analyzed correctly for VI. *Anal.* Calcd for $C_{12}H_9N_5O_5$: C, 47.54; H, 2.99; N, 23.09. Found: C, 47.58; H, 3.17; N, 22.96.

The nmr spectrum (DMSO-d_6), which was poorly resolved owing to decomposition, showed absorptions at δ 9.1 (~2.5 H, m), δ 7.4 (~5 H, s), and δ 3.5 (NH, br). The uv (MeOH) and ir (KBr) spectra showed absorptions at 217 and 388 nm and 1337, 1505, and 1530 cm^{-1}, respectively.

When a 10-equiv excess of phenylhydrazine was used, V could not be isolated, even though the reaction solution showed strong absorptions at 452 and 561 nm. A yellow precipitate of VI was formed within 6 hr. If the reaction was carried out in phenylhydrazine, VI precipitated within a few minutes (caution, exothermic).

Reaction of TNT and Phenylhydrazine.—When a 2-equiv excess of phenylhydrazine was added to a benzene solution of TNT, a yellow precipitate was formed after 12 hr. There was no evidence for formation of a σ complex, even immediately after mixing the reactants, as the visible spectrum of the solution showed no double maxima. Recrystallization of the yellow precipitate from benzene yielded yellow needles which exploded at 143.5°, and analyzed correctly for IX. *Anal.* Calcd for $C_{13}H_{11}N_5O_5$: C, 49.23; H, 3.49; N, 22.08. Found: C, 49.52, H, 3.53; N, 22.09.

The nmr spectrum (dioxane) showed absorptions at δ 8.1 (~1 H, s), δ 7.9 (~1 H, s), δ 6.7 (~5 H, m), and δ 2.5 (~3 H, s). This latter absorption could only be seen in DMSO-d_6. On the basis of the nonequivalence of the protons on the tetrasubstituted ring, the triazene oxide function has been assigned ortho to the

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[25] S. Joshi and D. Deorha, *J. Indian Chem. Soc.*, **34**, 77 (1957).

[26] E. H. Rodd, "Chemistry of Carbon Compounds," Vol. IIIA, Elsevier, New York, N. Y., 1954, p 307.

[27] C. Moberg and O. Wennerstrom, *Acta Chem. Scand.*, **25**, 2355 (1971).

[28] M. J. Strauss and S. P. B. Taylor, unpublished work.

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.

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[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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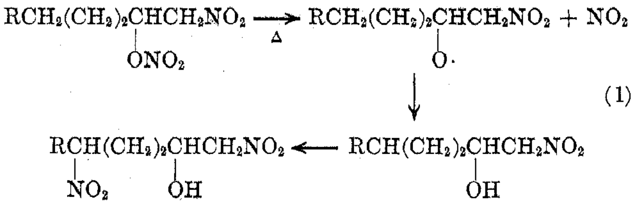
The decomposition of β-nitroalkyl nitrates in dilute hydrocarbon or halocarbon solution follows first-order kinetics (ΔH_a = 38–40 kcal mol^{-1}) to give dinitro or bromonitro alcohols derived from a 1,5 intramolecular hydrogen shift. For instance, 1-nitro-2-methyl-2-pentyl nitrate (**5**) rearranges 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.



$$\mathrm{R CH_2(CH_2)_2\underset{ONO_2}{CH}CH_2NO_2 \xrightarrow[\Delta]{} RCH_2(CH_2)_2\underset{O\cdot}{CH}CH_2NO_2 + NO_2}$$

$$\downarrow \qquad (1)$$

$$\mathrm{R\underset{NO_2}{CH}(CH_2)_2\underset{OH}{CH}CH_2NO_2 \longleftarrow R\dot{C}H(CH_2)_2\underset{OH}{CH}CH_2NO_2}$$

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

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[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.