perature for 3 days. Precipitate was collected by filtration. (In the preparation of compounds I and III (Table II), neutralization with hydrochloric acid was necessary for the precipitation of the condensation products.) The almost pure products were washed with water and ethanol and dried. One recrystallization from a suitable solvent, as given in Table II, gave the analytically pure compounds.

(c) **Neutral Method.**—A solution of 1.5 millimoles of dimeric 4,5-dimethyl-*o*-benzoquinone in 20 ml. of 95% ethanol was added to 3.0 millimoles of the pyrimidine sulfate[20] dissolved in 100 ml. of water and neutralized with 10% sodium hydroxide. The final *p*H of the combined solutions was adjusted to 7.0, and the mixture was heated on the steam-bath for 4 hr. and then allowed to stand at room temperature for 1–3 days. The precipitate was collected, washed and dried, as above. One recrystallization from the appropriate solvent (Table II) gave the analytically pure product.

CHICAGO 9, ILLINOIS

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

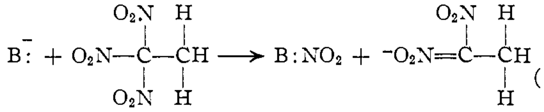
Various Reactions of Organic Bases with 1,1,1-Trinitroethane and 1-Halo-1,1-Dinitroethanes. 1,1-Dinitroethene as a Reaction Intermediate[1]

BY LAWRENCE ZELDIN[2] AND HAROLD SHECHTER[3]

RECEIVED MARCH 14, 1957

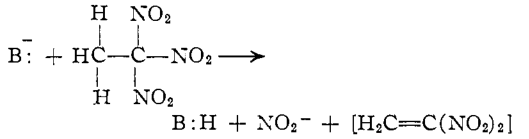
Bases undergo two reactions with 1,1,1-trinitroethane: (1) nucleophilic attack on one of the nitro groups effecting displacement of the 1,1-dinitroethane anion and (2) elimination of nitrous acid to give 1,1-dinitroethene, a reactive intermediate; 1,1-dinitroethene undergoes addition of the bases to yield β-substituted derivatives of 1,1-dinitroethane. Bases which react with 1,1,1-trinitroethane by sequence 1 are potassium salts of 2-nitropropane, 2,4-pentanedione and 1-butanethiol, respectively, and *n*-butyllithium. Bases which react by sequence 2 are potassium diethyl malonate, guanidine, piperidine and trimethylamine (and triethylamine); the products derived by addition to 1,1-dinitroethene are potassium ethyl 2-carbethoxy-4,4-dinitrobutyrate (I), 2-guanidino-1,1-dinitroethane (VI), 1,1-dinitro-2-piperidinoethane (VII) and trimethylammonium N-(2-nitroethyl-2-nitronate) (VIII). Exchange reactions of VIII with guanidine and with piperidine yield VI and VII. Reactions of piperidine with either 1-bromo-1,1-dinitroethane or 1-chloro-1,1-dinitroethane and of sodium diethyl malonate with 1-bromo-1,1-dinitroethane result in reductive attack on halogen with displacement of the 1,1-dinitroethane anion.

1,1,1-Trinitroethane undergoes two general reactions with bases: (1) attack of the base on one of the nitro groups (equation 1) resulting in displacement of the 1,1-dinitroethane anion[4a]; this reaction involves reduction of 1,1,1-trinitroethane and results in transfer of a (positive) nitro group[4b] to the attacking base, and (2) reaction of the base with a β-hydrogen resulting in elimination of nitrous acid and formation of 1,1-dinitroethene as an (unisolated) intermediate

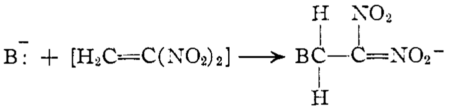


$$\mathrm{B\overset{-}{:}} + \mathrm{O_2N{-}\underset{O_2N}{\overset{O_2N}{C}}{-}\underset{H}{\overset{H}{C}}H} \longrightarrow \mathrm{B{:}NO_2} + \mathrm{{}^-O_2N{=}\overset{O_2N}{C}{-}\underset{H}{\overset{H}{C}}H} \quad (1)$$

Subsequent Michael addition of the base to 1,1-dinitroethene yields a β-substituted anion of 1,1-dinitroethane (equations 2 and 3).[4c,d] Thus reactions of 1,1,1-trinitroethane with aqueous potassium hydroxide[4a] or with hydroxylamine in potassium methoxide[4d] result in formation of potassium 1,1-dinitroethane in excellent yields (equation 1), whereas 1,1,1-trinitroethane reacts with potassium ethoxide[4c] or ethanolic potassium hydroxide,[4a] potassium methoxide[4c] and ethanolic potassium cyanide[4d] to give potassium salts of ethyl 2,2-dinitroethyl ether ($\sim$ 80%), methyl 2,2-dinitroethyl ether ($\sim$ 80%) and 3,3-dinitropropionitrile (80%), respectively.

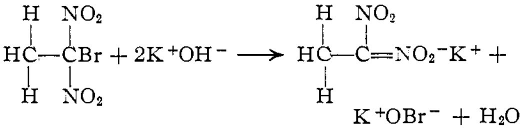


$$\mathrm{B\overset{-}{:}} + \mathrm{H\underset{H}{\overset{H}{C}}{-}\underset{NO_2}{\overset{NO_2}{C}}{-}NO_2} \longrightarrow \mathrm{B{:}H} + \mathrm{NO_2^-} + [\mathrm{H_2C{=}C(NO_2)_2}] \quad (2)$$



$$\mathrm{B\overset{-}{:}} + [\mathrm{H_2C{=}C(NO_2)_2}] \longrightarrow \mathrm{B\underset{H}{\overset{H}{C}}{-}\overset{NO_2}{C}{=}NO_2^-} \quad (3)$$

The reactions of 1-bromo-1,1-dinitroethane with aqueous or alcoholic potassium hydroxide[5a] (equation 4), aqueous potassium carbonate,[5a] hydrazine and potassium hydroxide[5b] and potassium iodide[5c] also have been investigated and are found to involve reductive attack on (positive) bromine and formation of potassium 1,1-dinitroethane. No evidence has been obtained for processes of the elimination–addition type involving formation of 1-bromo-1-nitroethene or 1,1-dinitroethene as reaction intermediates.



$$\mathrm{H\underset{H}{\overset{H}{C}}{-}\underset{NO_2}{\overset{NO_2}{C}}Br} + 2\mathrm{K^+OH^-} \longrightarrow \mathrm{H\underset{H}{\overset{H}{C}}{-}\overset{NO_2}{C}{=}NO_2^-K^+} + \mathrm{K^+OBr^-} + \mathrm{H_2O} \quad (4)$$

As a result of the facts that: (1) there are, as yet, at least two uncorrelated reactions of bases

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[1] This research was supported by the Office of Naval Research.

[2] (a) Deceased, September 3, 1955. (b) Taken in part from a dissertation submitted by L. Zeldin to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, June, 1951.

[3] To whom inquiries with respect to this research should be made.

[4] (a) A. Hantzsch and A. Rinckenberger, *Ber.*, **32**, 628 (1899). (b) This reaction is presumed to involve attack of the base on the positive nitrogen atom of a nitro group. An alternate possibility, though less attractive, involves displacement attack on oxygen of a nitro group to give the corresponding nitrito derivative. These two possible processes can not be differentiated from the results of present investigations. (c) J. Meisenheimer, *Ber.*, **36**, 434 (1903). (d) J. Meisenheimer and M. Schwarz, *ibid.*, **39**, 2543 (1906).

[5] (a) E. ter Meer, *Ann.*, **181**, 1 (1876); (b) E. L. Hirst and A. K. Macbeth, *J. Chem. Soc.*, **121**, 2169 (1922); (c) K. Klager, *Anal. Chem.*, **23**, 534 (1951).

with 1,1,1-trinitroethane, (2) reaction of 1,1,1-trinitroethane with certain bases allows formation *in situ* of the unusual dinitroölefin, 1,1-dinitroethene, subsequent reaction of which offers an attractive method for preparing β-substituted derivatives of 1,1-dinitroethane and (3) reactions of 1-bromo-1,1-dinitroethane with bases have not been found to give the elimination–addition sequence as does 1,1,1-trinitroethane, a study has been initiated of the actions of various organic bases with 1,1,1-trinitroethane and 1-halo-1,1-dinitroethanes. The results reported in the present research are those of reactions of 1,1,1-trinitroethane with potassium salts of diethyl malonate,[6] 2-nitropropane,[6] 2,4-pentanedione[6] and 1-butanethiol,[6] respectively, and with *n*-butyllithium, guanidine, piperidine,[6] triethylamine and trimethylamine, respectively. The reactions of 1-bromo-1,1-dinitroethane with piperidine[6] and with sodium diethyl malonate[6] and of 1-chloro-1,1-dinitroethane with piperidine[6] are also described.

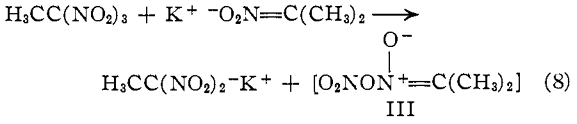
Reaction of 1,1,1-trinitroethane (one equivalent) with ethanolic potassium diethyl malonate (two equivalents) occurs rapidly at 78°, presumably by the elimination–addition sequence (equations 2 and 3) involving 1,1-dinitroethene,[7] to yield potassium ethyl 2-carbethoxy-4,4-dinitrobutyrate (I, 36%), potassium nitrite and ethyl malonate (equations 5 and 6). Identification of I was effected upon (1) preparation and analysis of silver ethyl 2-carbethoxy-4,4-dinitrobutyrate, and (2) acidification and then isolation of pure ethyl 2-carbethoxy-4,4-dinitrobutyrate (II). Reaction of II with potassium hydroxide, Michael addition of the anion to methyl acrylate and hydrolysis of the adduct in concentrated hydrochloric acid to give 4,4-dinitroheptanedioic acid[8] (30%, equation 7) serve as further confirmation of structure I.

$$H_3CC(NO_2)_3 + K^{+-}CH(CO_2C_2H_5)_2 \longrightarrow [H_2C{=}C(NO_2)_2] + K^+NO_2^- + H_2C(CO_2C_2H_5)_2 \quad (5)$$

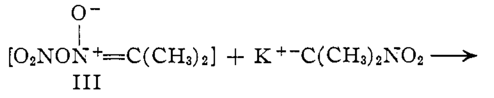
$$[H_2C{=}C(NO_2)_2] + K^{+-}CH(CO_2C_2H_5)_2 \longrightarrow \underset{\text{I}}{(H_5C_2O_2C)_2CHCH_2C(NO_2)_2^-K^+} \quad (6)$$

$$\underset{\text{II}}{(H_5C_2O_2C)_2CHCH_2CH(NO_2)_2} \xrightarrow[\text{3, HCl, H}_2\text{O}]{\text{1, KOH; 2, CH}_2\text{=CHCO}_2\text{CH}_3} (HO_2CCH_2CH_2)_2C(NO_2)_2 \quad (7)$$

Potassium 2-nitropropane (two equivalents) in anhydrous ethanol reacts exothermally with 1,1,1-trinitroethane (one equivalent) at 0° to yield potassium 1,1-dinitroethane (68%), 2,3-dimethyl-2,3-dinitrobutane (87%) and potassium nitrite. Reaction of potassium 2-nitropropane and 1,1,1-trinitroethane, therefore, does not follow the elimination–addition sequence (equations 2 and 3) as does potassium diethyl malonate, but rather the oxidation–reduction sequence (equation 1) involving attack on a (positive) nitro group of 1,1,1-trinitroethane and formation of the 1,1-dinitroethane anion (equation 8). Further reaction of the 2-nitropropane anion with the presumed intermediate III (an anhydride of nitric and 2-propanenitronic acids, a N-nitratoketoxime) by displacement involving carbon-alkylation (equation 9) may account for the formation of 2,3-dimethyl-2,3-dinitrobutane and potassium nitrite.[9]

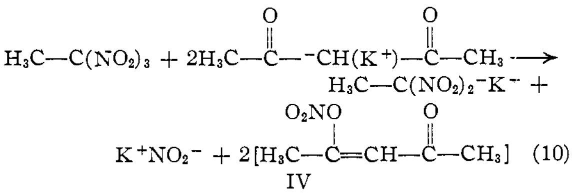


$$H_3CC(NO_2)_3 + K^+\ {}^-O_2N{=}C(CH_3)_2 \longrightarrow H_3CC(NO_2)_2^-K^+ + \underset{\text{III}}{[O_2NO\overset{\overset{\displaystyle O^-}{|}}{N}{}^+{=}C(CH_3)_2]} \quad (8)$$



$$\underset{\text{III}}{[O_2NO\overset{\overset{\displaystyle O^-}{|}}{N}{}^+{=}C(CH_3)_2]} + K^{+-}C(CH_3)_2NO_2 \longrightarrow K^+NO_2^- + (H_3C)_2CNO_2CNO_2(CH_3)_2 \quad (9)$$

The bases potassium 2,4-pentanedione, potassium 1-butanethioxide and *n*-butyllithium, each undergo reductive attack (equation 1) on a nitro group of 1,1,1-trinitroethane as does potassium 2-nitropropane. Thus, reaction of potassium 2,4-pentanedione in refluxing ethanol with 1,1,1-trinitroethane (equation 10) yields potassium 1,1-dinitroethane (64%), potassium nitrite (53%) and



$$H_3C{-}C(NO_2)_3 + 2H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}{}^-CH(K^+){-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 \longrightarrow H_3C{-}C(NO_2)_2^-K^- + K^+NO_2^- + 2\underset{\text{IV}}{[H_3C{-}\overset{\overset{\displaystyle O_2NO}{|}}{C}{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3]} \quad (10)$$

an unidentified high molecular weight product.[10] Potassium 1-butanethioxide, in contrast to potassium methoxide and ethoxide,[4c,d] reacts with 1,1,1-trinitroethane in refluxing ethanol to give potassium 1,1-dinitroethane (> 42%), potassium nitrite and di-*n*-butyl disulfide (71%) (equations 11 and 12).

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[6] These bases were chosen because they or their analogs undergo Michael addition with conjugated nitroölefins to yield β-substituted nitroalkanes; see, *e.g.*, C. T. Bahner, U. S. Patent 2,447,626, August 24, 1948, and R. L. Heath and J. D. Rose, *J. Chem. Soc.*, 1486 (1947).

[7] There were no efforts other than those described to isolate 1,1-dinitroethene in the present research.

[8] L. Herzog, M. H. Gold and R. D. Geckler, THIS JOURNAL, **73**, 749 (1951).

[9] Alternate paths (1′–3′, 4′–6′)[9b,c] involving oxidation–reduction and subsequent dimerization of intermediate radicals which may be written for reaction of 1,1,1-trinitroethane with 2-propanenitronate (A⊖) and 1-butanethioxide (A⊖) anions are:

$$H_3CC(NO_2)_3 + A^\ominus \longrightarrow A\cdot + \cdot NO_2 + H_3CC^\ominus(NO_2)_2 \quad (1')$$

$$\cdot NO_2 + A^- \longrightarrow NO_2^\ominus + A\cdot \quad (2')$$

$$2A\cdot \longrightarrow A{-}A \quad (3')$$

$$H_3CC(NO_2)_3 + A^\ominus \longrightarrow H_3CC(NO_2)_2 + NO_2^\ominus + A\cdot \quad (4')$$

$$H_3C\dot{C}(NO_2)_2 + A^\ominus \longrightarrow A\cdot + H_3CC^\ominus(NO_2)_2 \quad (5')$$

$$2A\cdot \longrightarrow A{-}A \quad (6')$$

Mechanisms involving heterolytic displacement processes in reactions of these bases with 1,1,1-trinitroethane have been employed in the body of this manuscript because of their simplicity and their general ability to correlate the experimental results. There is no evidence available however which will allow definite choice of these mechanisms over those of sequences 1′–3′ and 4′–6′. (b) Similar mechanisms[4e] may be written for reactions of 1-bromo-1,1-dinitroethane and 1-chloro-1,1-dinitroethane with sodium diethyl malonate; see subsequent Discussion and Experimental. (c) The author wishes to acknowledge the contribution of one of the referees for suggesting sequences 1′–6′.

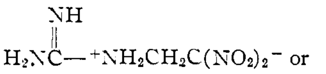
[10] This product is believed to arise from displacement of nitrite ion in reaction of potassium 2,4-pentanedione and the initial nitrated derivative IV of 2,4-pentanedione to give 1,1,2,2-tetraacetylethane and ultimately its polymeric aldol derivatives. The properties of this material are very similar to that of aldols derived from 1,1,2,2-tetraacetylethane and its yield is nearly quantitative based on 2,4-pentanedione.

$$H_3CC(NO_2)_3 + K^{+-}SCH_2CH_2CH_2CH_3 \longrightarrow \underset{\text{V}}{H_3CC(NO_2)_2{}^-K^+ + [O_2NSCH_2CH_2CH_2CH_3]} \quad (11)$$

$$CH_3CH_2CH_2CH_2S^-K^+ + [O_2NSCH_2CH_2CH_2CH_3] \longrightarrow K^+NO_2{}^- + (CH_3CH_2CH_2CH_2S)_2 \quad (12)$$

Similarly, reaction of *n*-butyllithium and 1,1,1-trinitroethane at 25–30° in ethyl ether yields lithium 1,1-dinitroethane (> 48%) and lithium nitrite.

Guanidine and the amines piperidine, triethylamine and trimethylamine in either ethanol or ethyl ether function similarly with respect to 1,1,1-trinitroethane in that they effect attack on β-hydrogen and elimination of nitrous acid. Thus, guanidine and piperidine react with 1,1,1-trinitroethane (equations 2 and 3) to give 2-guanidino-1,1-dinitroethane[11] (VI, 75%) and guanidinium nitrite (82%) and 1,1-dinitro-2-piperidinoethane (VII, 66%) and piperidinium nitrite, respectively.

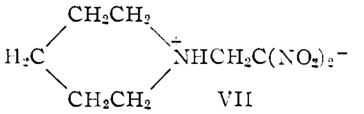


$$H_2N\overset{\overset{NH}{\|}}{C}—{}^+NH_2CH_2C(NO_2)_2{}^- \text{ or}$$

VI

$$(H_2N)_2C{=}{}^+NHCH_2C(NO_2)_2{}^-$$

VI



VII

The adducts VI (m.p. >> 196° dec.) and VII (m.p. 108.5°) are readily crystallizable solids and are quite stable when adequately purified. Their physical properties indicate that they exist, as expected, as dipolar ions[12]; thus, their ultraviolet spectra (Fig. 1, see Experimental), color, solubility behavior and crystalline form (monoclinic) resemble that of salts of 1,1-dinitroalkanes. The structure of VI is assigned on the basis of quantitative and ultraviolet spectral analyses (Fig. 1); the adduct is decidedly different in properties from that of authentic guanidinium 1,1-dinitroethane (see Experimental), an alternate product that might be obtained from a displacement reaction (Equation 1) involving 1,1,1-trinitroethane and guanidine. The proof of structure of VII is based on its analytical and spectral analyses (Fig. 1), its conversion to silver 1,1-dinitro-2-piperidinoethane (analyzed) and its synthesis[13] from dinitromethane and N-methylolpiperidine (94%).

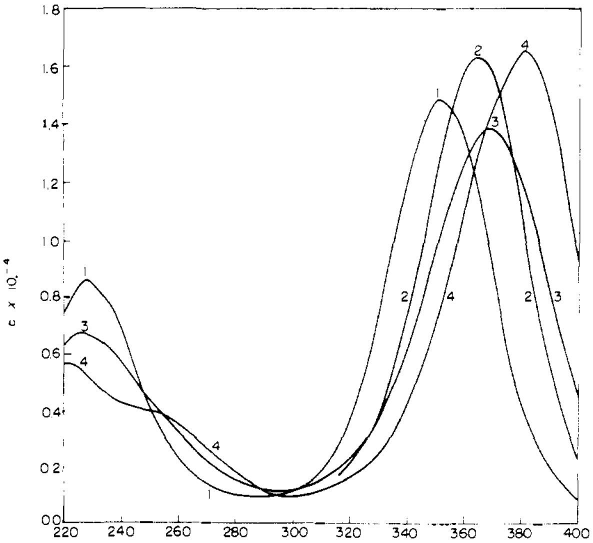


Fig. 1.—Ultraviolet absorption spectra of trimethylammonium-N-(2-nitroethyl-2-nitronate) (1), 2-guanidino-1,1-dinitroethane (2), 1,1-dinitro-2-piperidinoethane (3) and 1,1-dinitroethane (4) in aqueous base (10^{-4} *M* soln. in 10^{-3} *M* NaOH).

The reactions of triethylamine and of trimethylamine with 1,1,1-trinitroethane serve as most interesting cases since they might allow isolation of 1,1-dinitroethene[7] upon initial elimination of nitrous acid. Reaction of triethylamine and 1,1,1-trinitroethane in ethyl ether yields triethylammonium nitrite and a red, non-crystallizable and thermally unstable product; in refluxing benzene, N-nitrosodiethylamine (83%)[14] and the intractable product are obtained. It was thus concluded that triethylamine effects elimination of nitrous acid from 1,1,1-trinitroethane and that, in refluxing benzene, triethylammonium nitrite decomposes to N-nitrosodiethylamine[15]; it also became apparent that the principal unidentified product of reaction was not 1,1-dinitroethene nor its polymers but rather an instable adduct of triethylamine and 1,1-dinitroethene, possibly triethylammonium N-(2-nitroethyl-2-nitronate)[16] (a homolog of VIII). The reaction of trimethylamine and 1,1,1-trinitroethane in anhydrous ethyl ether at −18° then was investigated because the products are more readily isolable, and it was found that trimethylammonium N-(2-nitroethyl-2-nitronate)[16] (VIII, equations 13 and 14) is produced in 83–90% yield. The adduct VIII, an internal salt and a *gem*-dinitro analog of "betaine," $(H_3C)_3N^+CH_2CO_2{}^-$, is a yellow, fairly stable, crystalline solid, m.p. 107° dec., soluble in water and insoluble in non-polar solvents.

$$(H_3C)_3N + H_3CC(NO_2)_3 \longrightarrow (H_3C)_3\overset{+}{N}HNO_2{}^- + [H_2C{=}C(NO_2)_2] \quad (13)$$

$$(H_3C)_3N + [H_2C{=}C(NO_2)_2]^{15} \longrightarrow \underset{\text{VIII}}{(H_3C)_3\overset{+}{N}CH_2C(NO_2)_2{}^-} \quad (14)$$

Its ultraviolet spectrum (Fig. 1) is similar to that of VI, VII and potassium 1,1-dinitroethane. Its

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[11] It is possible for 2-guanidino-1,1-dinitroethane to exist in tautomeric modifications.

[12] These adducts give positive Liebermann tests for nitrite ion upon acidification with strong mineral acid in the presence of phenol. Salts of mono- and *gem*-dinitroalkanes on acidification with strong acids evolve nitrous acid and thus nitrosate phenol; the parent mono- and *gem*-dinitroalkanes do not give positive tests under these conditions.

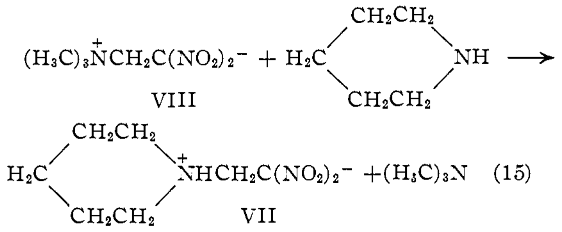
[13] A modification of the method of P. Duden, K. Bock and H. G. Reid, *Ber.*, **38**, 2036 (1905); see Experimental.

[14] The initial studies with triethylamine were conducted by Dr. Ralph Kaplan in this Laboratory. His many contributions throughout this investigation are warmly acknowledged.

[15] This reaction has been reported in 50% yield: German Patent 400,313, June 8, 1924; *Chem. Zentr.*, **96**, I, 293 (1925).

[16] This appears to be the first example of a Michael addition of a tertiary amine to an activated α,β-unsaturated compound. The marked electrophilic properties of 1,1-dinitroethane are perhaps to be expected on the basis of the powerful electron-attracting characteristics of nitro groups and on the relative stabilization derived upon formation of a 1-nitroalkanenitronate anion.

structure is verified by: (1) analysis, (2) conversion to a double salt with silver nitrate (analyzed) and (3) exchange with guanidine and with piperidine (equation 15) to yield VI (28%) and VII (96%); the conversions of VIII to VI and VII also serve as corroborative evidence for the structures assigned to VI and VII.

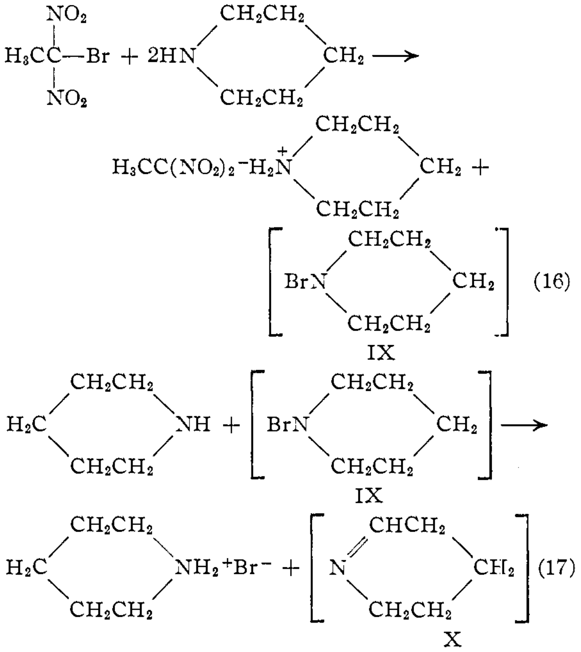

VIII

VII

(15)

Upon considering the results of the present and previous[4a,c,d] researches concerning reactions of bases with 1,1,1-trinitroethane and recognizing that many of the reactions have been effected in different environments, there is as yet no general correlation[2b,17] between the strength,[17b] nucleophilicity[17b,c] (at least with respect to carbon), steric requirements or ease of oxidation of a base and whether the base will attack 1,1,1-trinitroethane by displacement or elimination–addition processes. It has been established, however, that reaction of 1,1,1-trinitroethane involving elimination–addition is effected by simple alkoxides,[4c] aliphatic amines, guanidine (an amine analog) and cyanide[4d] and malonic ester anions. Since it has been previously observed that 1-bromo-1,1-dinitroethane reacts with simple bases only by attack on (positive) bromine and with formation of salts of 1,1-dinitroethane,[5] a study has been initiated of reactions of 1-halo-1,1-dinitroethanes with bases that result in elimination–addition upon reaction with 1,1,1-trinitroethane. These reactions may thus allow the formation of 1,1-dinitroethene or of 1-halo-1-nitroethenes (*in situ*) or give additional information[4c,4d,18] concerning the relative ease of reduction of (positive) halogen and of (positive) nitro groups in 1-halo-1,1-dinitroethanes.

Reaction of 1-bromo-1,1-dinitroethane with piperidine in ethyl ether at 0° (equations 16 and 17) results primarily in transfer of bromonium ion (as in equation 4) to yield piperidinium 1,1-dinitroethane (64%), piperidinium bromide (65%) and complex, unidentified, amine-like products (XI, 28%) apparently derived from polymerization of Δ^1-piperideine[19] (X). Piperidinium bromide and Δ^1-piperideine (and its subsequent polymers, XI) are believed to arise (equation 17) from reaction of piperidine and N-bromopiperidine (IX).[19] The action of 1-chloro-1,1-dinitroethane on piperidine is similar to that of 1-bromo-1,1-dinitroethane and piperidine in that attack on (positive) chlorine results in formation of piperidinium 1,1-dinitroethane (> 52%), piperidinium chloride (27%) and XI. There was no evidence for elimination–addition processes (equations 2 and 3) in reactions of 1-bromo-1,1-dinitroethane or 1-chloro-1,1-dinitroethane with piperidine.


(16)

IX

IX

(17)

X

1-Bromo-1,1-dinitroethane (two equivalents) and sodium diethyl malonate (one equivalent) in ethanol at 5–10° do not react by initial elimination–addition processes. Reaction involves displacement and (positive) bromine rather than a (positive) nitro group is transferred to the diethyl malonate anion. The products isolated are sodium 1,1-dinitroethane (68%), 1,1-dinitroethane (16%), tetraethyl 1,1,2,2-ethanetetracarboxylate (XII, 63%), tetraethyl ethylenetetracarboxylate (XIII, 3–4%) and sodium bromide (~ 100%). With one equivalent each of 1-bromo-1,1-dinitroethane and sodium diethyl malonate, the products obtained from reaction are: sodium 1,1-dinitroethane, 1,1-dinitroethane (~ 48%), diethyl bromomalonate (~ 10%), tetraethyl ethylenetetracarboxylate (XIII, 57%), sodium bromide (~ 100%), diethyl malonate (24%) and 1-bromo-1,1-dinitroethane (~ 6%). An equation sequence (equations 18–22) which accounts for the products obtained from 1-bromo-1,1-dinitroethane and sodium diethyl malonate is

$$H_3CC(NO_2)_2Br + Na^{+-}CH(CO_2C_2H_5)_2 \longrightarrow H_3CC(NO_2)_2{}^-Na^+ + BrCH(CO_2C_2H_5)_2 \quad (18)$$

$$(H_5C_2O_2C)_2CH^-Na^+ + BrCH(CO_2C_2H_5)_2 \longrightarrow Na^+Br^- + \underset{\text{XII}}{(H_5C_2O_2C)_2CHCH(CO_2C_2H_5)_2} \quad (19)$$

$$\underset{\text{XII}}{(H_5C_2O_2C)_2CHCH(CO_2C_2H_5)_2} + Na^{+-}CH(CO_2C_2H_5)_2 \longrightarrow (H_5C_2O_2C)_2C^-(Na^+)CH(CO_2C_2H_5)_2 + H_2C(CO_2C_2H_5)_2 \quad (20)$$

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(17) (a) Discussion of this problem will be deferred until the determining factors have been delineated further. (b) For discussion of related problems see J. Hine, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1956, pp. 136–142. (c) C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

(18) A. K. Macbeth and D. D. Pratt, *J. Chem. Soc.*, **119**, 1356 (1921), report that the reductive action of bases on chlorotrinitromethane and on trichloronitromethane results in attack on positive chlorine rather than on a nitro group.

(19) (a) E. Lellman and R. Schwaderer, *Ber.*, **12**, 1327 (1889), and M. Delepine, *Bull. soc. chim. France*, [3] **19**, 613 (1898), report that N-bromopiperidine loses hydrogen bromide readily. (b) Similar reactions of N-chloropiperidine yielding piperidinium chloride and trimeric and polymeric derivatives of Δ^1-piperideine are described by C. Schopf, A. Komzak, F. Braun, E. Jacobi, M. L. Bormuth, M. Bullenheimer and I. Hagel, *Ann.*, **559**, 1 (1948).

$$(H_5C_2O_2C)_2C^-(Na^+)CH(CO_2C_2H_5)_2 + Br(O_2N)_2CCH_3 \longrightarrow$$
$$[(H_5C_2O_2C)_2CBrCH(CO_2C_2H_5)_2] + Na^{+-}(O_2N)_2CCH_3 \quad (21)$$

$$[(H_5C_2O_2C)_2CBrCH(CO_2C_2H_5)_2] + Na^{+-}(O_2N)_2CCH_3 \longrightarrow$$
$$\underset{\text{XIII}}{(H_5C_2O_2C)_2C{=}C(CO_2C_2H_5)_2} + H_3CCH(NO_2)_2 + Na^+Br^- \quad (22)$$

The results involving halogen exchange in reaction of 1-bromo-1,1-dinitroethane and sodium diethylmalonate are analogous to that of reaction of 2-bromo-2-nitropropane and sodium diethyl ethylmalonate[20] to yield sodium 2-propanenitronate, 2,3-dimethyl-2,3-dinitrobutane, ethyl bromoethylmalonate and sodium bromide. Additional evidence for halogen exchange in reaction of certain bases with *gem*-halonitroalkanes is derived from the fact that 2,3-dimethyl-2,3-dinitrobutane and the appropriate anions are formed by reaction of sodium ethanenitronate or sodium 2-butanenitronate with 2-bromo-2-nitropropane[21] and of sodium 2-propanenitronate with 1-bromo-1-nitroethane[21] or 1,1-dichloro-1-nitroethane.[21]

Experimental

Materials.—Diethyl malonate, 2-nitropropane, 1-butanethiol, 2,4-pentanedione, guanidine, piperidine, triethylamine and trimethylamine were commercial products that were purified before use. 1,1,1-Trinitroethane, m.p. 53.5–55.0°, was prepared from tetranitromethane in 50% over-all yield by established procedures.[22] 1-Bromo-1,1-dinitroethane,[23] b.p. 49–50° (4.7 mm.), $n^{20}\mathrm{D}$ 1.4757, d_{20}^{20} 1.831; *MR*D calcd. 30.41, *MR*D found 30.64, was prepared in 70–90% yield by adding bromine to cold, aqueous sodium 1,1-dinitroethane. The lachrymatory oil was extracted with methylene chloride and washed with dilute sodium thiosulfate before vacuum distillation.

1-Chloro-1,1-dinitroethane.—Gaseous chlorine was bubbled through a stirred solution of 1,1-dinitroethane (15.0 g., 0.125 mole) and potassium hydroxide (8.4 g., 0.15 mole) in water (400 ml.) at 0–5°. The product separated as a yellow oil and was extracted with ether. The ether extract was washed with saturated sodium chloride, dried with calcium chloride and distilled to give **1-chloro-1,1-dinitroethane**, a colorless, lachrymatory oil (16.62 g., 86% yield), b.p. 59–61° (22 mm.), $n^{20}\mathrm{D}$ 1.4439, d^{20}_{20} 1.465; *MR*D calcd. 28.54, *MR*D found 28.01.

Anal. Calcd. for $C_2H_3N_2O_4Cl$: Cl, 22.95. Found: Cl, 22.40.

1,1,1-Trinitroethane and Potassium Diethyl Malonate.—A mixture of diethyl malonate (35.2 g., 0.22 mole) and potassium ethoxide (0.22 mole) in absolute ethanol (400 ml.) was heated to 78°. 1,1,1-Trinitroethane (16.5 g., 0.10 mole) in absolute ethanol (50 ml.) was then added at a rate such that the reaction mixture boiled gently. The solution color changed to deep red. Near the end of the addition, heat was applied to keep the solution refluxing. A yellow-orange salt soon precipitated. The reaction mixture was stirred and cooled at 0–5°, then filtered. The powdery salts obtained weighed 27.5 g. The salts were suspended in water (100 ml.), stirred and cooled to 0°. A mixture of aqueous urea–acetic acid (84 g., 0.23 mole each of urea and acetic acid in water)[24] was precooled to 0–3°, then added dropwise to the solution of salts. The acidified solution was extracted with ether; the ether extract was dried with calcium sulfate. Vacuum distillation, after removal of the solvent, yielded **ethyl 2-carbethoxy-4,4-dinitrobutyrate (II)** (10.09 g., 36.3% yield), b.p. 126–130° (1.1 mm.). Redistillation gave analytically pure material: b.p. 122.5–123.5° (0.5 mm.), $n^{20}\mathrm{D}$ 1.4498, d^{20}_{20} 1.280; *MR*D calcd. 58.31, *MR*D found 58.38.

Anal. Calcd. for $C_9H_{14}N_2O_8$: C, 38.81; H, 5.07; N, 10.07. Found: C, 38.80; H, 5.04; N, 10.01.

A sample of the crude salts from another experiment (1.10 g.) was washed with water (1.0 ml.) to remove impurities such as potassium nitrite and potassium diethyl malonate. **Potassium ethyl 2-carbethoxy-4,4-dinitrobutyrate (I)** (0.45 g.) was isolated upon filtering the red solution. The salt was dissolved in water, treated with an excess of saturated silver nitrate solution and cooled. The yellow silver salt that formed was filtered. After recrystallization from hot water, **silver ethyl 2-carbethoxy-4,4-dinitrobutyrate** (0.23 g.) was obtained.

Anal. Calcd. for $C_9H_{13}N_2O_8Ag$: C, 28.07; H, 3.40; N, 7.27; Ag, 28.01. Found: C, 27.57; H, 3.29; N, 7.65; Ag, 28.04.[25]

Proof of Structure of Ethyl 2-Carbethoxy-4,4-dinitrobutyrate (II).—A mixture of II (1.39 g., 0.005 mole) and water (14 ml.) was stirred at 0–5° while potassium hydroxide (11.5 ml., 0.0434 *N*, 0.00499 mole) and then methyl acrylate (1.30 g., 0.015 mole) were added. The solution was stirred at 0–5° for 2 hr., then at 25° for 18 hr. The color changed slowly from light yellow to deep amber, and a dense oil settled. The mixture was extracted with ether; the solvent was distilled from the extract. Concentrated hydrochloric acid (30 ml.) was added to the residue (methyl ethyl 2-carbethoxy-4,4-dinitroheptanedioate), and the mixture was heated to 135–140°. After 4 hr., the oil completely dissolved. The red mixture was heated for another hour; charcoal was added and the mixture then filtered. On evaporation of most of the filtrate, crude **4,4-dinitroheptanedioic acid** (0.375 g., 30% yield), m.p. 135–137.5°, crystallized. After recrystallization from hot water, the acid melted at 138.5–140°; neut. equiv. calcd. 125, neut. equiv. found 127. An authentic sample[8] melted at 138.5–139.5°; admixture of the two samples resulted in no depression of the melting point.

1,1,1-Trinitroethane and Potassium 2-Nitropropane.—A solution of potassium ethoxide (0.20 mole) in anhydrous ethanol (250 ml.) was cooled and stirred while 2-nitropropane (17.8 g., 0.20 mole) was added slowly. 1,1,1-Trinitroethane (7.6 g., 0.0455 mole) in anhydrous ethanol (50 ml.) was then poured into the cold solution of potassium 2-nitropropane. Heat was evolved, and the solution turned deepred in color. After several minutes, an orange precipitate formed. The reaction mixture was stirred at 0° for 2 hr. The product was then filtered, washed with ethanol–ether and air-dried; yield 15.0 g.

The filtrate was evaporated under vacuum. A white, water-insoluble solid (2.95 g.) and a yellow, water-soluble salt (19.95 g.) were obtained. The water-soluble salt was identified as potassium 2-nitropropane by acidifying it in the presence of potassium nitrite at −5°; greenish-white 2-nitro-2-nitrosopropane (5.45 g., 42.4% yield based on excess potassium 2-nitropropane), m.p. 74–76° (blue melt; dec.), was obtained; lit.[26] m.p. 76° (dec. to blue liquid). The water-insoluble compound was **2,3-dimethyl-2,3-dinitrobutane**, m.p. (after recrystallization from methanol) 210–212° dec. An authentic sample[27] melted at 209–211° dec. No depression of the melting point was observed when the two samples were mixed. The infrared spectra of the two samples were identical.

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

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

[22] (a) Potassium trinitromethane was prepared from tetranitromethane, aqueous hydrogen peroxide and potassium hydroxide. Acidification of potassium trinitromethane in petroleum ether with anhydrous hydrogen chloride yielded trinitromethane; K. Schimmelschmidt, Hunter Report BIOS 1919; 22/1G, July 3 (1946). (b) Silver trinitromethane was obtained by stirring trinitromethane with moist silver oxide in ether: W. S. Reich, G. G. Rose and W. Wilson, *J. Chem. Soc.*, 1234 (1947). (c) 1,1,1-Trinitroethane was prepared by adding methyl iodide to an ether solution of silver trinitromethane.[4a]

[23] E. ter Meer[5a] prepared 1-bromo-1,1-dinitroethane by titrating an aqueous solution of potassium 1,1-dinitroethane with bromine water. No physical constants were reported for 1-bromo-1,1-dinitroethane.

[24] N. Kornblum and G. E. Graham, THIS JOURNAL, **73**, 4041 (1951).

[25] For analysis of silver salts of 1,1-dinitroalkanes, the following procedure was used: 0.2–0.5 meq. of silver salt was suspended in water and 2 ml. of a saturated ferric ammonium sulfate solution in 5 *N* nitric acid was added. The acidic suspension was then titrated to a persistent pink end-point with ammonium thiocyanate. It was observed that variable titration results are obtained if the proportions of indicator and acid are varied.

[26] V. Meyer, *Ann.*, **175**, 123 (1875).

[27] H. Shechter and R. Kaplan, THIS JOURNAL, **75**, 3980 (1953).

Additional 2,3-dimethyl-2,3-dinitrobutane (0.57 g.) was obtained by extracting 2.13 g. of the orange precipitate with ether. The residue was recrystallized from hot water, and yellow **potassium 1,1-dinitroethane** (0.69 g.), m.p. 153° dec., was obtained. Potassium 1,1-dinitroethane was converted to its silver salt by reaction with aqueous silver nitrate.[25]

Anal. Calcd. for $C_2H_3N_2O_4Ag$: Ag, 47.5. Found: Ag, 47.4.

The yield of 2,3-dimethyl-2,3-dinitrobutane, based on 1,1,1-trinitroethane, was 87%; the yield of isolated potassium 1,1-dinitroethane was 68%.

1,1,1-Trinitroethane and Potassium 2,4-Pentanedione.—Potassium 2,4-pentanedione was prepared by adding 2,4-pentanedione (30.0 g., 0.30 mole) to a refluxing solution of potassium ethoxide (0.30 mole) in anhydrous ethanol (160 ml.). A solution of 1,1,1-trinitroethane (16.5 g., 0.10 mole) in anhydrous ethanol (50 ml.) was immediately added to the stirred mixture. A deep red color developed, and after several minutes a yellow solid began to precipitate. Refluxing was continued for 30 minutes; the mixture was then cooled and stirred at 0° for 14 hr. The salts were filtered, washed with ethanol and dried in a vacuum; yield 23.2 g. The product was washed with a mixture of methanol (36 ml.) and water (19 ml.) to dissolve potassium nitrite and excess potassium 2,4-pentanedione. The remaining salt was filtered, washed with methanol and methanol–ether and air-dried. This salt was **potassium 1,1-dinitroethane** (10.17 g., 64.4% yield), identified by conversion to its silver salt and analysis; Ag calcd. 47.5, Ag found 47.6.

The filtrate from the methanol–water wash was diluted with a 1:1 methanol–ether solution (*ca.* 200 ml.). The white salt that precipitated was filtered, washed with ether and then dried. The salt (7.38 g.) darkened on exposure to air, was soluble in water and evolved oxides of nitrogen on treatment with sulfuric acid. The salt was identified as impure **potassium nitrite**; analysis for nitrite ion[28] indicated that the salt was 61.4% pure. The yield of potassium nitrite was 53.2%.

The initial filtrate was evaporated to dryness. A reddish-brown tar remained (29 g., including traces of solvent; the theoretical yield for polymers[10] derived from 2,4-pentanedione was 30 g.). This product was soluble in water, ethanol and acetone, very slightly soluble in ether and insoluble in benzene. No identifiable reaction product could be recovered from this material.

1,1,1-Trinitroethane and Potassium 1-Butanethioxide.—1-Butanethiol (9.02 g., 0.10 mole) was added slowly to a hot solution of potassium ethoxide (0.10 mole) in anhydrous ethanol (100 ml.); the potassium 1-butanethioxide formed was practically all soluble at 80–85°. While the solution was at 80–85°, 1,1,1-trinitroethane (8.25 g., 0.05 mole) in anhydrous ethanol (30 ml.) was added dropwise (30 min.). A yellow salt precipitated; the supernatant liquid was light red in color. The reaction mixture was cooled to 25° and then stirred for 14 hr. Anhydrous ethyl ether (400 ml.) was added to the mixture to precipitate the alcohol-soluble salts. The suspension was cooled in a salt–ice-bath, then filtered; the filtrate was saved. A yield of 10.6 g. (88% crude yield based on potassium nitrite and potassium 1,1-dinitroethane) of salts was obtained. The product became somewhat gummy on exposure to the atmosphere.

The salts were washed with a solution of methanol (11 ml.) and water (6 ml.) to dissolve the potassium nitrite. The remaining salt was filtered, washed with methanol and ether, dried and identified as **potassium 1,1-dinitroethane** (3.34 g., 42.3% yield). The salt was converted to silver 1,1-dinitroethane by reaction with excess saturated silver nitrate solution; Ag calcd. 47.5, Ag found 47.6.

The initial filtrate was evaporated at reduced pressure. The residue (*ca.* 15 ml.) was extracted with ethyl ether and water. The ether extract was washed with saturated sodium chloride solution. After removing the solvent, the residue was vacuum distilled to yield **di-*n*-butyl disulfide** (6.37 g., 71.4% yield), b.p. 88.5–89° (5.5 mm.), $n^{20}D$ 1.4920, $d^{20}{}_{20}$ 0.9464; lit.[29] b.p. 88° (4 mm.), 90° (4.5 mm.); $n^{20}D$ 1.49208, 1.4926, $d^{20}{}_{20}$ 0.944. The tarry distillation residue (1.61 g.) contained nitrogen and sulfur; distillation of this material under high vacuum yielded traces of di-*n*-butyl disulfide.

1,1,1-Trinitroethane and *n*-Butyllithium.—A solution of 1,1,1-trinitroethane (8.3 g., 0.05 mole) in anhydrous ether (60 ml.) was added in 2 hr. to a stirred solution of *n*-butyllithium[30] (0.115 mole) in ethyl ether (100 ml.) under nitrogen. Reaction occurred immediately; the solution turned red and a precipitate formed. After the mixture had been stored for 8 hr., water (50 ml.) was added to dissolve the precipitate. The mixture was acidified with urea and acetic acid.[24] The ether layer was separated; the solvent was distilled and the residue converted to **potassium 1,1-dinitroethane** (3.78 g., 48% yield) by reaction with cold, methanolic potassium hydroxide (0.139 mole, 100 ml.). The salt was identified by its ultraviolet spectrum (λ_{max} 381 mμ, ϵ_{max} 16,350) and upon preparing silver 1,1-dinitroethane; Ag calcd. 47.5, Ag found 46.8.

1,1,1-Trinitroethane and Guanidine.—Guanidinium carbonate (12.60 g., 0.07 mole, 0.14 equiv.) was added to a stirred solution of sodium ethoxide (0.12 mole) in absolute ethanol (70 ml.). The suspension was cooled to 0–5° and stirred for 30 minutes. The sodium carbonate and excess guanidinium carbonate were filtered and washed with absolute ethanol (*ca.* 50 ml.) and then with ethanol–ether; the washings were combined with the filtrate.

The guanidine solution was stirred and cooled to 0–5°, and 1,1,1-trinitroethane (8.25 g., 0.05 mole) in absolute ethanol (40 ml.) was added dropwise (90 min.). The solution turned red and heat was evolved. The mixture was stirred at 25–30° for 10 hr. The suspension was cooled to 0° and filtered to isolate the orange product (9.16 g.) that precipitated. The product was refluxed in 95% ethanol (35 ml.), cooled to 0–5°, filtered, washed with absolute ethanol and ether and dried. The filtrates and washings were combined and saved. Powdery, orange **2-guanidino-1,1-dinitroethane (VI)** was isolated in 84.8% crude yield (7.50 g.); ultraviolet analysis of the product showed it to be 88.3%[31] pure. The impurity present is presumed to be guanidinium carbonate. Pure VI was crystallized as lustrous golden plates from hot water; it darkened at 196–199°, but no definite decomposition temperature or melting point could be determined.[32] The X-ray diffraction pattern of the compound is[33]: 6.20(s), 4.97(m), 3.86(s), 3.74(s), 3.42(s), 3.05(vs), 2.69, 2.58, 2.47 and 2.10 (no back reflection).

Anal. Calcd. for $C_3H_7N_5O_4$: C, 20.34; H, 3.98; N, 39.54. Found: C, 20.66; H, 3.93; N, 39.53.

On standing, the combined filtrates and washings deposited a red, crystalline product. The material was filtered (0.22 g.); on the basis of its ultraviolet spectrum, it contained 30.8% VI. The filtrate was evaporated to dryness at reduced pressure. A gummy, red solid remained which, after drying, weighed 7.06 g. Ultraviolet analysis of a 1×10^{-4} *M* solution of this product (in 10^{-3} *M* NaOH) indicates that VI is present to the extent of 8.2–9.7%. The major component of this product was **guanidinium nitrite**. It was identified in the following manner: (1) A

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[28] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1947, p. 603.

[29] S. F. Birch and W. S. Norris, *Ind. Eng. Chem.*, **21**, 1087 (1929); R. E. Stutz and R. L. Shriner, THIS JOURNAL, **55**, 1242 (1933); S. Bezzi, *Gazz. chim. ital.*, **65**, 693 (1935).

[30] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949), as modified by J. G. Traynham, private communication.

[31] A pure sample of VI, made up to concentrations of 1.00×10^{-6}, 5.00×10^{-6} and 1.00×10^{-5} *M* in 10-fold excess sodium hydroxide was used as the ultraviolet standard (Fig. 1); the average value found for the molecular extinction coefficient at 364–5 mμ was 16230 (±50). Over the range of concentrations studied, the compound obeyed Beer's law. Guanidinium carbonate and nitrate show no absorption in the 300–400 mμ region.

[32] The melting points (dec.) of VI, VII and VIII are affected markedly by the rates of heating. The X-ray diffraction patterns have been determined because they are of greater reliability than are melting points.

[33] The authors are indebted to Dr. M. Hoch and the Cryogenic Laboratory of The Ohio State University for assistance in obtaining the X-ray data. Chromium K_α radiation, $\lambda = 2.2850$ Å. at 32 kilovolts and 9–10 milliamp. for 19–20 hr. was used. The first figure is interplanar spacing (d) in Å. (calcd. from $\lambda = 2d \sin \theta$). The letter in parentheses indicates the relative intensity of medium (m), strong (s) and very strong (vs) lines.

sample weighing 0.5026 g. was dissolved in ethanol–water (10.3 ml.) and added to a solution of picric acid (2.2 g.) in absolute ethanol (*ca.* 40 ml.). The orange-yellow picrate was filtered, washed with ethanol and ether and dried to give guanidinium picrate (1.01 g.), m.p. 317° dec.; an authentic sample, lit.[34] m.p. 333°, melted at 319–320° dec. On the basis of the yield of guanidinium picrate, the original salt crop contained 5.23 g. of guanidinium nitrite (5.30 g. = theoretical yield). (2) On treating the salts with hydrochloric acid, nitrogen oxides were evolved; the salts also liberated iodine from a solution of potassium iodide and acetic acid. A solution of the product (1.006 g.) in distilled water (*ca.* 40 ml., *p*H of solution 9.6) was neutralized with dilute nitric acid (to *p*H 6.9), and concentrated silver nitrate (3.995 g. in *ca.* 6 ml. of water) was added. The gray-brown salt obtained weighed 1.15 g. (theoretical yield of silver nitrite 1.54 g.). A portion of this product (1.05 g.) was dissolved in water (80 ml.) at 60–70°, filtered and cooled to 0°. Silver nitrite (0.95 g.) crystallized; it gave a positive test for nitrite ion (iodide to iodine in acetic acid solution).

The results of the present experiment are summarized: the total yield of VI is 85%; the total yield of guanidinium nitrite, based on silver nitrite isolated, is 82.3%.

Properties of 2-Guanidino-1,1-dinitroethane (VI).—Pure VI is very slightly soluble in cold water (pale-yellow solution) and only slightly soluble in boiling water (approximately 1 part in 103 parts of water at 100°); it is insoluble in hot or cold acetone, acetonitrile, methanol, or piperidine. The *p*H of a cold aqueous solution is 5.4–5.5. The compound is soluble in acids (colorless solution) and in dilute bases (yellow solution). These properties are strongly indicative of an inner-salt structure. Additional evidence for the dipolar ion structure was adduced from spectral studies. The ultraviolet spectrum of VI in water or dilute bases is similar in intensity to that of the 1,1-dinitroethyl anion (Fig. 1); absorption maxima attributable to the *gem*-dinitro anion[35] at 364 mμ (ϵ_{max} 16,300) and at 225 mμ (ϵ_{max} 7460) were observed. The infrared spectrum[35] was determined in Nujol; two bands were observed at 5.98 and 6.08 μ. This absorption can be attributed to the C═N structure[36] and indicates the presence of the imino group or/and the nitronate ion. The absence of the sharp peak at 6.3 μ that is characteristic of *gem*-dinitroalkanes[35] serves as further evidence that VI exists as its dipolar ion.

Guanidinium 1,1-Dinitroethane.—1,1-Dinitroethane (2.4 g., 0.02 mole) was added to a stirred suspension of guanidinium carbonate (2.1 g., 0.012 mole) in methanol (20 ml.). Carbon dioxide was evolved. The yellow salt that precipitated was recrystallized from hot methanol to give **guanidinium 1,1-dinitroethane** (2.84 g., 79% yield), m.p. 97° dec. The product is soluble in water (5% by wt. at 20°) and hot alcohol, slightly soluble in cold alcohol. The ultraviolet spectrum of the compound exhibited maximum absorption at 381–382 mμ. The properties of guanidinium 1,1-dinitroethane are markedly different from those of VI.

Anal. Calcd. for $C_3H_9N_5O_4$: N, 39.10. Found: N, 38.86.

1,1,1-Trinitroethane and Piperidine.—A solution of 1,1,1-trinitroethane (16.50 g., 0.10 mole) in absolute ether (60 ml.) was added slowly (30 min.) to a stirred solution of piperidine (17.85 g., 0.21 mole) and absolute ether (50 ml.) cooled in an ice–water mixture. Sufficient heat was evolved to cause refluxing of the reaction mixture. A yellow-orange oil separated which crystallized on continued stirring. After 2 hr., the yellow salts were filtered, washed with ether and air-dried; crude yield 30.9 g. (92%). The mixture of salts was triturated with water (30 ml.) and filtered. The pale yellow salt that remained was washed with small portions of water, methanol and ether, crushed and dried. The yield was 12.80 g. The reaction mixture, on standing for several days, deposited additional product (0.54 g., after washing to remove the nitrite salt). The total yield of **1,1-dinitro-2-piperidinoethane (VII)** was 13.34 g. (65.6%), m.p. 104.5–105° dec.

1,1-Dinitro-2-piperidinoethane is practically insoluble in cold water, soluble in hot water, slightly soluble in methanol and insoluble in ether; it is readily soluble in aqueous acids and bases. The product recrystallizes from hot water as pale-yellow needles, m.p. 108.0–108.5° dec.[32] The solubility characteristics, color and ultraviolet spectrum of VII suggest that it exists primarily as the dipolar ion. The spectrum, in tenfold excess base (Fig. 1), shows absorption maxima characteristic of the *gem*-dinitro anion at 369 mμ (ϵ_{max} 13,900) and at 225 mμ (ϵ_{max} 6,800). In distilled water, the band at 369 mμ is shifted to 357 mμ, and the intensity is somewhat diminished (ϵ_{max} 11,200).[35] The X-ray diffraction pattern of this salt is: 11.35, 9.72, 7.90(s), 6.14, 5.96, 5.52(m), 4.84(s), 4.65(m), 4.46(s), 4.12, 3.94(vs), 3.67, 3.61, 3.44, 3.23(m), 3.16, 3.00, 2.95, 2.89, 2.63(m), 2.52, 2.42, 2.36, 2.29, 2.04; back reflection, 2.63.[31,32]

Anal. Calcd. for $C_7H_{13}N_3O_4$: C, 41.37; H, 6.45; N, 20.68. Found: C, 41.38; H, 6.44; N, 20.49.

Piperidinium nitrite, produced in the reaction of 1,1,1-trinitroethane with piperidine, was identified in the following manner: (1) The aqueous filtrate (from the trituration step) was acidified immediately with excess 4 *N* hydrochloric acid (approx. 0.2 mole). Oxides of nitrogen were evolved from the solution. The aqueous piperidinium chloride was covered with ether and treated with excess sodium hydroxide. Skellysolve B was added to the ether extract and the ether removed by distillation. On treating the remaining solution with excess phenyl isothiocyanate (*ca.* 15 g.), N-phenyl-N′-piperidinothiourea (22.2 g., quant. yield), m.p. 99.0–99.5°, lit.[37] m.p. 99°, was obtained. Admixture with an authentic sample resulted in no depression of the melting point. (2) A portion of the aqueous filtrate (from the trituration step of another experiment) was allowed to stand for several days. An oil separated. On treating the mixture with 6 *N* hydrochloric acid, oxides of nitrogen were evolved. The mixture was extracted with ether; the extract was evaporated. The residue (b.p. 210–215°) was distilled to yield N-nitrosopiperidine, b.p. 75–85° (13 mm.), $n^{20}{}_D$ 1.4927, $d^{20}{}_{20}$ 1.103, MR_D calcd. 31.08, MR_D found 30.59; lit.[38] b.p. 215–218° (760 mm.), 102° (13 mm.); $n^{18.5}{}_D$ 1.4933, $d^{18.5}{}_4$ 1.0631. The product gave a positive Liebermann (nitrosamine) test.

Proof of Structure of 1,1-Dinitro-2-piperidinoethane (VII).—It has been reported[15] that VII can be synthesized from N-methylolpiperidine and dinitromethane; no experimental procedures nor melting point were reported for the product. This alternate synthesis was effected to verify the structure of VII: Potassium dinitromethane (1.44 g., 0.01 mole) was suspended in water (7 ml.) and ether (40 ml.). The mixture was stirred at 0° while 0.50 *N* sulfuric acid (25 ml., 0.0125 equiv.) was added dropwise.[39] The pale-yellow ether layer was separated and immediately added[39] to an aqueous suspension of N-methylolpiperidine (prepared by adding 36% formaldehyde (2.0 g., 0.02 mole) to piperidine (1.2 g., 0.14 mole) in water (3 ml.) at 0°). The mixture was stirred at 0°. The pale yellow compound which formed was filtered, washed with ethanol and ether and air-dried. The yield of VII was 1.90 g. (94%), m.p. 107.5° dec., after recrystallization from hot water. This sample, when mixed with the product of reaction of 1,1,1-trinitroethane and piperidine, melted at 107.5° dec.; the X-ray diffraction patterns of the two products were identical.

Alkali metal salts of VII are very soluble in water and methanol. The silver salt was best prepared[40] by the following method: VII (0.58 g., 2.86 meq.) was suspended in water (2 ml.) and titrated with 2.70 *N* sodium hydroxide (1.00 ml., 2.70 meq.). The clear yellow solution was cooled to 0° and concentrated silver nitrate (1.16 g., 6.8 meq., in 1.5 ml. of water) was added. **Silver 1,1-dinitro-2-piperidinoethane** precipitated as a bright yellow salt. The prod-

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(34) H. Lidholm, *Ber.*, **46**, 160 (1913).

(35) A fuller interpretation of the ultraviolet spectra of these and other 1,1-dinitroalkane anions and of the infrared spectra of 1,1-dinitroalkanes will be the subject of a future communication from this Laboratory.

(36) N. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 5.

(37) O. Hecht, *Ber.*, **23**, 288 (1890).

(38) C. Schotten, *ibid.*, **15**, 425 (1882); A. Ladenburg and C. F. Roth, *ibid.*, **17**, 513 (1884); J. W. Bruhl, *Z. physik. Chem.*, **16**, 193 (1895).

(39) The free acid, dinitromethane, decomposes rapidly; see P. Duden, *Ber.*, **26**, 3003 (1893).

(40) Care must be taken to avoid an excess of alkali when preparing the silver salt. When excess base is present, the silver salt obtained is green (presence of silver oxide) and gives a high analytical value for silver.

uct was filtered, washed with water, methanol and ether and dried at room temperature and 1 mm. pressure; yield 0.84 g. (100%).

Anal. Calcd. for $C_7H_{12}N_3O_4Ag$: C, 27.11; H, 3.90; N, 13.55; Ag, 34.79. Found: C, 27.11; H, 3.78; N, 13.45; Ag, 35.20.

1,1,1-Trinitroethane and Triethylamine.—1,1,1-Trinitroethane (8.3 g., 0.05 mole), triethylamine (10.1 g., 0.10 mole) and benzene (120 ml.) were stirred at 27°. A mild exothermic reaction occurred; after 1.5 hr., the solution temperature was 37°. The solution was then refluxed for 24 hr. During this time, some oxides of nitrogen were evolved. After the reaction mixture had cooled, two layers formed. Distillation of the upper, deep-red layer at reduced pressure gave N-nitrosodiethylamine (4.25 g., 83.3% yield based on 1,1,1-trinitroethane), b.p. 55–60° (11–14 mm.), $n^{20}D$ 1.4369–1.4380, $d^{20}{}_{20}$ 0.961; lit.[41] b.p. 61–63° (12 mm.), $n^{19.9}D$ 1.43864, $d^{19.9}{}_4$ 0.943. The product gave a positive Liebermann test. The lower, reddish-black layer (4.52 g.) was dissolved in water, covered with ether and acidified with 3 *N* hydrochloric acid. The ether was removed and the residual amber solution slowly added to 10% methanolic potassium hydroxide in an attempt to isolate potassium 1,1-dinitroethane. The basic solution turned red in color, but no precipitate formed. All efforts to crystallize or purify adequately the adduct from triethylamine and 1,1-dinitroethene were unsuccessful.

1,1,1-Trinitroethane and Trimethylamine.—Trimethylamine (45.7 g., 0.78 mole), 1,1,1-trinitroethane (31.0 g., 0.20 mole), absolute ethanol (60 ml.) and anhydrous ether (60 ml.) were mixed at −80° and stored for 4 days, with occasional shaking, at −13°. The yellow precipitate that formed was filtered and washed repeatedly with ethanol-ether and then with ether and dried. The yield of pale yellow **trimethylammonium N-(2-nitroethyl-2-nitronate)** (VIII) was 29.4 g., 83%. An additional 2.5 g. of VIII (total yield 31.9 g., 90%) was obtained after storing the filtrate with additional trimethylamine (13.3 g.) at −18° for 4 more days. The product was recrystallized[42] by dissolving 1.00 g. in 10 ml. of water at 60°, filtering and cooling. The bright yellow, flat needles that precipitated weighed 0.68 g. and melted at 92–92.5° dec. The adduct VIII is soluble in water (approx. 3% at 20°), slightly soluble in ethanol and insoluble in ether. Its ultraviolet spectrum (Fig. 1) contained absorption maxima at 352 mμ (ϵ_{max} 14,900) and at 228 mμ (ϵ_{max} 8,600).[35]

Anal. Calcd. for $C_5H_{11}N_3O_4$: C, 33.90; H, 6.24; N, 23.72. Found: C, 33.76; H, 6.05; N, 23.90.

The product was converted to its **silver nitrate derivative** by adding a solution of silver nitrate (2.04 g., 0.012 mole) in water (2 ml.) to a saturated aqueous solution of VIII (1.06 g., 0.006 mole in 12 ml. of water) at 25°. The silver nitrate derivative precipitated as bright yellow needles. The salt was filtered, washed with water, dilute alcohol, absolute alcohol and ether and air-dried. The yield was 1.65 g. (79.3%). The salt is quite soluble in water and is difficult to recrystallize from this solvent. A satisfactory recrystallization procedure is to dissolve the silver salt in a minimum amount of cold water, filter, then reprecipitate by adding absolute alcohol. The melting point of the recrystallized salt is 107° dec.

Anal. Calcd. for $C_5H_{11}N_4O_7Ag$: C, 17.3; H, 3.19; N, 16.1; Ag, 31.1. Found: C, 17.6; H, 3.54; N, 15.4; Ag, 31.0.

Exchange Reaction of Trimethylammonium N-(2-Nitroethyl-2-nitronate) (VIII) and Guanidine.—Guanidinium carbonate (1.10 g., 0.006 mole) in water (10 ml.) was neutralized with aqueous sodium hydroxide (0.012 mole); VIII (1.77 g., 0.01 mole) in water (15 ml.) was then added. The clear yellow solution was stirred at 40–45° for 5 hr. and then heated to 80° for 3 hr. On cooling the mixture, a yellow solid precipitated. The product was filtered, washed with ethanol and ethyl ether and dried to give **2-guanidino-1,1-dinitroethane (VI)** (0.24 g., darkens at 185–192°). Evaporation of the filtrate to one-half of its original volume gave 0.26 g. of additional product; total yield 0.50 g. (28%). The X-ray diffraction pattern of the 2-guanidino-1,1-dinitroethane is identical with that of the product obtained from guanidine and 1,1,1-trinitroethane.

Exchange Reaction of Trimethylammonium N-(2-Nitroethyl-2-nitronate) (VIII) and Piperidine.—Piperidine (0.85 g., 0.01 mole) was added to a stirred mixture of VIII (0.885 g., 0.005 mole) in water (13 ml.) at 50–60°. The solution was stirred at 50–60° for 5 hr., then evaporated at reduced pressure. The yellow solid that remained was suspended in absolute ethanol, crushed and filtered. The yield of **1,1-dinitro-2-piperidinoethane (VII)** was 0.970 g. (95.6%), m.p. 110.5–111°. Admixture of this material with VII previously prepared resulted in no depression of the melting point; X-ray diffraction patterns of the samples were identical.

1-Bromo-1,1-dinitroethane and Piperidine.—Piperidine (17.0 g., 0.20 mole) was dissolved in ethyl ether (60 ml.) and cooled in an ice–water mixture. 1-Bromo-1,1-dinitroethane (19.9 g., 0.10 mole) in ether (70 ml.) was added dropwise (40 min.) to the stirred piperidine solution. The mixture immediately turned yellow, and a yellow, crystalline solid soon precipitated. The precipitate was filtered, washed with anhydrous ethyl ether and air-dried. Essentially pure **piperidinium 1,1-dinitroethane** (13.2 g., 64.3% yield) was obtained, m.p. 111–113°. Two recrystallizations (from ethanol) raised the melting point to 113–114°; authentic piperidinium 1,1-dinitroethane melts at 114.5–115°; mixed m.p. 113.5–114.5°. The ultraviolet spectra of the authentic salt (Fig. 1) and that obtained from 1-bromo-1,1-dinitroethane and piperidine were identical and exhibited an absorption maximum at 381–382 mμ (ϵ_{max} 16,300); the spectra of these samples differ considerably from that of VII.

The combined filtrates and washings on storage yielded a second crystalline product containing an ether-insoluble red oil. The product was diluted with absolute ethanol, evaporated to remove ether and then cooled to 0–5° for several days. The crystals obtained were filtered, washed with ethanol–ether and ether and dried. The product was identified as **piperidinium bromide** (8.3 g., 50% yield), white needles, m.p. 240.5–241.5°. Evaporation of the filtrate nearly to dryness followed by addition of ether, then ethanol (until the red oil all dissolved), resulted in isolation of additional piperidinium bromide (2.4 g.), m.p. 240–242°. An authentic sample was prepared from piperidine and hydrogen bromide; m.p. 238.5–239.5°, lit.[43] m.p. 235°. The mixed melting point of the product was not depressed.

The filtrate, upon evaporation at reduced pressure, left a red oily residue containing crystals and weighing 10.3 g. The residue was washed repeatedly with water to remove the piperidinium bromide; the residue (8.3 g., a polymer presumably composed of piperidine units, XI) could not be readily identified. The aqueous extract was evaporated at reduced pressure; on addition of ethanol to the residue, piperidinium bromide (0.43 g.), m.p. 226–233°, precipitated. On treating the filtrate with excess silver nitrate, silver bromide (1.48 g., equivalent to 1.31 g. of piperidinium bromide) was formed. The total yield of piperidinium bromide was thus 75%.

Piperidinium 1,1-Dinitroethane.—Piperidine (1.10 g., 0.0128 mole) was added to 1,1-dinitroethane (1.54 g., 0.0128 mole) in methanol at 25°. Heat was evolved and the solution turned yellow. Ether was added to precipitate the **piperidinium 1,1-dinitroethane**, bright yellow crystals (2.35 g., 89%), m.p. 114.5–115.5° dec.; very soluble in water, slightly soluble in cold ethanol, soluble in warm ethanol (the solubility characteristics of piperidinium 1,1-dinitroethane are quite different from those of 1,1-dinitro-2-piperidinoethane (VII)).

1-Chloro-1,1-dinitroethane and Piperidine.—1-Chloro-1,1-dinitroethane (15.5 g., 0.10 mole) was added rapidly to piperidine (17.0 g., 0.20 mole) in anhydrous ether (100 ml.) at 25°. After 1 hr., yellow needles began to precipitate; after 2 days, an oil began separating. The oily precipitate was filtered and washed with ether containing a small amount of ethanol (to dissolve the oil); the filtrate and washings (I) were combined and saved. The golden-yellow precipitate, after being dried, weighed 7.3 g.

The yellow precipitate was analyzed by ultraviolet methods and found to contain 4.27 g. of **piperidinium 1,1-dinitroethane**. The mixture of precipitated salts was then

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[41] E. Schmidt and R. Schumacher, *Ber.*, **54**, 1414 (1921); A. Guether, *Ann.*, **128**, 151 (1863); J. W. Bruhl, *Z. physik. Chem.*, **16**, 193 (1895).

[42] The product should be recrystallized immediately after isolation to minimize the danger of (rapid) decomposition caused by impurities.

[43] C. A. Bischoff, *Ber.*, **31**, 2841 (1898).

analyzed for piperidinium chloride in the following manner: A 5.00-g. aliquot of the salts was treated with excess silver nitrate. The mixture of silver salts formed was acidified with nitric acid in ethanol to dissolve the coprecipitated silver 1,1-dinitroethane. The silver chloride left, upon being filtered and dried, weighed 1.14 g. The silver chloride isolated is equivalent to 1.40 g. of piperidinium chloride in the original precipitate of salts.

Filtrate I was concentrated at reduced pressure; a residue remained which contained crystals and weighed 21.2 g. The residue was extracted with a mixture of water and ether; the aqueous extract, upon ultraviolet analysis of an aliquot portion, was found to contain 5.01 g. of piperidinium 1,1-dinitroethane. The aqueous extract (an aliquot) upon treatment with silver nitrate (as described previously) yielded silver chloride equivalent to 0.81 g. of piperidinium chloride. The ether extract of the residue, after removal of the solvent, was vacuum-distilled to yield 1-chloro-1,1-dinitroethane (1.0 g.), b.p. 58–61° (22 mm.). The distillates: fractions 2 (1.92 g., b.p. 72–85° (3 mm.), n^{20}D 1.4840) and 3 (2.98 g., b.p. 85–88° (3 mm.), n^{20}D 1.4891) and a residue (3.0 g.) were not identified further.

The yield of products of reaction of 1-chloro-1,1-dinitroethane and piperidine were: piperidinium 1,1-dinitroethane (9.28 g., 48.3%), piperidinium chloride (2.21 g., 21.2%) and 1-chloro-1,1-dinitroethane (1.0 g., 6.5% recovery); the material balance was 62.8%.

1-Bromo-1,1-dinitroethane and Sodium Diethyl Malonate.—(a) 1-Bromo-1,1-dinitroethane (19.9 g., 0.10 mole) was added dropwise in 1 hr. to a stirred solution of sodium diethyl malonate (36.6 g., 0.20 mole) in absolute ethanol (220 ml.) at 5–10°. A yellow precipitate formed almost immediately after addition. The mixture was stirred at 25° for 20 hr. and then poured into anhydrous ether (400 ml.). The salts (21.3 g., ppt. 1) that precipitated were filtered, washed with ether and dried. The filtrate was evaporated nearly to dryness. Upon addition of anhydrous ether (300 ml.) a second solid (3.7 g., ppt. 2) separated. The filtrate was evaporated to one-fifth its volume and diluted with Skellysolve F. A pale-yellow solid (ppt. 3) precipitated, was filtered, washed with 1:5 ether–Skellysolve F and dried. Precipitate 3 was identified as **tetraethyl ethane-1,1,2,2-tetracarboxylate** (19.8 g., 62.3% yield), m.p. 74.5–76° (recrystallized from absolute ethanol). An authentic sample of tetraethylethane-1,1,2,2-tetracarboxylate[44] melted at 74.5–75.5°; the melting point was not depressed when the two samples were mixed.

The filtrate (from ppt. 3) was freed of solvents under vacuum to leave a residue weighing 10.8 g. An aliquot of this residue was diluted to a concentration of 0.0158 g./l. in 10^{-3} *M* aqueous sodium hydroxide; ultraviolet analysis of this solution showed that the residue contained 1.88 g. (15.7% yield) of **1,1-dinitroethane.** A 5.00-g. aliquot of the residue was vacuum distilled; the distillate, b.p. 59–68° (5 mm.), weighed 1.75 g. and was identified as a mixture of diethyl malonate and 1,1-dinitroethane (infrared spectrum). The distillation residue, on treatment with absolute ethanol (2 ml.) and Skellysolve F (5 ml.) gave **tetraethyl ethylenetetracarboxylate**[44] (1.06 g., 3.4% yield), m.p. 46–48°. The non-crystallizable part of the distillation residue weighed 2.04 g., n^{20}D 1.4402; the infrared spectrum of this material showed the presence of an ester group.

Aqueous silver nitrate (17 g. in 50 ml. of water) was added to a 10.00-g. aliquot of ppt. 1 in water (130 ml.). The silver salts (13.8 g.) that were obtained were filtered and washed with water. The salts were suspended in 50% aqueous ethanol (100 ml.), and 5 *N* nitric acid (50 ml.) was added to dissolve the coprecipitated silver 1,1-dinitroethane. The remaining silver bromide was filtered, washed with water, ethanol and ether and dried; wt. 7.83 g. This corresponds to 9.14 g. of **sodium bromide** in ppt. 1. Analysis of a sample of ppt. 1 by ultraviolet methods showed that its sodium 1,1-dinitroethane content was 8.52 g. The mixed salts in ppt. 2 were analyzed in the same manner as described for ppt. 1. The weight of **sodium bromide** was 1.21 g.; the weight of **sodium 1,1-dinitroethane** was 1.15 g. Impure tetraethyl ethane-1,1,2,2-tetracarboxylate (0.15 g.) was also isolated, m.p. 67–68°.

The reaction of 1-bromo-1,1-dinitroethane and sodium diethyl malonate is summarized: the yield of sodium 1,1-dinitroethane was 68%, 1,1-dinitroethane (15.7%), tetraethyl ethane-1,1,2,2-tetracarboxylate (63%), tetraethyl ethylenetetracarboxylate (3.4%) and sodium bromide (100%).

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[44] A. Kotz and G. Stalmann, *J. prakt. Chem.*, [2] **68**, 156 (1903); C. A. Bischoff and C. Rach, *Ber.*, **17**, 2781 (1884).

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Thiazolidine Chemistry. III. The Preparation and Reduction of Some 2-Phenyl-3-*n*-alkyl-4-thiazolidinones[1-3]

BY IRVING R. SCHMOLKA AND PAUL E. SPOERRI[4]

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A series of 2-phenyl-3-*n*-alkyl-4-thiazolidinones was prepared and its properties studied. Upon treatment of these compounds with lithium aluminum hydride a reduction of the amide structure with rupture of the thiazolidine ring occurred. The structure of the cleavage product was proved by unequivocal syntheses.

As part of a program to study the effects of varying the heterocyclic ring of a series of quaternary salts, the preparation of N-alkyl-thiazolidines was undertaken. The synthesis of several 2,3-disubstituted-4-thiazolidinones had been reported previously.[5-7] In this paper we report on the synthesis of a series of thiazolidines in which the ring nitrogen was substituted with alkyl groups of increasing lengths. These are listed in Table I.

The products were colorless, ranging from a crystalline to a waxy appearance as the molecular weight increased and were unstable when exposed to sunlight.

The melting points of these compounds show a similar pattern when compared with the melting points of the amides of the aliphatic acid series.

The infrared curves for these compounds show the characteristic absorption bands for a disubstituted amide at 1680 cm.$^{-1}$ and for the thioether at 724 cm.$^{-1}$.

The use of lithium aluminum hydride, according to the reaction conditions of Uffer and Schlittler,[8]

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[1] Part II, *J. Org. Chem.* in press.

[2] Abstracted from the Ph.D. thesis of Irving R. Schmolka, Polytechnic Institute of Brooklyn, June, 1955.

[3] Presented before the Sixth Meeting-in-Miniature of the Metropolitan Long Island Subsection of the American Chemical Society, New York Section, Feb. 25, 1955.

[4] To whom inquiries should be sent.

[5] H. Erlenmeyer and V. Oberlin, *Helv. Chim. Acta*, **30**, 1329 (1947).

[6] H. D. Troutman and L. M. Long, THIS JOURNAL, **70**, 3436 (1948).

[7] A. R. Surrey, *ibid.*, **69**, 2911 (1947); **70**, 4262 (1948); **71**, 3150 (1949); **71**, 3354 (1949); **74**, 3450 (1952).

[8] A. Uffer and E. Schlittler, *Helv. Chim. Acta*, **31**, 1397 (1948).