

TABLE I
 REACTIONS OF SUBSTITUTED POLYNITRO ALKANES

Nitro compd	Reactant ^a (mol of reactants/0.01 mol nitro compounds)	Nitronate product	Yield, %
(O ₂ N) ₃ CCH ₂ Cl (1) ^b	KNO ₂ (0.1)	[(O ₂ N) ₂ CC(NO ₂) ₂] ²⁻ 2K ⁺ (2)	91
1	KNO ₂ (0.04), KOH (0.03)	2	31
1	KNO ₂ (0.03), KOH (0.002), KOAc (0.03)	2	ca. 100 ^c
1	KNO ₂ (0.04), KOAc (0.04)	2	85
1	KOH (0.03) or KI (0.024)	2	21
1	KOAc (0.08) or Piperidine or NaOMe	[HC(NO ₂) ₂] ⁻ K ⁺ (3)	76
ClC(NO ₂) ₂ CH ₂ Cl (4)	KNO ₂ (0.12)	2	12
4	KNO ₂ (0.09), KOAc (0.02)	2	17
4	KNO ₂ (0.04), KI (0.02)	2	57
4	Piperidine	3	ca. 30
4	NaOMe	2 + 3	
4	KNO ₂ (0.09), KOH (0.02)	2	35
(O ₂ N) ₃ CCH ₂ F (5)	KNO ₂ (0.06)	No precipitate ^d	
5	KNO ₂ (0.06), (KOH, KOAc, KCN) (0.01)	No precipitate	
5	KNO ₂ (0.06), KI (0.04)	2	70
5	NH ₃	3	ca. 50
(O ₂ N) ₃ CCH ₂ OAc (6)	KNO ₂ (0.06), KI (0.02)	2	89
6	KNO ₂ (0.06)	[(O ₂ N) ₃ C] ⁻ K ⁺ (7)	92
6	KNO ₂ (0.06), KOAc (0.02)	7	88
6	KI (0.06)	2 + [(O ₂ N) ₂ CCH ₂ C(NO ₂) ₂] ²⁻ 2K ⁺ (8)	
(O ₂ N) ₃ CCH ₂ OCOCF ₃ (9)	KNO ₂ (0.06) or KI (0.02) or KNO ₂ , KI	7	ca. 90
[(O ₂ N) ₃ CCH ₂ O] ₂ SO (10)	KI (0.04)	8	ca. 30
10	KNO ₂ (0.06)	7	90
(O ₂ N) ₃ CCH ₂ OTs (11)	KNO ₂ (0.06), KI (0.02), or KOAc (0.06)	7	ca. 90
ClC(NO ₂) ₂ CH ₂ OAc (12)	KNO ₂ (0.06), KI (0.02)	2	92
12	KNO ₂ (0.06), KOAc (0.02)	No precipitate	
12	KI (0.04)	8	15
ClCH ₂ C(NO ₂) ₂ CH ₂ Cl (13)	KNO ₂ or KNO ₂ + KI or KNO ₂ + KOH	No precipitate	
AcOCH ₂ C(NO ₂) ₂ CH ₂ OAc (14)	KNO ₂ or KNO ₂ + KOH or KI	No precipitate	
14	KNO ₂ (0.06), KI (0.02)	2	40
CH ₃ C(NO ₂) ₂ CH ₂ Cl (15)	KNO ₂ or KNO ₂ + KI or KNO ₂ + KOH	No precipitate	

^a Reactions were run in aqueous methanol (60%) except those using NaOMe in anhydrous MeOH. ^b Reference 2. ^c Crude product yield, not further purified. ^d In all cases where no precipitate formed, reaction did take place as evidenced by color changes. Products in these cases could be similar to the others reported by Ungnade and Kissinger (ref 3) and others [see P. Noble, Jr., F. G. Borgardt, and W. L. Reed, *Chem. Rev.*, **64**, 19 (1964), for discussions and other references].

Cl, -CH₂OAc, and -CN, and Y = -Cl, -F, -OAc, -OTs, and -OCOCF₃.

Previously reported studies on the reaction of 2,2,2-trinitrochloroethane (1) with bases indicated that the conversion of 1 to dipotassium tetranitroethane (2) is best effected in aqueous alcohol solution with excess nitrite ion.² The reaction is apparently base catalyzed since reactions run in the presence of potassium hydroxide were complete in less than 1 hr. The reaction with nitrite alone takes about 18 hr before the maximum yield is realized. Other additives such as iodide or cyanide ion also appear to accelerate the reaction but they, as well as hydroxide ion, result in lower yields of 2.

Results

Table I summarizes the results of the reactions of various substituted dinitroethyl compounds with bases. In this study no attempt was made to identify products other than the nitronate salts which could be readily precipitated out of the reaction mixture. Many of these reactions could have resulted in the formation of other aliphatic nitro derivatives similar to the production of 2,2-dinitroethyl methyl ether from 1,2-dichloro-1,1-dinitroethane (4)⁸ or the dinitroethylation reaction of Frankel.⁴ The identity of the nitronate salt products

was established through previously characterized halogen derivatives, decomposition points, and infrared and nmr spectra.

Discussion

Table I shows that a variety of nitronate products can be formed from the reaction of structurally related polynitro compounds with potassium nitrite. The nitronate product formed depends on the substituents on the polynitro compound as well as the nature and concentrations of potassium nitrite and other reactants. Several reaction paths can be written which explain the production of these different products.

In the case of polynitro compounds with easily hydrolyzed substituents, such as 2,2,2-trinitroethyl acetate (6), the dominant point of attack by aqueous base is at the carbonyl leading to loss of acetate followed by loss of formaldehyde from the intermediate nitro alcohol in a reverse Henry reaction.^{5,6}

The product trinitromethyl anion is isolated by precipitation from solution as the potassium salt 7 in nearly quantitative yield. Other esters of 2,2,2-trinitroethanol that were observed to behave similarly were the trifluoroacetate 9, the *p*-toluenesulfonate 11, and the sulfite 10. These compounds produce potassium

(3) H. E. Ungnade and L. W. Kissinger, *J. Org. Chem.*, **31**, 369 (1966).

(4) M. B. Frankel, *ibid.*, **23**, 813 (1958); L. J. Winters and W. E. McEwen, *Tetrahedron Suppl.*, **19**, 1, 49 (1963).

(5) N. S. Marans and R. P. Zelinsky, *J. Amer. Chem. Soc.*, **72**, 5329 (1950).

(6) T. N. Hall, *Tetrahedron, Suppl.*, **19**, 1, 115 (1963).

nitroform in reactions with potassium nitrite and potassium hydroxide or potassium iodide. The acetate 6 and 2-chloro-2,2-dinitroethyl acetate (12), however, produce the rearranged product 2 with potassium nitrite in the presence of iodide.

Esters of 2-chloro-2,2-dinitroethanol are expected to behave similarly. However, the presence of the labile positive halogen leads to competitive reactions possibly of the dinitroethylation type,⁴ which will be discussed below. In no case was a salt that corresponded to potassium chlorodinitromethane isolated.

However, difficultly hydrolyzed substituents, such as 2,2,2-trinitrochloroethane (1), with nitrogen bases or methoxide lead to the isolation of potassium dinitromethane (3). Most probably the initial attack of base is at the trinitromethyl group. This can be followed by acidic proton abstraction of hydrolysis of chloride resulting in the loss of one carbon as a derivative of formaldehyde. Sodium methoxide or nitrogen bases in reaction with 1, 2,2-dinitro-1,2-dichloroethane (4), and 2,2,2-trinitroethyl fluoride (5) produce this dinitromethane product. The fact that in no case was potassium trinitromethane formed and that in one case the rearranged product 2 was formed gives support to the speculation that the first point of attack occurs at the trinitromethyl group.

Discussion of the rearrangement of 2,2,2-trinitrochloroethane (1) to 2 was presented in ref 2. Since the 2,2,2-trinitroethyl acetate (6) and 2-chloro-2,2-dinitroethyl acetate (12) produce 2 only when reacted with potassium nitrite in the presence of iodide ion, it would seem more probable that a reaction path similar to that proposed in the dinitroethylation type reactions⁴ takes place with dinitroethylene as a common intermediate. Halogenation of intermediate nitronates by sources of positive halogen finds support in work reported by McEwen.⁴

Rearrangement to dipotassium 1,1,3,3-tetranitropropane (8) occurs in the absence of nitrite ion for compounds such as the chlorodinitroethyl acetate (12), the trinitroethyl acetate (6), and the sulfite 10 by reaction with iodide. Formation of the reactive intermediate dinitroethylene followed by Michael addition of 2,2-dinitroethyl acetate leads to the formation of 8.

From the reactions discussed above, it is obvious that many factors are responsible for directing the courses of the many processes involved and that much further study is needed to define the actual processes and steps involved. It is hoped that the speculation presented, along with the interesting chemical evidence, will spur additional fundamental work in the area of aliphatic nitro chemistry.

Experimental Section⁷

Preparation of Nitronate Salt Derivatives (Table I).—A solution of potassium nitrite (plus other reactants, if used) in 25 ml of 60% aqueous methanol was prepared (mole amounts given in Table I). To this solution was added 0.01 mol of nitro aliphatic compound, and the resulting solution was allowed to stand at room temperature for 24 hr. The precipitate was collected and washed with cold aqueous methanol and then air dried. The nitronate salt products were identified by their ir spectrum, melting (decomposition) points, and halogenated derivatives.

(7) Melting points and boiling points are uncorrected. *Caution:* many of the compounds described are explosives and are sensitive to impact, friction, etc.; *handle with care.* Microanalysis by Berkeley Analytical Laboratories; nmr by Varian Associates.

2,2,2-Trinitrochloroethane (1), 1,2-dichloro-2,2-dinitroethane (4), 2,2,2-trinitroethyl sulfite (10), 2,2-dinitrochloropropane (15), 1,3-dichloro-2,2-dinitropropane (13), dipotassium tetranitroethane (2), and potassium dinitromethane (3) were prepared as previously reported.²

2,2,2-Trinitroethyl acetate (6) was prepared as described by Morans and Zelinsky.⁵

2-Chloro-2,2-dinitroethyl acetate (12) was prepared by the method of Ungnade and Kissinger.³

2,2,2-Trinitroethyl Trifluoroacetate (9).—A solution of 36 g (0.2 mol) of 2,2,2-trinitroethanol in 50 g (0.24 mol) of trifluoroacetic anhydride was refluxed for 24 hr. The reaction mixture was fractionated under reduced pressure giving 47 g (85.5%) of product, bp 61–62° (4 mm), n_D^{25} 1.4051.

Anal. Calcd for $C_4H_2N_3O_8F_3$: C, 17.34; H, 0.73; N, 15.17. Found: C, 17.28, 17.37; H, 1.08, 1.01; N, 15.12, 15.14.

2,2,2-Trinitroethyl Tosylate (11).—2,2,2-Trinitroethanol (15 g, 0.082 mol) and *p*-toluenesulfonyl chloride (15 g, 0.078 mol) were heated at 85° for 7 days. After the first 2 hr of heating, 4 drops of pyridine were added. The crude product was recrystallized twice for benzene giving 10.5 g (24.7%) of product, mp 136.5–137°.

Anal. Calcd for $C_9H_9N_3O_8S$: C, 32.22; H, 2.68; N, 12.59; S, 9.56. Found: C, 32.23; H, 2.73; N, 12.62; S, 9.54.

2,2,2-Trinitrofluoroethane (5).—Trinitroethanol was fluorinated with sulfur tetrafluoride by the method of Baum.⁸ A 50% yield of 5 was obtained, bp 52–53° (13 mm). Proton nmr shows a doublet at 310 and 355 ppm from TMS. Principal infrared absorption was consistent with ref 8.

1,2-Difluorotetranitroethane.—Dipotassium tetranitroethane (2) was fluorinated by the aqueous fluorination method of Grakanskas.⁹ A 45% yield of 1,2-difluorotetranitroethane was obtained: bp 60° (35 mm); n_D^{25} 1.4152; F^{19} nmr shows a pentet at 97.3 ppm (relative intensity 1:2:3:2:1 split by 9 cps); principal infrared absorption at 1630 (s), 1340 (m), 1300 (m), 1275 (m), 820 (m), and 770 cm^{-1} (m).

Anal. Calcd for $C_2F_2N_4O_8$: C, 9.75; H, 22.76. Found: C, 9.77; N, 22.71.

1,3-Difluoro-1,1,3,3-tetranitropropane.—This compound was prepared by the aqueous fluorination procedure⁹ and produced a 58% yield of product: bp 75–77° (5 mm); n_D^{25} 1.4425; proton nmr shows a triplet with peaks at 291, 277, and 263 (relative intensity 1:2:1) from TMS; principal infrared absorption at 1620 (s) 1375 (w), 1310 (m), 1110 (w), 850 (w), and 820 cm^{-1} (w).

Anal. Calcd for $C_3H_2F_2N_4O_8$: C, 13.86; H, 0.78; N, 21.54. Found: C, 14.54; H, 0.90; N, 21.18.

Registry No.—1, 4100-02-1; 4, 4100-03-2; 5, 15892-91-8; 6, 4998-90-7; 9, 681-40-3; 10, 10596-61-9; 11, 26332-91-2; 12, 5917-55-5; 13, 4167-16-2; 14, 26329-29-3; 15, 4167-15-1; 1,2-difluorotetranitroethane, 20165-39-3; 1,3-difluoro-1,1,3,3-tetranitropropane, 22692-28-0.

(8) K. Baum, *J. Org. Chem.*, **33**, 1293 (1968).

(9) V. Grakanskas and K. Baum, *ibid.*, **33**, 3080 (1968).

Radical Reaction of Isocyanide with Disubstituted Phosphine

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A series of free-radical reactions of isocyanide have been found by us, which have been schematized by assuming an imido radical as the intermediate. As to the radical reaction of isocyanide with the heteroatom-

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