CHEMISTRY OF THE ALIPHATIC POLYNITRO COMPOUNDS AND THEIR DERIVATIVES[1]

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I. INTRODUCTION

This report reviews the recent chemistry of polynitroalkanes and their derivatives. All discussion is restricted to compounds containing at least two nitro groups, but excluding nitramines. The general and specialized methods of their preparation and their physical and chemical properties are reviewed. Mechanisms for the important reactions are discussed only where it was concluded that sufficient experimental data exist to support the reported hypotheses. The literature is covered extensively from about 1947 through 1962. Early work has been covered by Sidgwick (191), Hass and Riley (209), Rodd (164), Kirk and Othmer (210), and Levy and Rose (113), but they emphasize for the most part only the mononitroparaffins. An excellent survey of the chemistry of the mononitroparaffins was recently published by Kornblum (110).

A program initiated by the Office of Naval Research in 1947 to investigate the nitroaliphatics for potential use as explosives and propellants has been a big factor in expanding the chemistry of this often-ignored field. Gradually, as reports become declassified, much of this early work is appearing in the open literature. The first step toward releasing much of this information was accomplished by Professor H. Feuer, who, with the cooperation of the Office of Naval Research and the Department of Chemistry, Purdue University, organized a Symposium on Nitro Aliphatic Chemistry in 1961. Papers presented at this symposium were published in a special issue of *Tetrahedron.* Some of these papers are summaries of work covering approximately 10 years of work, but few or no experimental details are given. Portions of this work have since appeared elsewhere in the literature, and those with sufficient experimental data are covered in the appropriate sections of this review.

Caution. It should be understood that all polynitro compounds, and particularly the nitronate salts, must be considered to be hazardous materials and adequate safety precautions must be taken when handling these compounds. Distillations are particularly dangerous and must be conducted on as small a scale as possible, at low pressures and behind suitable barricades.

II. SYNTHETIC METHODS

A. NITRATION OF HYDROCARBONS

The liquid-phase nitration of both olefins and paraffins and the vapor-phase nitration of paraffins have been reviewed by Levy and Rose (113) and recently by Kirk and Othmer (210). Generally, the direct nitration of paraffins leads only to mononitro compounds, and the synthesis of nitroalkanes containing more than one nitro group is usually most successful when dinitrogen tetroxide is added to olefins, although nitric acid or mixed acids (nitric + sulfuric) have been used in special cases. A mechanism for the formation of *gem*-dinitro compounds by nitration of saturated hydrocarbons has been proposed by Titov (192).

Nikolaeva, Redkina, and Kamai (125) report that the nitration of 2,3-dibromopropene with mixed acids yields mainly 1,2-dibromo-1,1-dinitroethane, but also small amounts of 1,1-dinitro-2-bromoethane and, surprisingly, α,β-dibromo-α-nitropropionic acid. Frankel and Klager (55) have studied the nitration of 2-nitro-1-butene, 2-nitro-2-butene, and 2-nitro-1-propene with 70% nitric acid and report that only in the case of 2-nitro-2-butene was a product identified, namely, 2,2,3-trinitrobutane.

$$CH_3CH{=}C(NO_2)CH_3 \xrightarrow{70\%\ HNO_3} CH_3CH(NO_2)C(NO_2)_2CH_3$$

Cyclohexene has also been nitrated with 70% nitric acid; the product is mainly *trans*-dinitrocyclohexane (115, 123).

The most important use of mixed nitric and sulfuric acids for nitration has been the synthesis of tetranitromethane from acetylene (70). Recently, a modification of this process by Wetterholm (199) has resulted in an economically attractive process for producing nitroform. The process consists of the nitration of acetylene with concentrated nitric acid using a mercury catalyst and isolation of the nitroform by the distillation of a nitroform–water azeotrope. The process is continuous and gives an over-all yield of 73.6%.

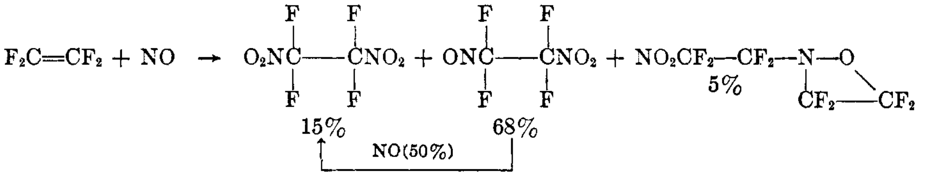
B. ADDITION OF NITROGEN OXIDES TO OLEFINS

The addition of nitrogen oxides to olefins has received only little attention in recent years. The compounds prepared by this method since earlier reviews (113, 163, 191) are summarized briefly in Table I. Significant work, however, has recently been concerned with the addition of nitrogen oxides to fluoroolefins. Tetrafluoroethylene yields 1,2-dinitrotetrafluoroethane with N_2O_4 (23), and nitric oxide gives a mixture of the dinitro compound, the nitrosonitro compound, and perfluoro-2-(2-nitrotetrafluoroethyl)-1,2-oxazetidine (16). The addition of N_2O_3 gives a mixture of the nitroso and dinitro deviatives (60).

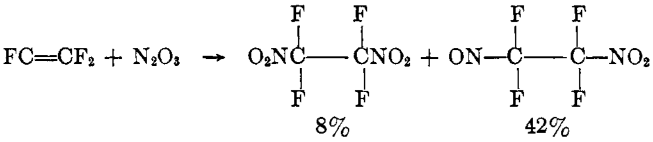
Birchall, *et al.* (16), also report that the nitronitroso compound is further converted to the dinitro compound in 50% yield with excess NO in the vapor phase. Park and co-workers (152) have studied the reaction of NO with chlorotrifluoroethylene and tetrafluoroethylene. In both cases, the expected nitronitroso and dinitro compounds were formed in the product mixture; in the case of the chlorotrifluoroethylene, however, the main product was polymeric.

Haszeldine (75) reports that tetrafluoroethylene, chlorotrifluoroethylene, and 1,1-dichloro-2,2-difluoroethylene when heated to 60–65° in an autoclave for 6 to 8 hours with N_2O_4 give mainly the dinitro compounds (see Table I).

$$F_2C{=}CF_2 + N_2O_4 \rightarrow O_2NCF_2CF_2NO_2$$



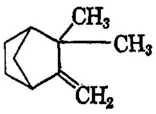
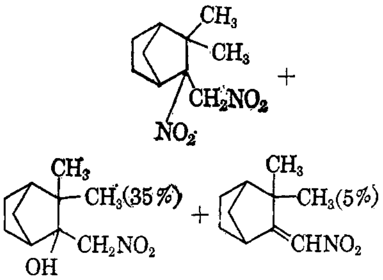
$$F_2C{=}CF_2 + NO \rightarrow \underset{15\%}{O_2NCF_2CF_2NO_2} + \underset{68\%}{ONCF_2CF_2NO_2} + \underset{5\%}{NO_2CF_2CF_2NOCF_2CF_2} \qquad ONCF_2CF_2NO_2 \xrightarrow{NO(50\%)} O_2NCF_2CF_2NO_2$$



$$FC{=}CF_2 + N_2O_3 \rightarrow \underset{8\%}{O_2NCF_2CF_2NO_2} + \underset{42\%}{ON{-}CF_2{-}CF_2{-}NO_2}$$

TABLE I

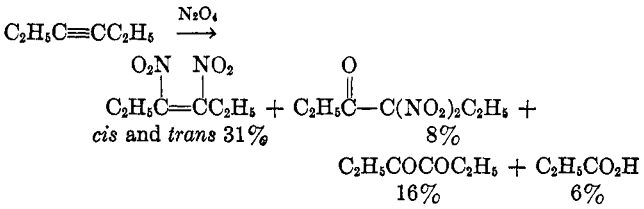
ADDITION OF NITROGEN OXIDES TO OLEFINS

Olefin	Nitrogen oxide	Products	Yield, %	B.p. (mm.) or m.p., °C., and/or n^t_D	Ref.
	N_2O_4	1,2-Dinitrocyclohexane (epimers)		110–114 (1);	124
	70% HNO_3	*trans*-Dinitrocyclohexane		46; n^{20}_D 1.4843	10, 115
	N_2O_4		30	141–143	182
$(C_2H_5)_2C{=}CH_2$	N_2O_4	$(C_2H_5)_2C(NO_2)CH_2NO_2$	86	91–92 (1); 14	159
		$(C_2H_5)_2C(OH)CH_2NO_2$	40	72.5–73 (1); n^{20}_D 1.453	
$C_6H_5CH{=}CHC_6H_5$	N_2O_4	$C_6H_5CH(NO_2)CH(NO_2)C_6H_5$ (*meso* and *dl*)	53	235–237^a; 149^b	182
		$C_6H_5CH(OH)CH(NO_2)C_6H_5$ (isomers)	29	98–99	
$C_6H_5CH_2CH{=}CH_2$	N_2O_4	$C_6H_5CH_2CH(NO_2)CH_2NO_2$	34	62	
		$C_6H_5CH_2CH(OH)CH_2NO_2$	45	n^{20}_D 1.5370	183
$(C_2H_5)_2C{=}CH_2$	N_2O_3	$(C_2H_5)_2C(NO_2)CH_2NO_2$	39		159
		$(C_2H_5)_2C(OH)CH_2NO_2$	25		
$CH_2{=}C(CH_3)C(CH_3){=}CH_2$	N_2O_4	$O_2NCH_2C(CH_3){=}C(CH_3)CH_2NO_2$	45	70 (760)	205
$CH_2{=}C(CH_3)CH_2C(CH_3)_3$	N_2O_4	$O_2NCH_2C(NO_2)(CH_3)CH_2C(CH_3)_3$		19.5; n^{20}_D 1.464	10
$(CH_3)_2C{=}CHC(CH_3)_3$	N_2O_4	$(CH_3)_2C(NO_2)CH(NO_2)C(CH_3)_3$		68 (0.5); 46	10
$F_2C{=}CF_2$	N_2O_4	$O_2NCF_2{-}CF_2NO_2$	53	58.5–59 (760); n^{25}_D 1.3265	23, 75
$F_2C{=}CFCl$	N_2O_4	$O_2NCF_2{-}CFClNO_2$	51	98.5–100 (760)	75
$F_2C{=}CCl_2$	N_2O_4	$O_2NCF_2{-}CCl_2NO_2$	47	81–83 (103)	75
$F_2C{=}CF_2$	N_2O_3	$ONCF_2{-}CF_2NO_2$	42	25 (760)	
		$O_2NCF_2{-}CF_2NO_2$	8	58 (760)	60
$F_2C{=}CF_2$	NO	$O_2NCF_2CF_2NO_2$	15		
		$ONCF_2CF_2NO_2$	68	24.2 (760)	16
		$O_2NCF_2CF_2NOCF_2CF_2$	5		16
$F_2C{=}CFCl$	NO	$F_2C(NO_2)CFClNO$		62 (630); n^{25}_D 1.349	
		$F_2C(NO_2)CFClNO_2$		94.5 (630); n^{25}_D 1.375	152
$F_2C{=}CFCF_3$	NO	$F_3CCF(NO_2)CF_2NO$		42 (630); n^{20}_D 1.306	152
		$F_3CCF(NO_2)CF_2NO_2$		68.5 (630); n^{20}_D 1.3220	
$C_2H_5C{\equiv}CC_2H_5$	N_2O_4	$C_2H_5C(NO_2){=}C(NO_2)C_2H_5$ (*trans*)	31	53–55 (1); n^{35}_D 1.4582	58
		(*cis*)		44–53 (0.1); 29–31; n^{35}_D 1.4692	
		$C_2H_5COC(NO_2)_2C_2H_5$	8	69–71 (1); n^{20}_D 1.4548	
$CH_3C{\equiv}CCH_3$	N_2O_4	$CH_3C(NO_2){=}C(NO_2)CH_3$ (*trans*)	34	70–72 (8); n^{20}_D 1.4678	58
		(*cis*)	7	96–100 (1.5); n^{20}_D 1.4776	
$CH_3C(NO_2){=}C(NO_2)CH_3$	N_2O_4	$CH_3C(NO_2)_2C(NO_2)_2CH_3$	31	162–163 dec.	69
$C_2H_5C(NO_2){=}C(NO_2)C_2H_5$	N_2O_4	$C_2H_5C(NO_2)_2C(NO_2)_2C_2H_5$	32	106–107	69

[a] *meso*. [b] *dl*.

In addition to the reactions summarized in Table I, the addition of N_2O_4 to alkylacetylenes is of interest. Freeman and Emmons (58) studied the reaction of N_2O_4 with 3-hexyne and 2-butyne.

In the case of 3-hexyne, two dinitro compounds were identified, namely *cis*- and *trans*-3,4-dinitro-3-hexene and 4,4-dinitro-3-hexanone. From 2-butyne, only the *cis*- and *trans*-2,3-dinitro-2-butene were identified,



$$C_2H_5C{\equiv}CC_2H_5 \xrightarrow{N_2O_4} \underset{\textit{cis and trans } 31\%}{C_2H_5\overset{O_2N}{\overset{|}{C}}{=}\overset{NO_2}{\overset{|}{C}}C_2H_5} + \underset{8\%}{C_2H_5\overset{O}{\overset{\|}{C}}{-}C(NO_2)_2C_2H_5} + \underset{16\%}{C_2H_5COCOC_2H_5} + \underset{6\%}{C_2H_5CO_2H}$$

because of the difficulty in working up the reaction mixture. The *cis*-2,3-dinitro-2-butene obtained by N_2O_4 addition is stated to be identical with that obtained by coupling chloronitroethane with base (17). The *cis–trans* configurations were assigned by infrared analysis.

Stevens (182) has studied the addition of N_2O_4 to camphene and stilbene. He finds that in the absence of oxygen the principal products are the dinitro compounds, 3-(nitromethyl)-3-nitrocamphenilane and dinitrobibenzyl, and the corresponding hydroxynitro compounds, which result from hydrolysis during work-up of the intermediate nitronitrites. When oxygen is used as the carrier gas, a different product distribution is observed. Dinitro compounds are not formed and, in addition to the 1,2-nitroalcohol, nitroketones and 1,2-nitronitrates were identified. Stevens (183) also studied the addition of N_2O_4 to allylbenzene (Table I).

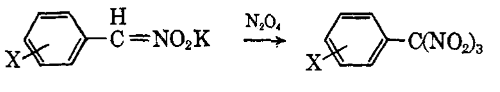
The addition of N_2O_4 to 2,3-dinitro-2-butene and 3,4-dinitro-3-hexene resulting in 2,2,3,3-tetranitrobutane and 3,3,4,4-tetranitrohexane, respectively, has been reported (69).

The complexity of reaction of N_2O_4 with olefins certainly indicates a free-radical mechanism. Mechanistic views are presented by Shechter and Conrad (169) and by Campbell, Shavel, and Campbell (20).

C. NITRATION OF ACIDIC HYDROGEN COMPOUNDS AND THEIR SALTS

Only a few pertinent examples of the nitration of compounds containing acidic hydrogens or their salts to give polynitro compounds have been reported (Table II). The nitrating agents used were $NO_2(N_2O_4)$, nitric acid, or, in one case, tetranitromethane.

Novikov (139) has nitrated several substituted phenylnitromethanes with N_2O_4 to the corresponding trinitrophenylmethanes. The *p*-nitro, *m*-nitro, and *p*-chloro derivatives were studied. The nitrolic acids were nitrated similarly and also give trinitrophenylmethane. The nitration of phenylnitromethane, with N_2O_4 in ether, to the dinitrophenylmethane in 22% yield is reported by Khmelnitskii (94). The liquid-phase nitration of 1,4-dimethylcyclohexane with NO_2 resulting in 1,4-dinitro-1,4-dimethylcyclohexane is reported by Smiley and McRae (180).



The use of tetranitromethane as a nitrating agent for aliphatic nitration is reported by Plummer (158) in the case of the salts of several nitropropanes.

$$NaO_2N{=}C(NO_2)CH_2CH_3 \xrightarrow{C(NO_2)_4} (NO_2)_3CCH_2CH_3 + NaO_2N{=}C(NO_2)_2$$

An interesting example of the direct nitration of acidic protons is the work of Kissinger and Ungnade (98). They report that the nitration of half esters of malonic acid with 70% HNO_3 produces the corresponding α,α-dinitro esters, although in poor yield.

$$C_2H_5OCOCH(R)CO_2H \xrightarrow[HNO_3]{70\%} C_2H_5OCOC(NO_2)_2R$$

Treatment of these α,α-dinitro esters with hydrazine hydrate yields the hydrazine salt of the 1,1-dinitroalkane.

$$RC(NO_2)_2COOC_2H_5 + 2H_2NNH_2 \xrightarrow{EtOH} [RC(NO_2)_2]^-[H_3NNH_2]^+ + H_2NNHCOOC_2H_5$$

In the case of the acetate ester, however, the hydrazine salt of the hydrazide is produced.

$$HC(NO_2)_2COOC_2H_5 \xrightarrow{H_2NNH_2} [C_2H_5OCOC(NO_2)_2]^-[H_3NNH_2]^+ \xrightarrow{H_2NNH_2} [H_2NNHCOC(NO_2)_2]^-[H_3NNH_2]^+$$

The synthesis of *gem*-dinitroalkanes by the nitration of alkylacetoacetic esters has been studied by Ershova, Gogitidze, and Belikov (208).

$$CH_3COCH(R)COOC_2H_5 \xrightarrow{HNO_3} RCH(NO_2)_2 + CH_3COOH + CO_2 + C_2H_5ONO_2$$

However, the yields are low (4–9%). The series 1,1-dinitropropane to 1,1-dinitrodecane, prepared by this method, are included in Table II.

Parker, Emmons, Rolewicz, and McCallum (155) have improved the synthesis of trinitroacetonitrile (73–77% yield) by carrying out the nitration in the presence of carbon tetrachloride.

$$NCCH_2COOH + 3HNO_3 + 3SO_3 \xrightarrow{CCl_4} NCC(NO_2)_3 + CO_2 + 3H_2SO_4$$

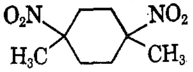
In solution, trinitroacetonitrile can be safely utilized for the preparation of dinitroacetonitrile derivatives. Although dinitroacetonitrile is unstable, it has been isolated as the tetrahydrate and its sodium, potassium, and silver salts. The sodium or potassium salt of dinitroacetonitrite is prepared by reduction of trinitroacetonitrile with hydrogen bromide in ethanol, followed by neutralization with the appropriate methanolic base. These salts are also prepared by cleavage of dinitrocyanoacetate esters (154), which are prepared by nitration of the oximinocyanoacetate esters.

$$NCC(NOH)COOR + HNO_3 \xrightarrow{H_2SO_4} NCC(NO_2)_2COOR + H_2O$$

$$NC(NO_2)_2COOR + ROH \xrightarrow{K^+} [NCC(NO_2)_2]^-K^+ + ROCOOR$$

TABLE II

NITRATION OF COMPOUNDS CONTAINING ACIDIC HYDROGEN AND THEIR SALTS

Compound	Nitrating agent	Product	B.p. (mm.) or m.p., °C., and/or n^{t}D	Yield, %	Ref.
$(NO_2)_2CHCH_2CH_3$	$C(NO_2)_4$	$(NO_2)_3CCH_2CH_3$	n^{22}D 1.4432	32	158
$C_6H_5CH_2CH_2CH_2NO_2$	$C(NO_2)_4$	$C_6H_5CH_2CH_2CH(NO_2)_2$	37.5–38.5	31.6	158
$C_6H_5CH_2CH_2CH(NO_2)_2$	$C(NO_2)_4$	$C_6H_5CH_2CH_2C(NO_2)_3$	35–36	32.6	158
	$NO_2(N_2O_4)$		178–179	15–20	168
$C_6H_5CH_2NO_2$	N_2O_4	$C_6H_5CH(NO_2)_2$	79–80	22	94, 139
p-$NO_2C_6H_4CH_2NO_2$	N_2O_4	p-$NO_2C_6H_4C(NO_2)_3$	46–47	58	139
m-$NO_2C_6H_4CH_2NO_2$	N_2O_4	m-$NO_2C_6H_4C(NO_2)_3$	63–64	60	139
$C_6H_5C(NO_2)=NOH$	N_2O_4	$C_6H_5C(NO_2)_3$	13; n^{20}D 1.5548	77	139
p-$NO_2C_6H_4C(NO_2)=NOH$	N_2O_4	p-$NO_2C_6H_4C(NO_2)_3$	46–47	58	139
m-$NO_2C_6H_4C(NO_2)=NOH$	N_2O_4	m-$NO_2C_6H_4C(NO_2)_3$	63–64	84	139
$C_2H_5OCOCH_2COOH$	70% HNO_3	$C_2H_5OCOC(NO_2)_2H$	n^{25}D 1.4321	11	98
$C_2H_5OCOCH(CH_3)COOH$	70% HNO_3	$C_2H_5OCOC(NO_2)_2CH_3$	45 (0.1); n^{25}D 1.4327	17	98
$C_2H_5OCOCH(C_2H_5)COOH$	70% HNO_3	$C_2H_5OCOC(NO_2)_2C_2H_5$	50 (0.1); n^{25}D 1.4340	17	98
$C_2H_5OCOCH(n\text{-}C_4H_9)COOH$	70% HNO_3	$C_2H_5OCOC(NO_2)_2C_4H_9$	60 (0.1); n^{25}D 1.4393	8	98
$KNO_2C(NO_2)C(NO_2)NO_2K$	H_2SO_4/HNO_3	$(NO_2)_3CC(NO_2)_3$	150 dec.	92	126
$CH_3COCH(C_2H_5)COOC_2H_5$	HNO_3	$CH_3CH_2CH(NO_2)_2$	77 (11); n^{20}D 1.4334	6	208
$CH_3COCH(C_3H_7)(COOC_2H_5)$	HNO_3	$CH_3(CH_2)_2CH(NO_2)_2$	86 (11); n^{20}D 1.4354	7	208
$CH_3COCH(C_4H_9)COOC_2H_5$	HNO_3	$CH_3(CH_2)_3CH(NO_2)_2$	103 (13); n^{20}D 1.4384	8	208, 194
$CH_3COCH(C_5H_{11})COOC_2H_5$	HNO_3	$CH_3(CH_2)_4CH(NO_2)_2$	89 (5); n^{20}D 1.4409	6	208
$CH_3COCH(C_6H_{13})COOC_2H_5$	HNO_3	$CH_3(CH_2)_5CH(NO_2)_2$	81 (1); n^{20}D 1.4432	5	208
$CH_3COCH(C_7H_{15})COOC_2H_5$	HNO_3	$CH_3(CH_2)_6CH(NO_2)_2$	88 (1); n^{20}D 1.4444	4	208
$CH_3COCH(C_8H_{17})COOC_2H_5$	HNO_3	$CH_3(CH_2)_7CH(NO_2)_2$	101–102 (1); n^{20}D 1.4468	9	208
$CH_3COCH(C_9H_{19})COOC_2H_5$	HNO_3	$CH_3(CH_2)_8CH(NO_2)_2$	113–115 (1); n^{20}D 1.4486	5	208

D. OXIDATION AND NITRATION OF NITROGEN DERIVATIVES

The nitration of certain oximes gives the corresponding *gem*-dinitro derivatives, although the method requires quite drastic nitrating conditions and gives poor yields. Gabriel, Bisgrove, and Clapp (69) prepared 2,2,3,3-tetranitrobutane from dimethylglyoxime. Ungnade and Kissinger (195, 100) have studied the nitration of α-oximinoesters and α-oximinonitriles. The α-oximinonitriles were prepared from the corresponding α-hydroxyaminonitriles (100) by dehydrogenation with *p*-benzoquinone in benzene; nitration was effected with 100% nitric acid in the presence of ammonium nitrate. The resulting α,α-dinitronitriles can be converted to the 1,1-dinitroalkane (ammonium salt) with ammonia (Table III).

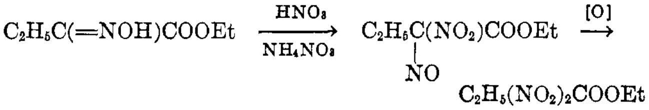
$$RCH(NHOH)CN \xrightarrow[\text{benzene}]{p\text{-benzoquinone}} RC(CN)=NOH \xrightarrow[NH_4NO_3]{100\%\ HNO_3}$$
$$RC(NO_2)_2CN \xrightarrow{NH_3} [RC(NO_2)_2]^-NH_4^+$$

TABLE III

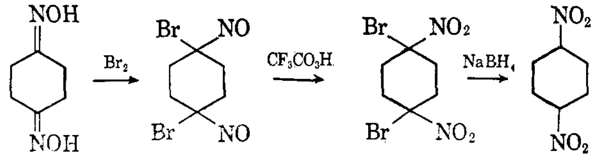
THE NITRATION OF α-OXIMINONITRILES (100)
$[RC(NO_2)_2CN]$

R	Yield, %	B.p. (mm.), °C.	M.p. dec. NH_4^+ salt of dinitroalkane	n^{25}D
CH_3	8	45 (7)	116	1.4390
C_2H_5	12	40 (2)	117	1.4372
C_3H_7	22	45 (2)	128	1.4377
C_4H_9	—	—	131	—

The nitration of the oximino ester proceeds by the α,α-nitronitroso ester intermediate, which is easily oxidized to the α,α-dinitro ester (195).

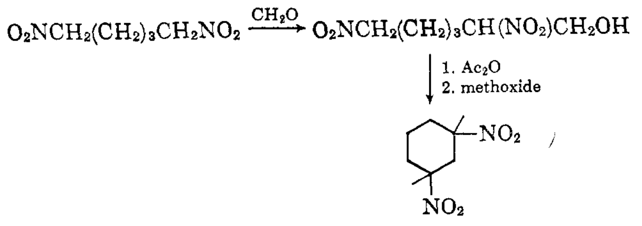


$$C_2H_5C(=NOH)COOEt \xrightarrow[NH_4NO_3]{HNO_3} C_2H_5\underset{NO}{\underset{|}{C}}(NO_2)COOEt \xrightarrow{[O]} C_2H_5(NO_2)_2COOEt$$



$$\xrightarrow{Br_2} \quad \xrightarrow{CF_3CO_3H} \quad \xrightarrow{NaBH_4}$$

The preparation of the mixed isomers of 1,4- and 1,3-dinitrocyclohexanes in low yield by oxidation of the corresponding dioxime with peroxytrifluoroacetic acid has been reported by Nielsen (122). He also has synthesized 1,4-dinitrocyclohexane by the bromination of the oxime and oxidation of the intermediate dibromodinitroso compound, followed by reduction with sodium borohydride. Nielsen (122) also prepared the 1,3-dinitrocyclohexane from 1,5-dinitropentane as follows.

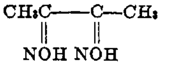
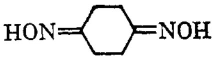
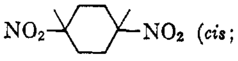
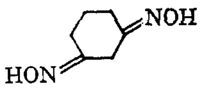
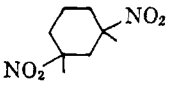
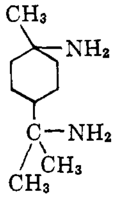
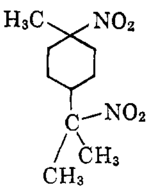


$$O_2NCH_2(CH_2)_3CH_2NO_2 \xrightarrow{CH_2O} O_2NCH_2(CH_2)_3CH(NO_2)CH_2OH$$

A summary of the polynitro compounds prepared from oximes is given in Table III (α-oximinonitriles) and Table IV, including one example of the oxidation of a diamine, namely, 1,8-diamino-*p*-menthane (109).

TABLE IV

OXIDATION AND NITRATION OF OXIMES

Oxime	Oxidizing or nitrating agent	Nitro compound	Yield, %	M.p., °C	Ref.
$C_6H_5CH{=}NOH$	N_2O_4	$C_6H_5CH(NO_2)_2$	45[a]	78–79	95
p-$ClC_6H_4CH{=}NOH$	N_2O_4	p-$ClC_6H_4CH(NO_2)_2$	46[a]	55	95
 $CH_3\underset{NOH}{\underset{\Vert}{C}}-\underset{NOH}{\underset{\Vert}{C}}-CH_3$	HNO_3/H_2SO_4	$CH_3C(NO_2)_2C(NO_2)_2CH_3$	12	162–163	69
$CH_3C({=}NOH)C({=}NOH)Cl$	HNO_3	$CH_3C(NO_2)_2C({=}NOH)Cl$	27	49–50	197
	CF_3CO_3H	 (*cis*; *trans*)	—	130–170	122
	CF_3CO_3H	 (epimers)	6	45–58	122
$C_2H_5({=}NOH)COOC_2H_5$	HNO_3/NH_4NO_3	$C_2H_5C(NO_2)_2COOC_2H_5$	—		195
	$KMnO_4$	 (epimers)	61	104–106	109

[a] From intermediate nitronitroso compound. [b] B.p., 45–50° (0.1 mm.); n^{25}_{D} 1.4356.

E. DISPLACEMENT OF HALOGEN

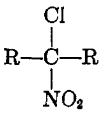
1. *Ter Meer Reaction*

The synthesis of *gem*-dinitro compounds from 1-nitro-1-haloalkanes by the displacement of halogen with nitrite ion in basic media is well known.

$$RCH(NO_2)Cl \xrightarrow[OH^-]{NO_2} \xrightarrow{H^+} RCH(NO_2)_2$$

Recent examples include the preparation of the potassium salt of dinitromethane (29), 2,2-dinitroethanol from 2-bromo-2-nitroethanol (66), and 1,1,4,4-tetranitrobutane from 1,4-dibromo-1,4-dinitrobutane (31). The general applicability of the ter Meer reaction to higher α,ω-dibromo-α,ω-dinitroalkanes has not been studied for two reasons: (1) the oxidative nitration method (93), to be discussed later, is more convenient, and (2) good yields of these higher 1,1-dinitroalkanes require the isolation of dry nitronate salts, which may be hazardous. A procedure for chlorinating 1-nitroalkanes that gives only the desired 1-chloro-1-nitroalkane and not the dichloro derivative was recently reported by Levering (211).

Another limitation of the ter Meer reaction is the fact that the secondary nitrohaloalkanes of the type



$$R-\overset{\displaystyle Cl}{\underset{\displaystyle NO_2}{\overset{|}{\underset{|}{C}}}}-R$$

such as 2-chloro-2-nitropropane, do not give the expected *gem*-dinitro compounds (see IF, Oxidative Nitration).

The mechanism of the ter Meer reaction has been studied by Hawthorne (76). He reports that the reaction between 1-chloro-1-nitroethane and nitrite ion to produce 1,1-dinitroethane displays first-order dependence on both nitrite ion and chloronitroethane. He states that the reaction is inhibited by the addition of strong base and that, under the conditions of the high nitrite ion concentration studied, the rate-determining process is the nitrite ion (general base) catalyzed ionization of the chloronitroethane. The mechanism suggested is the isomerization of the chloronitroethane to its *aci*-form followed by nucleophilic displacement of halogen by nitrite ion. The evidence as presented seems to substantiate the mechanism as written.

2. *α,ω-Dinitroalkanes (Victor Meyer Reaction)*

The synthesis of α,ω-dinitroalkanes by the displacement of halogen with silver nitrite (Victor Meyer) is best accomplished with the diiodides (36) or bromides (151) (Table V). Recently, however, a modification of this method in which sodium nitrite is substituted for silver nitrite and dimethylformamide (or dimethyl sulfoxide) as solvent was introduced by Kornblum (108). Kornblum (110) has recently reviewed the scope and limitations for the reaction of sodium nitrite with alkyl halides. His method has been successfully applied to the synthesis of α,ω-dinitroalkanes by Stille and Vessel (184) and improved upon by Takayama (186), who used a mixture of dimethyl sulfoxide and methyl ethyl ketone as the solvent system.

F. OXIDATIVE NITRATION (SHECTER–KAPLAN REACTION)

A new and very useful method for preparing *gem*-dinitro compounds has been discovered by Kaplan and

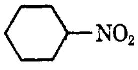
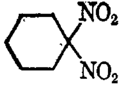
TABLE V

SYNTHESIS OF α,ω-DINITROALKANES

Dihaloalkane	Reagent	Dinitroalkane	B.p. (mm.) or m.p., °C., and/or n^t_D	Yield, %	Ref.
$I(CH_2)_3I$	$AgNO_2$	$O_2N(CH_2)_3NO_2$	108–110 (1); n^{20}_D 1.465	36	36
$Br(CH_2)_3Br$	$AgNO_2$	$O_2N(CH_2)_3NO_2$	104–105 (2); n^{20}_D 1.4646	20	151
$Br(CH_2)_3Br$	$NaNO_2$/DMF	$O_2N(CH_2)_3NO_2$	100–101 (0.5); n^{25}_D 1.4635	6	184
$I(CH_2)\ I$	$AgNO_2$	$O_2N(CH_2)_4NO_2$	33–34	46	36
$Br(CH_2)_4Br$	$AgNO_2$	$O_2N(CH_2)_4NO_2$	34–35	37	151
$Br(CH_2)_4Br$	$NaNO_2$/DMF	$O_2N(CH_2)_4NO_2$	33.5–34.5	33	184
$I(CH_2)_5I$	$AgNO_2$	$O_2N(CH_2)_5NO_2$	134 (1.2); n^{20}_D 1.461	45	36
$Br(CH_2)_5Br$	$AgNO_2$	$O_2N(CH_2)_5NO_2$	147–148 (2); n^{20}_D 1.4610	53	151
$Br(CH_2)_5Br$	$NaNO_2$/DMF	$O_2N(CH_2)_5NO_2$	113–115 (0.2); n^{20}_D 1.4597	29	184
$I(CH_2)_6I$	$AgNO_2$	$O_2N(CH_2)_6NO_2$	36.5–37.5	48	36
$Br(CH_2)_6Br$	$NaNO_2$/DMF	$O_2N(CH_2)_6NO_2$	36–37	42	184
$Br(CH_2)_{10}Br$	$AgNO_2$	$O_2N(CH_2)_{10}NO_2$	48–49	100	151
$CH_3CHBr(CH_2)_2CHBrCH_3$	$NaNO_2$/DMF	$CH_3CH(NO_2)(CH_2)_2CH(NO_2)CH_3$	51–52	7	184

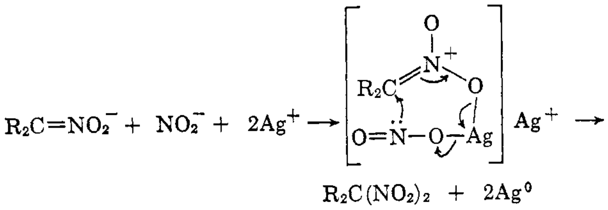
TABLE VI

gem-DINITRO COMPOUNDS PREPARED BY OXIDATIVE NITRATION

Nitro compound	Product	B.p. (mm.) or m.p., °C., and/or n^t_D	Yield, %	Ref.
$CH_3CH_2NO_2$	$CH_3CH(NO_2)_2$	55.5–56 (4.5); n^{20}_D 1.4341	78	93
$CH_3CH_2CH_2NO_2$	$CH_3CH_2CH(NO_2)_2$	68 (2.5); n^{25}_D 1.4321	86	127
$(CH_3)_2CHNO_2$	$(CH_3)_2C(NO_2)_2$	54	93	93
$CH_3(CH_2)_3NO_2$	$CH_3(CH_2)_2CH(NO_2)_2$	67–68 (1); n^{25}_D 1.4344	60	93, 127
$CH_3CH_2CH(NO_2)CH_3$	$CH_3CH_2C(NO_2)_2CH_3$	78 (10); n^{20}_D 1.4354	81	93
		67 (0.7); 36–37	75	93
$[CH_3CH(NO_2)]_2CH_2$	$[CH_3C(NO_2)_2]_2CH_2$	87.5	*a*	93
$(CH_3)_2C(NO_2)CH(CH_3)CH(NO_2)CH_3$	$(CH_3)_2C(NO_2)CH(CH_3)C(NO_2)_2CH_3$	83	*a*	93
$CH_3CH(NO_2)CH_2OH$	$CH_3C(NO_2)_2CH_2OH$	90	80	93
$(HOCH_2)_2CHNO_2$	$(HOCH_2)_2C(NO_2)_2$	146–147	77	93, 127
$O_2N(CH_2)_4CHO$	$CH(NO_2)_2(CH_2)_3CHO$	97 (0.8); n^{20}_D 1.4650	*a*	93
$O_2NCH_2CH_2COOCH_3$	$(O_2N)_2CHCH_2COOCH_3$	78–81 (0.6); n^{20}_D 1.4490	*a*	93
$CH_3CH(NO_2)CH(OH)CH_3$	$CH_3C(NO_2)_2CH(OH)CH_3$	73–75 (2); n^{20}_D 1.4588	70	93
$(O_2NCH_2)_2C(CH_3)_2$	$(CH_3)_2CCH_2(NO_2)CH(NO_2)_2$	122	61	93
cyclo-$PrCH(NO_2)CH_3$	cyclo-$PrC(NO_2)_2CH_3$	99 (10)	*a*	93

[a] Exact yields not given.

Shechter (93). It is especially useful when access to the required 1-chloro-1-nitroalkane is not easily available for the ter Meer reaction or for the preparation of secondary *gem*-dinitro compounds, where the ter Meer reaction fails. The reaction in general consists of an oxidation–reduction that proceeds rapidly in homogeneous solution at 0–30°. The intermediate is apparently an addition complex, which decomposes into the gem-dinitro compound. The intermediate silver complex is also supported by the work of Wright and Levering (202).



The reaction proceeds smoothly in alkaline, aqueous media with silver nitrate and inorganic nitrites. Although mercuric nitrate was found to be the only other cationic oxidant, it has several disadvantages, among which is lower yield. The general applicability of the reaction is illustrated by the *gem*-dinitro compounds that have been prepared (Table VI) and the fact that the silver can be recovered quantitatively.

An interesting application of the Shechter–Kaplan reaction has been used by Feuer (31) to prepare the heretofore inaccessible $\alpha,\alpha,\omega,\omega$-tetranitroalkanes. Although the oxidative nitration directly upon the α,ω-dinitroalkane does not occur until the nitro groups are separated by at least three methylene groups, surprisingly enough when the corresponding bis-methylol derivative is used the reaction takes place in good yield when the separation is only two methylene groups (Table VII). The diols can easily be cleaved by base to the tetranitroalkanes (see Henry Reaction, IIIB1a.)

TABLE VII

SYNTHESIS OF $\alpha,\alpha,\omega,\omega$-TETRANITROALKANES BY OXIDATIVE NITRATION (31)

$(O_2N)_2CH(CH_2)_nCH(NO_2)_2$

n	M.p., °C.	Yield, % Direct	Yield, % From diol
1	13–15[a]	0	0
2	87–88	0	49
3	69–70	10	25
4	66–68	84	70
5	Crude liquid	(89)	—

[a] Ref. 107.

TABLE VIII

MICHAEL-TYPE ADDITIONS OF NITROPARAFFINS

Nitroalkane	Michael addend[a]	Product	Yield, %	B.p. (mm.) or m.p., °C., and/or n^tD	Ref.
$(CH_3)_2CHNO_2$	$CH_3CH_2CH(NO_2)CH_2OCOCH_3$	$CH_3CH_2CH(NO_2)CH_2CH(NO_2)(CH_3)_2$	49–87	77 (0.75); n^{20}D 1.4530	9, 40, 181
$CH_3CH_2CH_2NO_2$	$CH_3CH_2CH(NO_2)CH_2OCOCH_3$	$CH_3CH_2CH(NO_2)CH_2CH(NO_2)CH_2CH_3$	13–19	82–86 (0.7); 33	6, 9, 40, 181
$(CH_3)_2CHNO_2$	$CH_3CH_2CH_2{=}CHNO_2$	$O_2NCH_2CH(C_2H_5)CNO_2(CH_3)_2$	85	Crude; n^{20}D 1.463	9
$(NO_2)_2CHCH_3$	$CH_3CH_2CH(NO_2)CH_2OCOCH_3$	$CH_3C(NO_2)_2CH_2CH(NO_2)CH_2CH_3$	65	90–92 (0.2); 29; n^{20}D 1.4667	40
$O_2NCH(CH_2OH)_2$	$CH_3CH_2CH(NO_2)CH_2OCOCH_3$	$(HOCH_2)_2C(NO_2)CH_2CH(NO_2)C_2H_5$	27	101–102	40
$(CH_3)_2CHNO_2$	$O_2NCH_2CH(CH_3)CH_2OCOCH_3$	$(CH_3)_2C(NO_2)CH_2CH(CH_3)CH_2NO_2$	25–71	80 (0.5); n^{20}D 1.4650	40
$(CH_3)_2CHNO_2$	$CH_2CH(NO_2)(CH_2)_2CH(NO_2)CH_2$ | | $OCOCH_3$ CH_3COO	$[(CH_3)_2C(NO_2)CH_2CH(NO_2)CH_2]_2$	98	193–194	40
$(NO_2)_2CH_2C_2H_5$	$CH_2CH(NO_2)(CH_2)_2CH(NO_2)CH_2$ | | $OCOCH_3$ CH_3COO	$[CH_3CH_2C(NO_2)_2CH_2CH(NO_2)CH_2]_2$	94	161–163	40
CH_3NO_2	$CF_3CF_2CF_2CH{=}CHNO_2$	$CF_3CF_2CF_2CH(CH_2NO_2)_2$	68	62	24
		Michael Additions of Nitroparaffins to Olefins Derived from Mannich Bases			
$CH_3CH_2NO_2$	$[CH_2{=}CHNO_2]$[b]	$(CH_3CHNO_2)_2CH_2$	4.0	43–44	6
$CH_3(CH_2)_3NO_2$	$[CH_3CH_2CH{=}CHNO_2]$	$[CH_3(CH_2)_2CHNO_2]_2CH_2$	20.7	55–56	6
$(CH_3)_2CH(CH_2)_2NO_2$	$[(CH_3)_2CHCH{=}CHNO_2]$	$[(CH_3)_2CHCH_2CH(NO_2)]_2CH_2$	15.7	121–122[c]	6
			13.3	55–57[c]	6
n-$C_6H_{13}CH_2NO_2$	n-$C_5H_{11}CH{=}CHNO_2$	$(n\text{-}C_6H_{13}CHNO_2)_2CH_2$	13.0	70[c]	6
			12.0	44[c]	

[a] The acetates give the corresponding olefins *in situ* under the reaction conditions. [b] The olefins in brackets are formed from the Mannich base intermediate (see section IIH). [c] Diastereomers.

$$O_2N(CH_2)_4NO_2 \xrightarrow{CH_2O} HOCH_2CH(NO_2)CH_2CH_2CH(NO_2)CH_2OH \xrightarrow{NO_2^-,\ Ag^+} HOCH_2C(NO_2)_2CH_2CH_2C(NO_2)_2CH_2OH \xrightarrow[2.\ HCl]{1.\ OH^-} (O_2N)_2CHCH_2CH_2CH(NO_2)_2$$

G. ALKALINE NITRATION

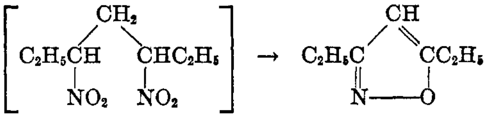
The alkaline nitration of cyclic ketones has been studied by Klager (103) and more extensively by Feuer (46). The reaction of cyclopentanone is a typical example. The intermediate dipotassium dinitrocyclopentanone is converted by bromination to 1,1,4,4-tetrabromo-1,4-dinitrobutane, which can be reduced to 1,4-dinitrobutane with sodium borohydride (103). A recent review by Kornblum (110) adequately discusses the scope of the alkaline nitration with respect to the cyclic ketones. Recently, Feuer and Anderson (28) have converted the dipotassium salts of the dinitrocyclic ketones to the monopotassium salts with glacial acetic acid followed by hydrolytic cleavage to the α,ω-dinitroalkanes. This is a useful method for obtaining α,ω-dinitroalkanes in good yield that cannot readily be obtained by the Victor Meyer reaction.

The alkaline nitration of dinitriles has also been studied by Feuer (44) and reviewed by Kornblum (110). Feuer and Savides (44) report that the alkaline nitration of acetone and methyl ethyl ketone gives the salts of α,α-dinitroketones, which were purified by precipitation from aqueous solution with methanol. The product from the alkaline nitration of 4-heptanone was isolated by bromination of the intermediate salt to 3,5-dinitro-3,5-dibromo-4-heptanone. The alkaline nitration of diketones and α,ω-diesters has not been reported.

H. MICHAEL ADDITIONS OF NITROALKANES TO NITROOLEFINS

Although the synthesis of 1,3-dinitroparaffins by Michael additions of nitroparaffins to low molecular weight nitroolefins is known (15), the *in situ* formation of the nitroolefin at mild temperatures by Feuer and Miller (40) greatly increased the scope of the reaction. They have studied quite extensively the addition of primary and secondary nitroparaffins and nitramines to 2-nitrobutyl acetate, 3-nitro-2-butyl acetate, 1,6-diacetoxy-2,5-dinitrohexane, and 2-acetoxy-2-butanone. A proposed reaction path based upon the observations and the results of these reactions is given (*cf.* Kornblum, ref. 110). The factors studied that influence the course of these Michael additions are: (a) number of reaction centers (positions for salt formation) of either the starting nitroparaffin or expected adduct, (b) number of active hydrogen atoms in the nitroparaffin, (c) relative acidities of the nitroparaffin, and (d) solubility of the Michael adduct. The results of this study are included in Table VIII, which is a compilation of recent Michael adducts derived from nitroalkanes and nitroolefins. The low yield of 3,5-dinitroheptane is caused by the rearrangement of the product to the isoxazole in the presence of a trace of base.[2] Michael additions of polynitroalkanes are discussed in section III.

$CH_3CH_2C(NO_2){=}CH_2 + CH_3CH_2CH{=}NO_2K \rightarrow$



Also, 1,3-dinitroparaffins can be prepared by the reaction of Mannich bases of primary nitroalkanes with a nitroalkane.

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[2] H. Feuer, private communication.

$$R_2NH + CH_2O + RCH_2NO_2 \rightarrow [RCH(NO_2)CH_2NR_2] \rightarrow [RC(NO_2)_2{=}CH]_2 \xrightarrow{R'CH_2NO_2} RCH(NO_2)CH_2CH(NO_2)R'$$

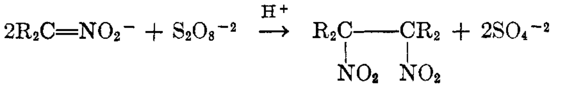
The intermediate Mannich bases of primary nitroalkanes are unstable because of the acidic hydrogen and easily eliminate the amine to yield the olefin, which then undergoes the Michael reaction.

Snyder and Hamlin (181) prepared 2-methyl-2,4-dinitrohexane and 3,5-dinitroheptane in this manner, and Bachmann and Atwood (6) prepared 2,4-dinitropentane, 4,6-dinitrononane, 2,8-dimethyl-4,6-dinitrononane, and 7,9-dinitropentadecane, as well as 3,5-dinitroheptane (Table VIII). One reason for the low yields reported is apparently the formation of the isoxazole side product,[2] which can easily be formed from 1,3-dinitroalkanes containing tertiary hydrogens.

I. MISCELLANEOUS METHODS

1. *Oxidative Dimerization*

Shechter and Kaplan (170) have studied the action of several chemical oxidants upon primary and secondary nitroalkanes. Oxidation under alkaline conditions of secondary nitro compounds with sodium persulfate results in the formation of *vic*-dinitroalkanes and ketones.



$$2R_2C{=}NO_2^- + S_2O_8^{-2} \xrightarrow{H^+} R_2C(NO_2){-}CR_2(NO_2) + 2SO_4^{-2}$$

$$R_2C{=}NO_2^- + 2S_2O_8^{-2} \xrightarrow[H^+]{2H_2O} R_2C{=}O + 4H^+ + NO_3^- + 4SO_4^{-2}$$

Thus, 2,3-dimethyl-2,3-dinitrobutane (51–62%) and acetone (8–27%), 3,4-dimethyl-3,4-dinitrohexane (37%) and 2-butanone (48%), and 1,1′-dinitrobicyclohexyl (26–30%) and cyclohexanone (66%) are obtained from the salts of 2-nitropropane, 2-nitrobutane, and nitrocyclohexane, respectively, at 0–5°. Other oxidizing agents, such as peroxide, ferricyanide, bromate, and permanganate, were less effective. The method fails with 1,1-dinitroethane, nitroform, and nitroethane.

2. *Electrolytic Methods*

The electrolytic coupling of primary and secondary nitroalkanes in basic media has been reported by Bahner (7, 8). Nitrocyclohexane, 2-nitropropane, and 2-nitrobutane were studied. In addition to the coupled product, small yields of the *gem*-dinitroalkanes were produced in the presence of excess nitrite ion.

The electrolytic preparation of *gem*-dinitroparaffins using a silver anode has been studied by Wright and Levering (202). This method is similar to the chemical reduction of Kaplan and Shechter (93), the silver ion being generated at the anode. The reactions taking place in the cell are

anode: $2Ag^0 \rightarrow 2Ag^+ + 2e$
anode compartment: $2Ag^+ + CH_3CH{=}NO_2^- + NO_2^- \rightarrow 2Ag^0 + CH_3C(NO_2){=}NO_2^- + H^+$
cathode: $2H_2O + 2e \rightarrow 2OH^- + 2H_2$

Under optimum conditions, nitroethane is converted to 1,1-dinitroethane in 80% yield. The preparation of 1,1-dinitropropane and 2,2-dinitropropane was also reported by this method. A cell containing a bed of powdered silver as the anode, permitting continuous operation, has been designed.

The conversion of 1,1-dinitroalkanes to 1,1,1-trinitroalkanes by electrolysis in basic solution and in the presence of excess nitrite ion has also been reported (74). The 1,1,1-trinitroethane, -propane, and -butane were prepared, although in poor yield (10–20%), from the corresponding *gem*-dinitroalkanes.

III. REACTIONS OF POLYNITRO COMPOUNDS

A. REACTIONS INVOLVING ONE OR MORE NITRO GROUPS

1. *Hydrolysis in Neutral or Mineral Acid Media*

It is well known from early work that the nitronate salts of compounds containing a terminal dinitromethyl group can generally be converted to the free *gem*-dinitromethyl compounds in good yield upon treatment with mineral acid (113, 164). The exceptions seem to be those cases where the free polynitro compound is not isolable, *e.g.*, dinitromethane and *sym*-tetranitroethane. The Nef reaction, conversion of the nitronate salt of a mononitroparaffin to a carbonyl group upon neutralization with dilute mineral acid, is not found to occur in compounds containing nitronitronate groups. An excellent review of this reaction pertaining to mononitro compounds is given by Noland (128). Feuer and Aguilar (27) reported that disodium 5,9-dinitro-2,12-tridecanedione when treated with dilute sulfuric acid undergoes the Nef reaction to give 2,5,9,12-tridecanetetraone. In general, the polynitroalkanes are stable to water or mineral acid hydrolysis; the important exceptions will be discussed below.

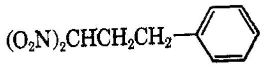
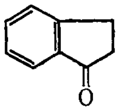
Kamlet and co-workers (92) investigated the effect of prolonged heating of polynitroalkanes in constant boiling hydrochloric acid. It was found that compounds containing a terminal *gem*-dinitromethyl group were hydrolyzed under these conditions to the corresponding carboxylic acid.

$$KO_2N{=}C(NO_2)CH_2CH_2CONH_2 \rightarrow HOOCCH_2CH_2COOH$$

Further examples of hydrolysis reactions are given in Table IX. In contrast to the terminal *gem*-dinitromethyl group, the internal *gem*-dinitromethylene group is not affected under these conditions nor under neutral or basic conditions. Therefore, esters containing an internal *gem*-dinitromethylene group can readily be converted to their corresponding carboxylic acids (172). This reaction will be discussed further in section IIIB.

TABLE IX

HYDROLYSIS OF POLYNITRO COMPOUNDS

Polynitro compound	Conditions	Product	Yield, %	Ref.
Terminal *gem*-trinitro compounds				
$KO_2N{=}C(NO_2)CH_2CH_2CONH_2$	*a*	$HOOCCH_2CH_2COOH$	80	92
$KO_2N{=}C(NO_2)CH{=}CHCONH_2$	*a*	$HOOCCH{=}CHCOOH$	34^b	89
$KO_2N{=}C(NO_2)CH{=}CHCOOMe$	*a*	$HOOCCH{=}CHCOOH$	10^b	92
$(O_2N)_2CHC_6H_4NO_2$-*m*	*a*	$HOOCC_6H_4NO$ -*m*	80	92
$(O_2N)_2CH(CH_2)_2C_6H_3(NO_2)_2$-2,4	*a*	$HOOC(CH_2)_2C_6H_3(NO_2)_2$-2,4	77	92
	*a*		72	92
Trinitromethyl compounds				
$(O_2N)_3CCH_2CH(COOH)CH_2COOH$	*e*	$HOOCCH_2CH(COOH)CH_2COOH$	—	48
$(O_2N)_3CCH_2CH_2COOH$	*c*	$HOOCCH_2CH_2COOH$	—	48
$(O_2N)_3CCH_2OCOR(-NHCOR)$	*c*	$(O_2N)_3CH + HCHO$	—	48
$(O_2N)_3CCH_2C_6H_4NO_2$-*p*	*a*	*p*-$NO_2C_6H_4CHO$	85	92
$(O_2N)_3CCH(C_6H_5)CH_2NO_2$	*a*	C_6H_5COOH	46	92
Miscellaneous compounds				
$NCC(NO_2)_2CH_2CH_2COOMe$	*a*	$HOOCCH_2CH_2COOH$	91	156
$O_2NCBr_2CH_2CH_2CBr_2NO_2$	*a*	$HOOCCH_2CH_2COOH$	73.5	45

[a] Refluxing aqueous hydrochloric acid. [b] Yield up to 80% under milder conditions. [c] Hot water.

Factors governing the acid hydrolysis of terminal trinitromethyl groups are more complex (92). Methyl 4,4,4-trinitrobutyrate is readily converted to 4,4,4-trinitrobutyric acid (>95%) by refluxing with 10% aqueous hydrochloric acid; prolonged heating did not affect the nitro groups. Similarly, 1-(2,4-dinitrophenyl)-3,3,3-trinitropropane was recovered (90%) unchanged after 24 hours of refluxing. However, 1-(4-nitrophenyl)-2,2,2-trinitroethane was converted to *p*-nitrobenzaldehyde (85%) after 24 hours of refluxing, and 2-phenyl-1,1,1,3-tetranitropropane was converted to benzoic acid (46%).

In general, the effect of hot mineral acid on polynitro compounds can be summarized as (92)

Nitro compound	Product
$R'RC(NO_2)_2$	No reaction
$RCH(NO_2)_2$	$RCOOH$
$RR'CHC(NO_2)_3$ (CH not activated)	No reaction
$RR'CHC(NO_2)_3$ (CH activated)	$RR'C{=}O$

The hydrolysis of a compound containing the cyanodinitromethyl group was reported by Parker and coworkers (156).

$$NCC(NO_2)_2CH_2CH_2COOMe \xrightarrow{HCl(aq)} HOOCCH_2CH_2COOH \; 91\%$$

Feuer and Savides (45) reported that hydrolysis of 1,4-dinitro-1,1,4,4-tetrabromobutane with hot aqueous hydrochloric acid gave succinic acid.

Feuer and co-workers (48) found that although 2,2,2-trinitroethylsuccinic acid is stable toward solutions of strong acids, it is decomposed rapidly in hot water, giving 1,2,3-propanetricarboxylic acid.

$$(O_2N)_3CCH_2CH(COOH)CH_2COOH \xrightarrow{H_2O} HOOCCH_2CH(COOH)CH_2COOH$$

This appears to be a general reaction of compounds containing a trinitromethyl group. The exceptions seem to be those cases where 2,2,2-trinitroethanol can be formed.

$$(O_2N)_3CCH_2\text{-}Y \xrightarrow{H_2O} [(O_2N)_3CCH_2OH \rightleftharpoons (O_2N)_3CH + HCHO]$$

where Y = -OCOR, -NHCOR.

2. Reactions with Base and Other Anions

Nitroform and compounds containing a terminal *gem*-dinitromethyl group are readily converted to the corresponding nitronate salts by the action of base. Early work also points out that a "positive" nitro group in tetranitromethane or compounds containing a trinitromethyl group is readily lost upon reaction with base (116, 164). Zeldin and Shechter (203) made a thorough investigation of the action of bases on 1,1,1-trinitroethane and reported that two general types of reactions occurred: (a) attack on a positive nitro group

$$CH_3C(NO_2)_3 + KOH \xrightarrow{\text{(aqueous)}} CH_3C(NO_2){=}NO_2K$$

and (b) attack on an acidic proton

$$CH_3C(NO_2)_3 + KOEt \xrightarrow{\text{(EtOH)}} EtOCH_2C(NO_2){=}NO_2K$$

$$CH_3C(NO_2)_3 + KCN \xrightarrow{\text{(EtOH)}} NCCH_2C(NO_2){=}NO_2K$$

The mechanism of reaction path a must involve a direct reductive attack on the trinitromethyl group, whereas path b must involve a prior attack on a proton of the methyl group.

$$(O_2N)_3CCH_3 + EtO^- \rightarrow [(O_2N)_3CCH_2^-] + EtOH$$

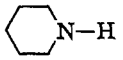
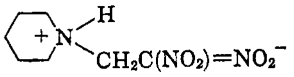
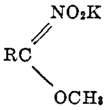
The resulting carbanion could lose nitrite ion to give 1,1-dinitroethylene as a reactive transitory intermediate, which could undergo Michael additions with any nucleophilic species present.

$$[(O_2N)_3CCH_2^-] \xrightarrow{-NO_2^-} [(O_2N)_2C{=}CH_2] \xrightarrow{:Y} {}^-O_2N{=}C(NO_2)CH_2Y$$

Reaction of 1,1,1-trinitroethane with nitrogen bases leads to the formation of interesting zwitterionic compounds (88, 203).

TABLE X

REACTIONS OF POLYNITRO COMPOUNDS WITH BASE

Nitro compound	Base	Product	Yield, %	Ref.
Reductive attack on a "positive" nitro group				
$CH_3C(NO_2)_3$	KOH/H_2O	$CH_3C(NO_2)=NO_2K$	High	203
$CH_3C(NO_2)_3$	H_2NOH/K^+	$CH_3C(NO_2)=NO_2K$	High	203
$CH_3C(NO_2)_3$	$2KO_2N=C(CH_3)_2$	$CH_3C(NO_2)=NO_2K$ +	68	203
		$(CH_3)_2C(NO_2)C(NO_2)(CH_3)_2$	87	203
$CH_3C(NO_2)_3$	$KCH(COCH_3)_2$	$CH_3C(NO_2)=NO_2K$	64.4	203
$CH_3C(NO_2)_3$	n-BuSK	$CH_3C(NO_2)=NO_2K$	42.3	203
$CH_3C(NO_2)_3$	n-BuLi	$CH_3C(NO_2)=NO_2Li$	48[a]	203
Attack on an acidic proton				
$CH_3C(NO_2)_3$	KOEt	$EtOCH_2C(NO_2)=NO_2K$	~80	203
$CH_3C(NO_2)_3$	KOMe	$MeOCH_2C(NO_2)=NO_2K$	~80	203
$CH_3C(NO_2)_3$	KOH/EtOH	$EtOCH_2C(NO_2)=NO_2K$	~80	203
$CH_3C(NO_2)_3$	KCN/EtOH	$NCCH_2C(NO_2)=NO_2K$	~80	203
$CH_3C(NO_2)_3$	$KCH(COOEt)_2$	$(EtOOC)_2CHCH_2(NO_2)=NO_2K$	36.3[b]	203
$CH_3C(NO_2)_3$	 $H_2N\overset{\overset{\displaystyle NH}{\|}}{C}NH_2$	 $H_2N-\overset{\overset{\displaystyle {}^+NH}{\|}}{C}-NHCH_2C(NO_2)=NO_2^-$	84.8	203
$CH_3C(NO_2)_3$			92	203
$CH_3C(NO_2)_3$	$N(CH_3)_3$	$(CH_3)_3\overset{+}{N}-CH_2C(NO_2)=NO_2^-$	90	203
$CH_3C(NO_2)_3$	NH_3	$H_3\overset{+}{N}-CH_2C(NO_2)=NO_2^-$	85	88
$CH_3C(NO_2)_3$	$(CH_3)_2NH$	$(CH_3)_2\overset{+}{N}HCH_2C(NO_2)=NO_2^-$	65	88
$(O_2N)_3CCH_2CH_2NO_2$	KOAc	$KO_2N=C(NO_2)CH_2C(NO_2)=NO_2K$[c]	33.4	89, 132, 133
$(O_2N)_3CCH_2CH(NO_2)CH_3$	KOAc	$KO_2N=C(NO_2)CH_2C(NO_2)_2CH_3$	34.5	133
$(O_2N)_3CCH_2CH(NO_2)CH_2CH_3$	KOAc	$KO_2N=C(NO_2)CH_2C(NO_2)_2CH_2CH_3$	34.5	133
$(O_2N)_3CCH_2CH_2CONH_2$	NH_3/K^+	$KO_2N=C(NO_2)CH=CHCONH_2$	64	89
$(O_2N)_3CCH_2CH_2NO_2$	KI	$KO_2N=C(NO_2)CH_2CH_2NO_2$	23	89
$(O_2N)_3CCH_2CH_2NO_2$	KOH/H_2O_2	$KO_2N=C(NO_2)CH_2C(NO_2)=NO_2K$ + $KO_2N=C(NO_2)CH=CHNO_2$	39 d	89
Miscellaneous reactions				
$(O_2N)_2CHCH_2C(NO_2)_2CH_2CH_2COOCH_3$	KOH	$HOOCCH_2CH_2COOH$	67	107
$RC(NO_2)=C(NO_2)R$	NH_3	$RCH(NO_2)C(R)=NH$ (R = Me, Et)	—	22
$RC(NO_2)=C(NO_2)R$	KOH/CH_3OH	 R = Me, Et	—	22

[a] Yield of the potassium salt. [b] Yield of distilled dinitro compound. [c] Other products also formed (89). [d] Only a small amount formed.

$$(CH_3)_3N + CH_3C(NO_2)_3 \rightarrow (CH_3)_3N^+CH_2C(NO_2)=NO_2^-$$

Kamlet and Dacons (88) report that the zwitterionic products from ammonia or dimethylamine and 1,1,1-trinitroethane react with potassium hydroxide.

$$H_3N^+CH_2C(NO_2)=NO_2^- + KOH \rightarrow [KO_2N=C(NO_2)CH_2]_2NH + [KO_2N=C(NO_2)]_2CH_2$$

$$(CH_3)_2N^+HCH_2C(NO_2)=NO_2^- + KOH \rightarrow KO_2N=C(NO_2)CH_2N(CH_3)_2$$

Further examples of reactions of types a and b are given in Table X.

Novikov and co-workers (132, 133) report that an interesting isomerization takes place when 1,1,1,3-tetranitroalkanes are treated with weak bases.

$$(O_2N)_3CCH_2CH_2NO_2 \xrightarrow[\text{2. } K^+]{\text{1. } NH_4OH} KO_2N=C(NO_2)CH_2C(NO_2)=NO_2K + \text{other products}$$

$$(O_2N)_3CCH_2CH(NO_2)CH_3 \xrightarrow{KOAc} KO_2N=C(NO_2)CH_2C(NO_2)_2CH_3$$

$$(O_2N)_3CCH_2CH(NO_2)CH_2CH_3 \xrightarrow{KOAc} KO_2N=C(NO_2)CH_2C(NO_2)_2CH_2CH_3$$

Kamlet and co-workers (89) confirmed the isomerization of 1,1,1,3-tetranitropropane to dipotassium 1,1,3,3-tetranitropropane; however, the identity of the other products and the proposed mechanistic path was shown to be in error.

Potassium 1,1,3-trinitropropane, identified by Novikov and co-workers (132, 133) as one of the products, was supposedly prepared by an independent method, namely, treatment of 1,1,1,3-tetranitropropane with dimethylamine and then potassium chloride. However, Kamlet and co-workers (89) proved this compound to be potassium 1,1,3-trinitro-2-propene by direct and independent synthesis of all compounds in question.

$$(O_2N)_3CCH_2CH_2NO_2 \xrightarrow{OH^-} KO_2N=C(NO_2)CH_2C(NO_2)=NO_2K + KO_2N=C(NO_2)CH=CHNO_2$$

$$(O_2N)_3CCH_2CH_2NO_2 \overset{KI}{\rightarrow} KO_2N=C(NO_2)CH_2CH_2NO_2$$

$$KO_2N=C(NO_2)CH_2OH + CH_2=CHNO_2 \rightarrow [HOCH_2C(NO_2)_2(CH_2)_2NO_2] \rightarrow KO_2N=C(NO_2)(CH_2)_2NO_2$$

TABLE XI

CONVERSION OF TRINITROMETHYL GROUPS TO *gem*-NITRONITRONATE GROUPS

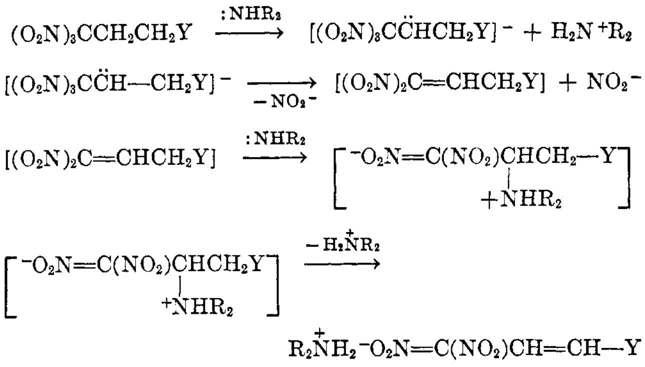
Trinitromethyl compound	Anion	Yield, % KI[a] (63)	Yield, % KOH/H_2O_2[b] (62)
$(O_2N)_3CCH_3$	${}^-O_2N{=}C(NO_2)CH_3$	81	99.8
$(O_2N)_3CCH_2CH_3$	${}^-O_2N{=}C(NO_2)CH_2CH_3$		100.9
$(O_2N)_3CCH_2CH_2CH_2CH_3$	${}^-O_2N{=}C(NO_2)CH_2CH_2CH_2CH_3$		99.4
$(O_2N)_3CCH_2CH_2COOH$	${}^-O_2N{=}C(NO_2)CH_2CH_2COO^-$		100.3
$(O_2N)_3CCH_2CH_2COOMe$	${}^-O_2N{=}C(NO_2)CH_2CH_2COOMe$	77	100.0
$(O_2N)_3CCH_2CH_2COC_6H_5$	${}^-O_2N{=}C(NO_2)CH_2CH_2COC_6H_5$	17	98.2
$(O_2N)_3CCH_2CH_2COCH_3$	${}^-O_2N{=}C(NO_2)CH_2CH_2COCH_3$	40	97.8
$(O_2N)_3CCH(C_6H_5)CH_2NO_2$	${}^-O_2N{=}C(NO_2)_2$[c]		100.2
$(O_2N)_3CCH_2CH_2COOCH_2C(NO_2)_3$	${}^-O_2N{=}C(NO_2)CH_2CH_2COO^-$, ${}^-O_2N{=}C(NO_2)_3$		99.8

[a] Isolated yield. [b] Spectrophotometrically determined yield. [c] Nitroform anion is species obtained, arising through a reverse Michael reaction (85).

An exact analogy for the formation of the olefin in the rearrangement of 1,1,1,3-tetranitropropane with base is found in the following reaction.

$$(O_2N)_3CCH_2CH_2CONH_2 \xrightarrow[2.\ K^+]{1.\ NH_3} KO_2N{=}C(NO_2)CH{=}CHCONH_2\ (64\%)$$

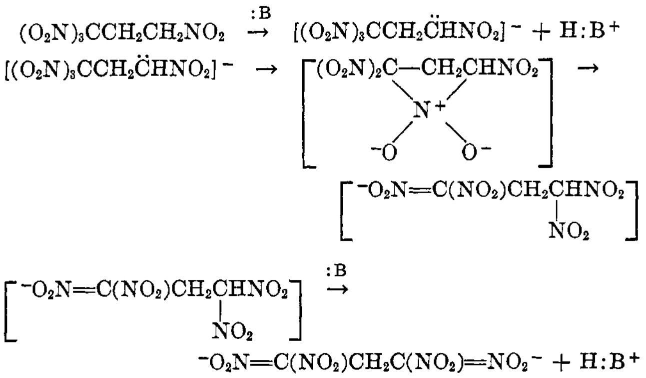
The mechanisms proposed by Kamlet and co-workers (89) for the formation of the observed products conform to all experimental evidence and find support in the previous work on the conversion of 1,1,1-trinitroethane to zwitterionic derivatives of 2,2-dinitroethylamine by reaction with nitrogen bases (88, 203). The mechanisms are: formation of the olefins



$$(O_2N)_3CCH_2CH_2Y \xrightarrow{:NHR_2} [(O_2N)_3C\ddot{C}HCH_2Y]^- + H_2N^+R_2$$
$$[(O_2N)_3C\ddot{C}H\text{—}CH_2Y]^- \xrightarrow[-NO_2^-]{} [(O_2N)_2C{=}CHCH_2Y] + NO_2^-$$
$$[(O_2N)_2C{=}CHCH_2Y] \xrightarrow{:NHR_2} \left[{}^-O_2N{=}C(NO_2)\underset{+NHR_2}{C}HCH_2\text{—}Y\right]$$
$$\left[{}^-O_2N{=}C(NO_2)\underset{+NHR_2}{C}HCH_2Y\right] \xrightarrow{-H_2\overset{+}{N}R_2} R_2\overset{+}{N}H_2{}^-O_2N{=}C(NO_2)CH{=}CH\text{—}Y$$

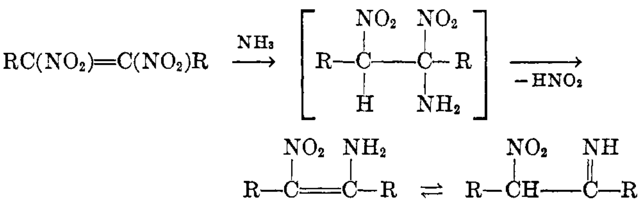
Y = -NO₂, -CONH₂

and rearrangement.



$$(O_2N)_3CCH_2CH_2NO_2 \xrightarrow{:B} [(O_2N)_3CCH_2\ddot{C}HNO_2]^- + H{:}B^+$$
$$[(O_2N)_3CCH_2\ddot{C}HNO_2]^- \rightarrow \left[\begin{array}{c}(O_2N)_2C\text{—}CH_2CHNO_2\\ \diagdown\quad\diagup\\ N^+\\ \diagup\quad\diagdown\\ {}^-O\qquad O^-\end{array}\right] \rightarrow \left[{}^-O_2N{=}C(NO_2)CH_2\underset{NO_2}{C}HNO_2\right]$$
$$\left[{}^-O_2N{=}C(NO_2)CH_2\underset{NO_2}{C}HNO_2\right] \xrightarrow{:B} {}^-O_2N{=}C(NO_2)CH_2C(NO_2){=}NO_2^- + H{:}B^+$$

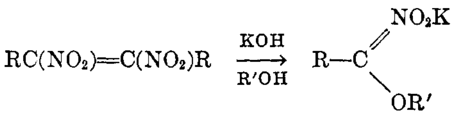
Clapp and co-workers (22) reported that the reaction of *vic*-dinitroolefins with ammonia led to the formation of a nitroimine.



$$RC(NO_2){=}C(NO_2)R \xrightarrow{NH_3} \left[R\text{—}\overset{NO_2}{\underset{H}{C}}\text{—}\overset{NO_2}{\underset{NH_2}{C}}\text{—}R\right] \xrightarrow[-HNO_2]{} R\text{—}\overset{NO_2}{C}{=}\overset{NH_2}{C}\text{—}R \rightleftharpoons R\text{—}\overset{NO_2}{C}H\text{—}\overset{NH}{\overset{\|}{C}}\text{—}R$$

R = Me, Et

However, reaction with potassium hydroxide in alcohol led to different products.



$$RC(NO_2){=}C(NO_2)R \xrightarrow[R'OH]{KOH} R\text{—}C\begin{array}{l}/\!\!/ NO_2K\\ \backslash\, OR'\end{array}$$

Table X lists various reactions of polynitro compounds with base.

Glover and Kamlet (63) reported the conversion of trinitromethyl groups to the corresponding nitronitronate groups by reductive attack of potassium iodide. More recently, Glover reported the quantitative reductions of many trinitromethyl compounds to the corresponding dinitro anions with basic hydrogen peroxide (62) and has used this reaction as the basis for spectrophotometric quantitative analysis of trinitromethyl compounds. The exceptions were cases in which trinitroethanol could be formed; here a quantitative conversion to potassium nitroform was effected and analyzed spectrophotometrically. Table XI lists typical examples of the two methods for comparison. It is interesting to note that 2,2,2-trinitroethyl 4,4,4-trinitrobutyrate gave a quantitative conversion to an equimolar mixture of nitroform and 4,4-dinitrobutyric acid.

Tetranitromethane under basic conditions has been used effectively as a nitrating agent for aromatic compounds such as azulene (3), and somewhat less effectively for the nitration of aliphatic nitro compounds as described in a patent by Plummer (158) (see section II).

Tetranitromethane also reacts with tertiary amines to give secondary N-nitrosamines (111). The secondary nitrosamine can be hydrogenated to the free secondary amine, thus providing a convenient method for degrading a tertiary amine to a secondary amine.

3. Reduction of Polynitro Compounds

a. Catalytic Reduction

The catalytic reduction of *vic*-dinitroolefins was studied by Clapp and co-workers (22) using high-pressure (3000 p.s.i.) hydrogen with Raney nickel or platinum oxide.

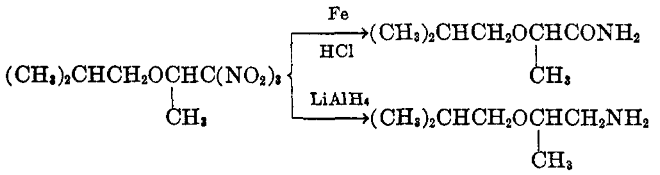
$$R\text{—}C(NO_2)\text{=}C(NO_2)R \xrightarrow[Ni(W\text{-}6)]{H_2} RCH(NH_2)CH(NH_2)R \qquad \underset{33\%}{R = Me} \quad \underset{25\%}{Et}$$

$$R\text{—}C(NO_2)\text{=}C(NO_2)R \xrightarrow[PtO_2]{H_2} RCH(NH_2)CH(NH_2)R \qquad \text{—} \quad 23\%$$

Grabiel and co-workers (69) reported that the reduction of 2,2,3,3-tetanitrobutane with Adams catalyst under 1 atmosphere pressure gave a 70% yield of 2,3-diaminobutane. A similar reduction of 3,3,4,4-tetranitrohexane gave a 70% yield of 3,4-diaminohexane.

b. Chemical Reduction

Shechter and Cates (168) have studied the chemical reductions of a trinitromethyl-substituted ether.



$$(CH_3)_2CHCH_2O\underset{\displaystyle CH_3}{\underset{|}{C}}HC(NO_2)_3 \begin{cases} \xrightarrow[HCl]{Fe} (CH_3)_2CHCH_2O\underset{\displaystyle CH_3}{\underset{|}{C}}HCONH_2 \\ \xrightarrow{LiAlH_4} (CH_3)_2CHCH_2O\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2NH_2 \end{cases}$$

The reduction of *gem*-dinitro- and trinitromethyl compounds with titanium(III) chloride has been studied in an effort to develop an analytical technique for the determination of polynitro compounds (26). However, the results vary randomly, and the technique at best can be used only for assay of specific compounds; in fact, it is more applicable to nitramines (204).

c. Electrochemical Reduction

The electrochemical characteristics of several polynitro compounds have been determined by Glicksman and Morehouse (61). With the data obtained, they have extended to nitroalkanes the theory which had been used to explain the effect of substituent groups and their positions on the operating potential of aromatic nitro compounds. This theory is based on the electron density in the vicinity of a reducible nitro group. The high theoretical ampere-minute capacity, together with the high operating potentials of the polynitroalkanes, shows that these compounds may have use as cathode materials in primary cells.

The polarographic behavior and controlled potential electrolysis of polynitro compounds have been investigated by several workers (117–119, 160, 185). The results indicate that if a *gem*-dinitro group also has a proton on the same carbon, reduction takes place mainly through conversion of one nitro group into the *aci*-form without C–N bond fission. For compounds without a proton on the carbon carrying the nitro groups, the first step involves C–N bond fission to produce nitrite ion and an *aci*-nitro compound. Nitroform at pH 6 and pH 2 undergoes a 12-electron change and gives as a product, dihydroxyguanidine. At pH 12, a 14-electron change takes place to give hydroxyguanidine. At pH 6 or pH 2, 1,1,1-trinitroethane undergoes a 6-electron change to give a hydroxyamidoxime $CH_3C\text{=}NOH(NHOH)$, and at pH 12 an 8-electron change to give an amidoxime $CH_3C\text{=}NOH(\text{-}NH_2)$.

4. Effect of Radiation

Light, particularly at λ_{max} of the nitronitronate ion in aqueous solution, promotes the decomposition of aliphatic nitro compounds and their salts (177). The decomposition causes increasing acidity of the solution.

γ-Radiation of nitro compounds has been studied by Henglein and co-workers (78–80). The decomposition of tetranitromethane by Co^{60} γ-radiation gives nitroform as a first product ($G = 3.73$). The nitroform undergoes further decomposition to dinitromethane and further degradation products. The rate of decomposition of tetranitromethane by γ-radiation is not affected by dissolved oxygen but decreases with increasing pH.

5. Analytical Methods

Analytical methods suitable for the quantitative determination of polynitro compounds have been described in the literature (12, 26, 62, 204), although no single method is applicable to all types of polynitro compounds. Reduction of the nitro compound with $TiCl_3$ (26, 204) may be applicable, but the quantity of reagent consumed varies with the conditions and the compound to be reduced.

Glover (62) has described a general method for the spectrophotometric determination of the dinitromethyl anion generated from a trinitromethyl compound by alkaline hydrogen peroxide. The mechanism, scope, and limitations of the method are discussed.

B. REACTIONS NOT AFFECTING NITRO GROUPS

1. Carbonyl Condensation Reactions

Because of the acidic nature of the protons α to a nitro group, nitroalkanes undergo many of the condensation reactions common to compounds such as β-keto esters. Three general types of condensations will be discussed: (a) the Henry reaction—the condensation of a polynitroalkane having an α-proton, with an aldehyde to produce a β-nitro-substituted alkanol; (b) the Aldol condensation—the condensation of a nitroalkane with an aldehyde, followed by elimination of water to give an olefin; (c) the Mannich reaction—the condensation of a nitroalkane with an aldehyde and an amine to produce a β-nitro-substituted alkylated amine.

a. Henry Reaction

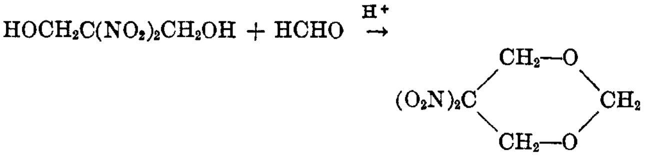
One of the first polynitroalkanes reported to undergo the Henry reaction was nitroform, which when reacted with formaldehyde gave 2,2,2-trinitroethanol (116). The product was probably isolated as a hydrate which was hygroscopic and difficult to purify. Feuer and Kucera (35) recently described a convenient procedure to obtain pure anhydrous 2,2,2-trinitroethanol (m.p. 72°), which is not hygroscopic. The reaction, which is acid-catalyzed, is reversed in base (pH >5.5 in the case of 2,2,2-trinitroethanol) to give the salt of the nitro compound and formaldehyde, a reaction referred to as "demethylolation."

The condensation of dinitromethane and 1,1-dinitroethane with glyoxalic acid was reported by Kissinger and co-workers (96). The reaction gave the expected α-hydroxyacid; however, when the condensation was attempted with glyoxal, the *same* α-hydroxyacid was obtained as the product.

$$KO_2N{=}CHNO_2 + OCHCOOH \rightarrow (O_2N)_2CHCH(OH)COOH$$

$$CH_3CH(NO_2)_2 + OCHCOOH \rightarrow CH_3C(NO_2)_2CH(OH)COOH$$

Feuer and co-workers (29) reported that the bismethylol derivative of dinitromethane, 2,2-dinitropropanediol, was readily prepared by treating potassium dinitromethane with excess formalin in the presence of acetic acid. The reaction is reversed in two distinct steps on treatment with base. The first product, the salt of 2,2-dinitroethanol, is obtained in excellent yield by the action of one mole of base at room temperature. Demethylolation of the salt of 2,2-dinitroethanol is effected only by heating with excess base, resulting in slow conversion to the salt of dinitromethane. Gold and co-workers (66) reported that, contrary to reports in the older literature, 2,2-dinitroethanol can be liberated from its salts by treatment with mineral acid and that the product can be distilled in a molecular still and stored for reasonably long periods of time at −20°. They also found that 2,2-dinitropropanediol will undergo further condensation with formaldehyde to the cyclic formal, 5,5-dinitro-1,3-dioxan.

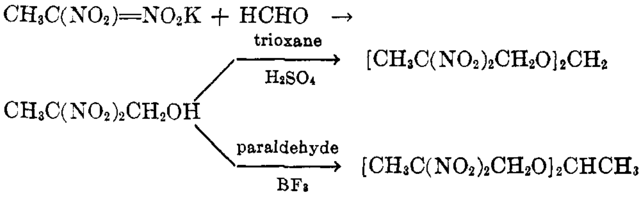


Klager and co-workers (107) prepared the bismethylol derivative of 1,1,3,3-tetranitropropane, 2,2,4,4-tetranitro-1,5-pentanediol. Klager also reported (104) that, contrary to other dinitromethylalkanes and derivatives, bis(potassium 2,2-dinitroethyl)amine or its N-substituted derivatives did not give methylol derivatives when treated with formaldehyde.

Feuer and co-workers (43) and Nielsen (124) reported the synthesis and properties of the various methylol derivatives of α,ω-dinitroalkanes. Separation and identification of the epimers of the α,ω-dinitro-α,ω-dimethylolalkanes was effected. The mechanism of the acid-catalyzed isomerization through the *aci*-nitro tautomer has also been reported (42, 43).

Novikov and co-workers (134) reported that the condensation of acetaldehyde and propionaldehyde with dinitromethane gave the expected dinitromethyl-substituted alkanols, isolated as the 3,5-dinitrobenzoates; however, necessary experimental data are lacking.

A recent article describes the process for the production of nitroplasticizers (4). The process involves the conversion of potassium 1,1-dinitroethane to 2,2-dinitropropanol, which is then converted to the bisformal and bisacetal derivatives.



A summary of the polynitroalcohols obtained from the Henry reaction is given in Table XII. A review through 1957 of the preparation and properties of many nitro alcohols is given by Shvekhgeimer, Pyatakov, and Novikov (174).

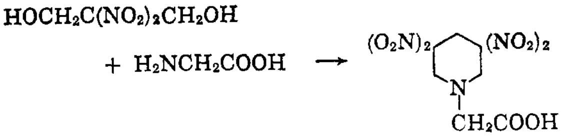
b. Aldol Condensations

Zonis and Perekalin (206) reported that the condensation of α,ω-dinitroalkanes with aromatic aldehydes in the presence of ethylenediamine or ammonium acetate–acetic acid catalysts produced α,ω-diaryl-α,ω-dienes.

$$O_2NCH_2CH_2CH_2CH_2NO_2 + C_6H_5CHO \rightarrow C_6H_5CH{=}C(NO_2)CH_2CH_2C(NO_2){=}CHC_6H_5$$

c. Mannich Reaction

The Mannich reaction has been extended to polynitroalkanes and provides an extremely useful method for the preparation of polynitroamines and derivatives. Feuer, Bachman, and May (30) reported that the condensation of 2,2-dinitropropanediol or sodium 2,2-dinitroethanol (methylol derivatives of dinitromethane) with glycine at pH 4 resulted in the formation of a cyclic product, 3,3,5,5-tetranitropiperidine-N-acetic acid. However, ethylglycine hydrochloride or ethanolamine under the same conditions did not give cyclic products.



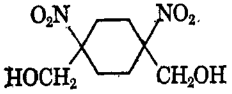
$$NaO_2N{=}C(NO_2)CH_2OH + HCl\cdot H_2NCH_2COOEt \rightarrow (O_2N)_2CHCH_2NHCH_2COOEt$$

$$HOCH_2C(NO_2)_2CH_2OH + H_2NCH_2CH_2OH \rightarrow (O_2N)_2CHCH_2NHCH_2CH_2OH$$

Treatment of 5,5-dinitro-3-aza-1-pentanol with acetyl

TABLE XII

THE HENRY REACTION $[RCH(NO_2)_2 + HCHO \xrightarrow{H^+} RC(NO_2)_2CH_2OH]$

Nitro compound	Carbonyl compound	Product	M.p., °C.	Yield, %	Ref.
C_1					
$KO_2N{=}CHNO_2$	HCHO	$HOCH_2C(NO_2)_2CH_2OH$	142	66	29, 66
$KO_2N{=}CHNO_2$	$HCOCO_2H$	$(O_2N)_2CHCH(OH)COOH$	124–127 dec.	66	96
$KO_2N{=}CHNO_2$	EtOCH(OH)COOEt	$(O_2N)_2CHCH(OH)COOEt$	Oil	90	96
$(O_2N)_3CH$	HCHO	$(O_2N)_3CCH_2OH$	72	80	35
C_2					
$CH_3CH(NO_2)_2$	HCHO	$CH_3C(NO_2)_2CH_2OH$	95–96	—	196, 213
$CH_3CH(NO_2)_2$	$HCOCO_2H$	$CH_3C(NO_2)_2CH(OH)COOH$	101–102	40	96
$CH_3CH(NO_2)_2$	EtOCH(OH)COOEt	$CH_3C(NO_2)_2CH(OH)COOEt$	44–45	61	96
$HOCH_2CH(NO_2)_2$	HCHO	$HOCH_2C(NO_2)_2CH_2OH$	142	76	66
$HC(NO_2)_2CN$	HCHO	$HOCH_2C(NO_2)_2CN$	Oil; n^{20}_D 1.4470	95	156
$HC(NO_2)_2CONH_2$	HCHO	$HOCH_2C(NO_2)_2CONH_2$	104–107	39.4	153
C_3					
$[KO_2N{=}C(NO_2)]_2CH_2$	HCHO	$HOCH_2C(NO_2)_2CH_2C(NO_2)_2CH_2OH$	97–99 dec.	35	107
C_4					
$O_2NCH_2CH_2CH_2CH_2NO_2$	HCHO	$(HOCH_2)_2C(NO_2)CH_2CH_2C(NO_2)(CH_2OH)_2$	180–182	91	**43**
$O_2NCH_2CH_2CH_2CH_2NO_2$	HCHO	$HOCH_2CH(NO_2)CH_2CH_2CH(NO_2)CH_2OH$	[a]	77	**43**
$O_2NCH_2CH_2CH_2CH_2NO_2$	HCHO	$HOCH_2CH(NO_2)CH_2CH_2CH_2NO_2$	Oil	48	43
$(O_2N)_2CHCH_2C(NO_2)_2CH_3$	HCHO	$HOCH_2C(NO_2)_2CHC(NO_2)_2CH_3$	66–67	—	50
C_5					
$O_2N{-}(CH_2)_5{-}NO_2$	HCHO	$O_2NCH_2CH_2CH_2CH_2CH(NO_2)CH_2OH$	Oil; n^{20}_D 1.4745	44	43, 122
$O_2N{-}(CH_2)_5{-}NO_2$	HCHO	$HOCH_2CH(NO_2)(CH_2)_3CH(NO_2)CH_2OH$	[a]	38	43
Others					
$[KO_2N{=}C(CN)CH_2]_2$	HCHO	$[HOCH_2C(CN)(NO_2)CH_2]_2$	[a]	—	44
	HCHO		[a]	98.5	124

[a] Mixture of epimers.

chloride resulted in the formation of N-acetyl-β-aminoethanol by acetolysis (30).

Frankel and Klager (54) studied the reaction of various 2,2-dinitro-1-alkanols with ammonia, glycine, and hydrazine. It was observed that little or no Mannich-type product was formed with ammonia unless the reaction mixture was buffered with ammonium acetate. The condensation of methylglycine and 2,2-dinitropropanol at pH 7 gave 5,5-dinitro-3-azahexanoate whereas at pH 9 or higher, the product was bis(2,2-dinitropropyl)glycine. When hydrazine was used as the base, 2,2-dinitropropanol gave the symmetrical bis condensation product. It is obvious from the work of Feuer and Frankel that the course of the reaction is greatly dependent upon pH. Recently, Frankel and Klager (57) have extended this reaction to include polynitroaliphatic primary amines and diamines as the base.

It has been generally observed that the Mannich base products from polynitro compounds are unstable. In many cases, the products are converted to the more stable nitraza derivative by treatment with mixed acid (HNO_3–H_2SO_4). A convenient procedure for the isolation of the nitraza derivative of an amino alcohol is described by Wolfrom and co-workers (201). Feuer and Swarts (47) extended this procedure to polynitro-substituted nitraza alcohols.

$$(O_2N)_3CH + HCHO + H_2NCH_2CH_2OH \rightarrow [(O_2N)_3CCH_2NHCH_2CH_2OH]$$

$$[(O_2N)_3CCH_2NHCH_2CH_2OH] + HNO_3 \xrightarrow{H_2SO_4} (O_2N)_3CCH_2N(NO_2)CH_2CH_2ONO_2$$

$$(O_2N)_3CCH_2N(NO_2)CH_2ONO_2 + Ac_2O \xrightarrow{H_2SO_4} (O_2N)_3CCH_2N(NO_2)CH_2CH_2OAc$$

$$(O_2N)_3CCH_2N(NO_2)CH_2CH_2OAc + HCl(g) \xrightarrow{MeOH} (O_2N)_3CCH_2N(NO_2)CH_2CH_2OH$$

Direct hydrolysis of the nitrate ester in acid media leads to the decomposition of the product (47), and basic hydrolysis cannot be applied because of the instability of the trinitromethyl group toward base (see section IIIA2).

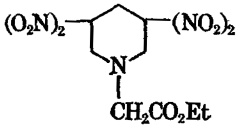
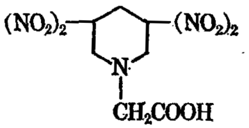
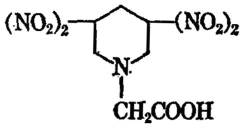
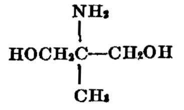
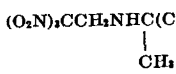
Feuer and Lynch-Hart (38) observed that, although nitroform does not react with methacrylamide and formaldehyde to give the expected Mannich product, the product was realized by treating nitroform with N-methylolmethacrylamide. Novikov and co-workers (134) have extended the reaction to aliphatic aldehydes other than formaldehyde.

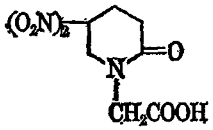
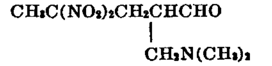
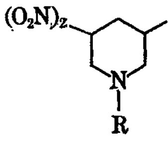
Frankel and Klager (53, 57) reported many examples of the use of the Mannich reaction in the preparation of polynitroaliphatic nitramines. Hamel (72) reported obtaining Mannich-type products using such intermediates as a polynitroaldehyde, a fluoroalkylamine, and a silyl-substituted alkylamine.

An early patent to Schenck (166) claims the formation of tris condensation products from 2,2,2-trinitroethanol and ammonia. Later patents (167), however, show that the product is actually bis(2,2,2-trinitroethyl)-amine. Reaction of trinitroethanol with urea produces bis(2,2,2-trinitroethyl)urea (167). Murray and Sauer (120) claim that condensation of nitroform with hexamethylenetetramine also gives bis(2,2,2-trinitroethyl)-amine. Table XIII gives a summary of Mannich reactions involving polynitroalkanes and derivatives.

TABLE XIII

THE MANNICH REACTION

Nitro compound	Base	Aldehyde	Product	m.p., °C.	Yield, %	$N\text{-}NO_2$ m.p., °C.	Ref.
Dinitromethyl							
$(O_2N)_2CH_2$	NH_3	CH_3CH_2CHO	$(O_2N)_2CH—CH(CH_2CH_3)NH_2$	117 dec.	46	—	134
$(O_2N)_2CH_2$	NH_3	$CH_3CH_2CH_2CHO$	$(O_2N)_2CH—CH(CH_2CH_2CH_3)NH_2$	112 dec.	46	—	134
$(O_2N)_2CH_2$	CH_3NH_2	CH_3CHO	$(O_2N)_2CHCH(CH_3)NHCH_3$	100–101 dec.	77.9	—	134
$(O_2N)_2CH_2$	CH_3NH_2	CH_3CH_2CHO	$(O_2N)_2CHCH(CH_2CH_3)NHCH_3$	97 dec.	66.5	—	134
$(O_2N)_2CH_2$	CH_3NH_2	$CH_3CH_2CH_2CHO$	$(O_2N)_2CHCH(CH_2CH_2CH_3)NHCH_3$	82.3 dec.	65.5	—	134
$(O_2N)_2C(CH_2OH)_2$	$EtO_2CCH_2NH_2 \cdot HCl$	$(HCHO)^a$		126–127	20	—	134
$(O_2N)_2C(CH_2OH)_2$	$HO_2CCH_2NH_2$	(HCHO)		145–146	52	—	30
$NaO_2N{=}C(NO_2)CH_2OH$	$HO_2CCH_2NH_2 \cdot HCl$	(HCHO)		147	25	—	30
$NaO_2N{=}C(NO_2)CH_2OH$	$EtO_2CCH_2NH_2 \cdot HCl$	(HCHO)	$(O_2N)_2CHCH_2NHCH_2CO_2Et$	102–103 dec.	65	41–42	30
$(O_2N)_2C(CH_2OH)_2$	$H_2NCH_2CH_2OH$	(HCHO)	$(O_2N)_2CHCH_2NHCH_2CH_2OH$	115–116 dec.	82	—	30
$NaO_2N{=}C(NO_2)CH_2OH$	$H_2NCH_2CH_2OH$	(HCHO)	$(O_2N)_2CHCH_2NHCH_2CH_2OH$	117 dec.	69	—	30
$(O_2N)_2C(CH_2OH)_2$	$CH_3N(NO_2)CH_2CH_2NH_2$	(HCHO)	$(O_2N)_2C[CH_2NHCH_2CH_2N(NO_2)CH_3]_2$	110–115	63	—	72
$(O_2N)_2C(CH_2OH)_2$	$CH_3C(NO_2)_2CH_2CH_2NH_2$	(HCHO)	$(O_2N)_2C[CH_2NHCH_2CH_2C(NO_2)_2CH_3]_2$	95–110	74.2	137–139	57
$(O_2N)_2C(CH_2OH)_2$	$(O_2N)_3CCH_2CH_2NH_2$	(HCHO)	$(O_2N)_2C[CH_2NHCH_2CH_2C(NO_2)_3]_2$	70–80	83.8	157–159	57
$KO_2N{=}C(NO_2)CH_2OH$	NH_3	(HCHO)	$[KO_2N{=}C(NO_2)CH_2]_2NH$	—	—	78	104
Trinitromethyl							
$(O_2N)_3CH$	$CH_2{=}C(CH_3)CONHCH_2OH$	(HCHO)	$CH_2{=}C(CH_3)CONHCH_2C(NO_2)_3$	74–75	87	128–128.5	38
$(O_2N)_3CH$	$CH_2{=}CHCONHCH_2OH$	(HCHO)	$CH_2{=}CHCONHCH_2C(NO_2)_3$	90.5–91	—	179–179.5	38
$(O_2N)_3CH$	$(O_2N)_3CCH_2CH_2CONHCH_2OH$	(HCHO)	$(O_2N)_3CCH_2CH_2CONHCH_2C(NO_2)_3$	150–151	80	—	38
$(O_2N)_3CH$	$CH_2{=}C(CH_3)CONHCH_2OCOC_6H_5$	(HCHO)	$CH_2{=}C(CH_3)CONHCH_2C(NO_2)_3$	73–74	64	—	39
$(O_2N)_3CH$	$[C_6H_5CO_2CH_2NHCOCH{=}]_2$	(HCHO)	$(O_2N)_3CCH_2NHCOCH{=}CHCONHCH_2C(NO_2)_3$	197 dec.	47	—	39
$(O_2N)_3CH$	$H_2NCH_2CH_2OH$	(HCHO)	$(O_2N)_3CCH_2NHCH_2CH_2OH$	—	33.9	74	47
$(O_2N)_3CH$	$H_2NCH_2CH_2CH_2OH$	(HCHO)	$(O_2N)_3CCH_2NHCH_2CH_2CH_2OH$	—	56.4	50–50.5	47
$(O_2N)_3CH$	 $HOCH_2\overset{\overset{\textstyle NH_2}{\mid}}{\underset{\underset{\textstyle CH_3}{\mid}}{C}}—CH_2OH$	(HCHO)	 $(O_2N)_3CCH_2NH\underset{\underset{\textstyle CH_3}{\mid}}{C}(CH_2OH)_2$	—	10.6^b	116–117 dec.	47
$(O_2N)_3CH$	$C_6H_{12}N_4$	(HCHO)	$[(O_2N)_3CCH_7]_2NH$	114	60–70	—	120
$(O_2N)_3CCH_2OH$	NH_3	(HCHO)	$[(O_2N)_3CCH_2]_2NH$	107	90	—	167
$(O_2N)_3CCH_2OH$	$CH_3C(NO_2)_2CH_2CH_2NH_2$	(HCHO)	$CH_3C(NO_2)_2CH_2CH_2NHCH_2C(NO_2)_3$	Oil	71.7	105–107	57
$(O_2N)_3CCH_2OH$	$(O_2N)_3CCH_2CH_2NH_2$	(HCHO)	$(O_2N)_3CCH_2NHCH_2CH_2C(NO_2)_3$	64–65	79	114–115	57
$(O_2N)_3CCH_2OH$	$CH_2(NH_2)_2$	(HCHO)	$CH_2[NHCH_2C(NO_2)_3]_2$	100–105	93.1	84–85	57
$(O_2N)_3CCH_2OH$	$(O_2N)_2C(CH_2CH_2NH_2)_2$	(HCHO)	$(O_2N)_2C[CH_2CH_2NHCH_2C(NO_2)_3]_2$	93–95	65.7	170–175	57
$(O_2N)_3CCH_2OH$	$O_2N—N(CH_2CH_2NH_2)_2$	(HCHO)	$O_2N—N[CH_2CH_2NHCH_2C(NO_2)_3]_2$	Gum	33	158–159	57
$(O_2N)_3CCH_2OH$	$[CH_2N(NO_2)CH_2CH_2NH_2]_2$	(HCHO)	$[CH_3N(NO_2)CH_2CH_2NHCH_2C(NO_2)_3]_2$	100–105	100	166–167	57

$(O_2N)_3CCH_2OH$	$N(NO_2)[CH_2C(NO_2)_2CH_2CH_2NH_2]_2$	(HCHO)	$O_2N{-}N[CH_2C(NO_2)_2CH_2CH_2NHCH_2C(NO_2)_3]_2$	90–100	31.3	186–187	57
$(O_2N)_3CCH_2OH$	H_2NCONH_2	(HCHO)	$[(O_2N)_3CCH_2NH]_2CO$	191	82	—	167
1,1-Dinitroethane							
$CH_3C(NO_2)_2CH_2OH$	NH_3	(HCHO)	$NH[CH_2C(NO_2)_2CH_3]_2$	67–68	90.4	—	54
$CH_3C(NO_2)_2CH_2OH$	$CH_3O_2CCH_2NH_2 \cdot HCl$	(HCHO)	$CH_3C(NO_2)_2CH_2NHCH_2CO_2Me$	Oil	77.3	80–81	54
$CH_3C(NO_2)_2CH_2OH$	H_2NCH_2COOH	(HCHO)	$[CH_3C(NO_2)_2CH_2]_2NCH_2COOH$	123–124	92	—	54
$CH_3C(NO_2)_2CH_2OH$	H_2NNH_2	(HCHO)	$CH_3C(NO_2)_2CH_2NHNHCH_2C(NO_2)_2CH_3$	85–86	73	—	54
$CH_3C(NO_2)_2CH_2OH$	$H_2NCH_2CH(OH)CH_2OH$	(HCHO)	$CH_3C(NO_2)_2CH_2NHCH_2CH(OH)CH_2OH$	—	11	60	11
$CH_3CH(NO_2)_2$	NH_3	CH_3CHO	$[CH_3C(NO_2)_2CH(CH_3)]_2NH$	72–73	70	—	134
$CH_3C(NO_2)_2CH_2OH$	$H_2NCH_2CH_2OH$	(HCHO)	$CH_3C(NO_2)_2CH_2NHCH_2CH_2OH$	Oil	21.2[c]	59–60	68
					48		72
$CH_3C(NO_2)_2CH_2OH$	$(O_2N)_3CCH_2CH_2NH_2$	(HCHO)	$CH_3C(NO_2)_2CH_2NHCH_2CH_2C(NO_2)_3$	Oil	100	109–109.5	57
$CH_3C(NO_2)_2CH_2OH$	$(O_2N)_2C(CH_2CH_2NH_2)_2$	(HCHO)	$(O_2N)_2C[CH_2CH_2NHCH_2C(NO_2)_2CH_3]_2$	Oil	100	206–208	57
$CH_3C(NO_2)_2CH_2OH$	$CF_3CH_2NH_2$	(HCHO)	$CH_3C(NO_2)_2CH_2NHCH_2CF_3$	Oil	86	—	72
$CH_3C(NO_2)_2CH_2OH$	$(CH_3)_3SiCH_2NH_2$	(HCHO)	$CH_3C(NO_2)_2CH_2NHCH_2Si(CH_3)_3$	[d]	77	—	72
Cyanodinitromethane							
$HC(NO_2)_2CN$	$C_6H_5CONHCH_2OH$	(HCHO)	$C_6H_5CONHCH_2C(NO_2)_2CN$	76.5–77.5	33	—	156
$HC(NO_2)_2CN$	$CH_2{=}C(CH_3)CONHCH_2OH$	(HCHO)	$CH_2{=}C(CH_3)CONHCH_2C(NO_2)_2CN$	74–5	27	—	156
$HC(NO_2)_2CN$	$CH_2{=}CHCONHCH_2OH$	(HCHO)	$CH_2{=}CHCONHCH_2C(NO_2)_2CN$	77–8	20	—	156
$HC(NO_2)_2CN$	$HOCH_2NHCONHCH_2OH$	(HCHO)	$NCC(NO_2)_2CH_2NHCONHCH_2C(NO_2)_2CN$	134	4	—	156
$HC(NO_2)_2CONH_2$	$CH_2{=}C(CH_3)CONHCH_2OH$	(HCHO)	$CH_2{=}C(CH_3)CONHCH_2C(NO_2)_2CONH_2$	116–117	18.3	—	153
Other polynitro compounds							
$CH_3CH_2CH(NO_2)_2$	NH_3	CH_3CHO	$[CH_3CH_2C(NO_2)_2CH(CH_3)NH]_2CHCH_3$	90	21	—	134
$CH_3CH_2C(NO_2)_2CH_2OH$	NH_3	(HCHO)	$[CH_3CH_2C(NO_2)_2CH_2]_2NH$	66–67	99	—	54
$CH_3CH_2CH_2C(NO_2)_2CH_2OH$	NH_3	(HCHO)	$[CH_3CH_2CH_2C(NO_2)_2CH_2]_2NH$	100–100.5	85.2	—	54
$CH_3O_2CCH_2CH_2C(NO_2)_2CH_2OH$	NH_3	(HCHO)	$[CH_3O_2CCH_2CH_2C(NO_2)_2CH_2]_2NH$	79–80	88	—	54
$CH_3O_2CCH_2CH_2C(NO_2)_2CH_2OH$	$H_2NCH_2CO_2H$	(HCHO)		128–130	61.5	—	54
$O_2NCH_2CH_2OOCCH_3$	N_2H_4	(HCHO)	$O_2NCH_2CH_2NHN(CH_2CH_2NO_2)_2$	127[e]	41	—	72
....	$CH_3C(NO_2)_2CH_2CH_2NH_2$	$HOCH_2CN$	$CH_3C(NO_2)_2CH_2CH_2NHCH_2CN$	83–85	84	—	72
$CH_3C(NO_2)_2CH_2CH_2CHO$	$(CH_3)_2NH$	(HCHO)	 $CH_3C(NO_2)_2CH_2\underset{\substack{\vert\\ CH_2N(CH_3)_2}}{CH}CHO$	[f]	35	—	72
$HOCH_2C(NO_2)_2CH_2C(NO_2)_2CH_2OH$	RNH_2	(HCHO)	 R				
			H–	108–112 dec.	54	—	72
			CF_3CH_2–	95–96	37	—	
			$(CH_3)_3SiCH_2$–	88–90	17	—	
			$CH_3N(NO_2)CH_2CH_2$–	96–98	68	—	
$HOCH_2N(NO_2)CH_2N(NO_2)_2CHOH$	$CH_3C(N_2O)_2CH_2CH_2NH_2$	(HCHO)		118–120	89	—	72

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[a] (HCHO) = formaldehyde present as methylol derivative of polynitroalkane or of the amine. [b] Yield as nitraza alcohol. [c] Yield as nitrate ester of alcohol. [d] B.p. 64° (16 mm.). [e] Melting point of the amine hydrochloride. [f] B.p. 104° (100 mm.).

2. Addition Reactions

a. Michael Reaction

A general discussion of the Michael reaction is given by Bergmann, Ginsberg, and Pappo (15). This is a general survey of the literature through October, 1955, covering the scope and limitations of the reaction. However, relatively few examples of the reaction involving polynitro compounds appeared in the literature to that time.

Herzog and co-workers (81) were the first to report the extension of the Michael reaction to aliphatic *gem*-dinitro compounds. They reported that condensation of potassium dinitromethane with methyl acrylate and acrylonitrile gave dimethyl 4,4-dinitroheptanedioate and 4,4-dinitroheptanedinitrile, respectively, as bis adducts. Shechter and Zeldin (172) studied the Michael reactions of 1,1-dinitroethane with α,β-unsaturated esters, aldehydes, ketones, and sulfones. They also reported the addition of 1,1-dinitroethane to 2-nitropropene. The reactions are base-catalyzed, and in most cases excellent yields of the Michael products are realized. Klager (101) reported the Michael addition of potassium 2,2-dinitroethanol to methyl acrylate. He found that, if the pH is controlled to 5–6, the intermediate methyl 5-hydroxy-4,4-dinitrovalerate can be isolated. In the presence of excess base, demethylolation occurs, giving the salt of methyl 4,4-dinitrobutyrate which can undergo further Michael condensations.

$$\mathrm{KO_2N{=}C(NO_2)CH_2OH + CH_2{=}CHCOOMe \xrightarrow{pH\ 5\text{–}6} HOCH_2C(NO_2)_2CH_2CH_2COOMe}$$

$$\mathrm{HOCH_2C(NO_2)CH_2CH_2COOMe + NaOMe \rightarrow NaO_2N{=}C(NO_2)CH_2CH_2COOMe}$$

$$\mathrm{NaO_2N{=}C(NO_2)CH_2CH_2COOMe}\left.\begin{array}{l}\xrightarrow{\mathrm{CH_2{=}CHCOOMe}} \mathrm{MeOOCCH_2CH_2C(NO_2)_2CH_2CH_2COOMe}\\ \xrightarrow{\mathrm{CH_2{=}CHCN}} \mathrm{NC{-}CH_2CH_2C(NO_2)_2CH_2CH_2COOMe}\end{array}\right.$$

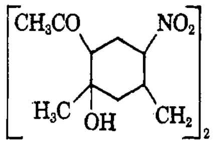
Klager (104) found that potassium bis(2,2-dinitroethyl)amine and its N-substituted derivatives did not give the expected Michael adducts with methyl acrylate. Instead, dimethyl 4,4-dinitro-1,7-heptanedioate, the 2:1 adduct of methyl acrylate and dinitromethane, was formed as the result of the disproportionation of the original nitro compounds.

The kinetics of the Michael addition of nitroform to β-nitrostyrene and the reverse decomposition of the Michael adduct have been studied by Hine and Kaplan (85). The decomposition reaction was found to be subject to general base catalysis. In strong acid the *decomposition* of the intermediate carbanion is rate determining, whereas in pyridine-buffered solutions the *formation* of the carbanion is rate determining.

Feuer and Harmetz (32) reported some "abnormal" Michael additions of α,ω-dinitroparaffins to methyl vinyl ketone.

$$\mathrm{O_2NCH_2CH_2CH_2CH_2NO_2 + 2CH_2{=}CHCOCH_3 \xrightarrow{^{-}OH} [CH_3COCH_2CH_2CH(NO_2)CH_2]_2}$$

$$\mathrm{O_2NCH_2CH_2CH_2CH_2NO_2 + 4CH_2{=}CHCOCH_3 \xrightarrow{^{-}OH}}$$



The cyclic product is obtained by an internal aldol condensation of the tetrakis adduct. The tetrakis adducts of methyl acrylate and acrylonitrile were isolated in good yield with no cyclization occurring. Michael-type additions of primary or secondary nitroparaffins, 1,1-dinitroparaffins, and nitramines with nitroolefins, generated *in situ* by elimination of acetic acid from the corresponding nitro acetates, have been reported by Feuer and co-workers (37, 40).

The dinitroethylation reaction reported by Frankel (50), which involves reacting 2-bromo-2,2-dinitroethyl acetate with an anion such as sodium 1,1-dinitroethane, could involve as an active intermediate 1,1-dinitroethylene to which the dinitroethane anion would add in a Michael-type reaction. Further work by Winters and McEwen (200) gave support to the suggested intermediate 1,1-dinitroethylene. A more detailed account of dinitroethylation will be given in section IIIB3.

Klager and co-workers (107) found that partial acidification of potassium 2,2-dinitroethanol led to the formation of potassium 2,2,4,4-tetranitro-1-butanol. Its formation is postulated to involve a Michael addition of potassium 2,2-dinitroethanol to 1,1-dinitroethylene generated *in situ* by elimination of water.

$$\mathrm{KO_2N{=}C(NO_2)CH_2OH + H_2SO_4 \rightarrow HC(NO_2)_2CH_2OH + KHSO_4}$$

$$\mathrm{HC(NO_2)_2CH_2OH \xrightarrow{-H_2O} [CH_2{=}C(NO_2)_2]}$$

$$\mathrm{KO_2N{=}C(NO_2)CH_2OH + [CH_2{=}C(NO_2)_2] \rightarrow KO_2N{=}C(NO_2)CH_2C(NO_2)_2CH_2OH}$$

The reaction is quite sensitive to pH, and the best yield results at pH 4. When the tetranitrobutanol is treated with excess potassium hydroxide, demethylolation occurs to give dipotassium 1,1,3,3-tetranitropropane. Treatment of the dipotassium tetranitropropane with methyl acrylate led to the formation of the mono-Michael adduct, potassium methyl 4,4,6,6-tetranitrohexanoate; no bis adduct was isolated. Feuer and co-workers (37) studied the Michael condensations of the higher homologs in the $\alpha,\alpha,\omega,\omega$-tetranitroalkane series and found that bis adducts were obtained in all cases. The 1,1,3,3-tetranitropropane compound is apparently the only exception in the series. Further examples of Michael-type reactions involving polynitro compounds were reported in summaries of work presented to the Symposium on Nitro Aliphatic Chemistry by Frankel (53) and Hamel (72). Table XIV lists examples of Michael-type reactions of polynitro compounds where sufficient data were reported to characterize the product.

b. 1,2-Addition Reactions

Little work has been reported on reactions involving 1,2-addition of a polynitro compound to an olefinic double bond. Shechter and Cates (168) have studied the addition of nitroform to α,β-unsaturated ethers, which produces α-trinitromethyl ethers in good yield. The direction of addition was determined by the reduction of the product with lithium aluminum hydride to an amine (IIIA3), which was independently synthesized by an alternate unequivocal route.

A recent report by Rondestvedt and co-workers (165) described the synthesis of α-trinitromethyl ethers by the nitroform–aldehyde–alcohol reaction, a reaction first discovered by Hartman and Tawney. A more convenient synthetic method involves treating an acetal with nitroform (165). The kinetics of the nitroform–aldehyde–alcohol and the acetal–nitroform reactions were investigated, and the rate expressions obtained were interpreted in terms of a mechanism involving several equilibria (165). Tawney (189) described the addition of nitroform to vinyl ethers and also gave an example of the aldehyde–nitroform–alcohol reaction.

Tawney and Schaffner (190) described a process for the addition of nitroform to vinyl acetate using boron trifluoride etherate as the catalyst. Anspon (1, 2) claims the addition of bromotrinitromethane to isopropyl vinyl ether and methyl vinyl ketone. Table XV lists examples of 1,2-additions and the acetal–nitroform reaction.

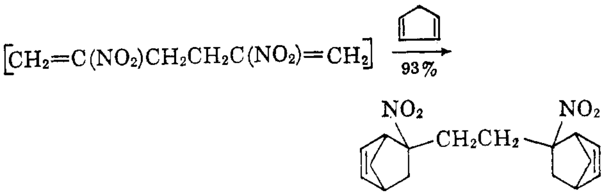
c. Diels–Alder Reactions

Only two examples of Diels–Alder reactions involving polynitro compounds have appeared in the literature to date. Gold and co-workers (66) found that addition of a solution of 2,2-dinitroethanol to a refluxing solution of cyclopentadiene in chlorobenzene produced a waxy crystalline compound, 6,6-dinitrobicyclo[2.2.1]-2-heptene. The 2,2-dinitroethanol apparently dehydrates, giving 1,1-dinitroethylene as a reactive dienophile which immediately reacts with the cyclopentadiene present.

$$HC(NO_2)_2CH_2OH \overset{\Delta}{\rightarrow} [CH_2{=}C(NO_2)_2] + H_2O$$

Feuer, Miller, and Lawyer (41) reported an example of a bis adduct.

$$AcOCH_2CH(NO_2)CH_2CH_2CH(NO_2)CH_2OAc \xrightarrow{NaOAc} [CH_2{=}C(NO_2)CH_2CH_2C(NO_2){=}CH_2]$$



3. *Reactions with Base*

a. Formation of Nitro Salts and Halogen Derivatives

In general, there are three methods for the formation of *gem*-nitronitronate salts: (1) the reverse Henry reaction, which is pH dependent (see section IIIB1a)

$$RC(NO_2)_2CH_2OH \rightleftharpoons RCH(NO_2)_2 + HCHO \overset{:B}{\rightarrow} RC(NO_2){=}NO_2^- + B^+{:}H$$

(2) the neutralization of the acidic proton on terminal dinitromethyl groups with base (to be discussed in section IV)

$$RCH(NO_2)_2 + {:}B \rightarrow RC(NO_2){=}NO_2^-B^+{:}H$$

(3) the reduction of terminal halodinitro groups with base or iodide ion

$$RCX(NO_2)_2 \xrightarrow[\text{or } I^-]{^-OH} RC(NO_2){=}NO_2^- + X^- + I_2$$

In contrast to mononitronate salts, which upon acidification with mineral acid undergo the Nef reaction (128), *gem*-nitronitronate salts upon acidication generally give the free dinitroalkane.

Klager (102) reported a procedure for the quantitative determination of terminal dinitromethyl groups or bromine in compounds containing terminal bromodinitromethyl groups. The procedure involves a titration with thiosulfate of the iodine liberated by reaction of the bromodinitromethyl group with potassium iodide.

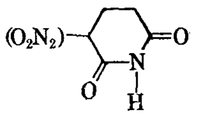
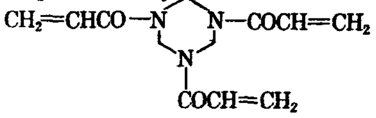
$$RCBr(NO_2)_2 + 2KI \rightarrow RC(NO_2){=}NO_2K + KBr + I_2$$

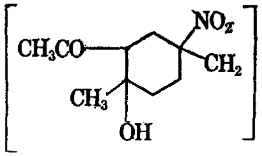
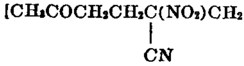
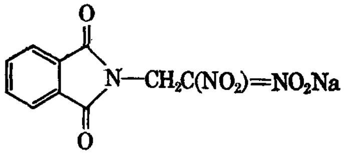
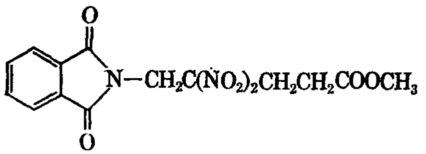
The titrations are carried out at pH 6–7 using a starch indicator in 50% aqueous alcohol solution. Novikov and co-workers (135) extended the procedure to include chlorodinitromethyl groups with titrations carried out in 30% aqueous alcohol using boric or acetic acids to adjust the pH.

The reactions of 1-halo-1,1-dinitroethanes with various organic bases have been studied by Zeldin and Shechter (203). Apparently all these reactions involve reductive attack on the positive halogen, as compared with proton removal and elimination of nitrite ion in

TABLE XIV

THE MICHAEL REACTION

Nitro compound	Acceptor	Adduct	Yield, %	B.p. (mm.) or m.p., °C., and/or n^t_D	Ref.
C_1					
$KO_2N=CHNO_2$	$2CH_2=CHCOOMe$	$(O_2N)_2C(CH_2CH_2COOMe)_2$	60.4	44.5–45	81
$KO_2N=CHNO_2$	$2CH_2=CHCN$	$(O_2N)_2C(CH_2CH_2CN)_2$	35	79	81
$CH_2(NO_2)_2$	$C_6H_5COCH=CH_2$	$C_6H_5COCH_2CH_2CH(NO_2)_2$	49	77–78	143
$CH_2(NO_2)_2$	$2C_6H_5COCH=CH_2$	$(C_6H_5COCH_2CH_2)_2C(NO_2)_2$	48	135–136	143
$CH_2(NO_2)_2$	$C_6H_5CH=CHCOCH_3$	$(O_2N)_2CHCH(C_6H_5)CH_2COCH_3$	60	94	140
$HC(NO_2)_3$	$CH_2=C(CH_3)NO_2$	$(O_2N)_3CCH_2CH(CH_3)NO_2$	73	51–51.2	142
$HC(NO_2)_3$	$C_6H_5CH=CHNO_2$	$(O_2N)_3CCH(C_6H_5)CH_2NO_2$	41	87–88	85
$HC(NO_2)_3$	$(CH_2=CHCONH)_2CH_2$	$[(O_2N)_3CCH_2CH_2CONH]_2CH_2$	80	183–184	38
$HC(NO_2)_3$	$[CH_2=C(CH_3)CONH]_2CH_2$	$[(O_2N)_3CCH_2CH(CH_3)CONH]_2CH_2$	64	179–179.5	38
$HC(NO_2)_3$	$CH_2=CHCONHCH_2OOCC_6H_5$	$(O_2N)_3CCH_2CH_2CONHCH_2OOCC_6H_5$	83	133–133.5	39
$HC(NO_2)_3$	$CH_2=C(COOH)CH_2COOH$	$(O_2N)_3CCH_2CH(COOH)CH_2COOH$	75	175	48
$HC(NO_2)_3$	$CH_2=C(COOMe)CH_2COOMe$	$(O_2N)_3CCH_2CH(COOMe)CH_2COOMe$	47	137–140 (3); n^{20}_D 1.4643	48
$HC(NO_2)_3$	$[CH_2=CHCOCH_3]^a$	$(O_2N)_3CCH_2CH_2COCH_3$	40	43–43.5	112
$HC(NO_2)_3$	$[HOCH_2COCH=CH_2]^a$	$(O_2N)_3CCH_2CH_2COCH_2OH$	74	77	112, 67, 53
$HC(NO_2)_3$	$C_6H_5CH=CHCOCH_3$	$(O_2N)_3CCH(C_6H_5)CH_2COCH_3$	80	91	140
$HC(NO_2)_3$	$C_6H_5COCH=CH_2$	$C_6H_5COCH_2CH_2C(NO_2)_3$	70	80–81	143
$HC(NO_2)_3$	$CH_2=CHCONH_2$	$(O_2N)_3CCH_2CH_2CONH_2$	63	95–96	89
C_2					
$CH_3CH(NO_2)_2$	$CH_2=CHCOOMe$	$CH_3C(NO_2)_2CH_2CH_2COOMe$	72	94–97 (0.6); n^{20}_D 1.4556	172
$CH_3CH(NO_2)_2$	$CH_2=C(NO_2)CH_3$	$CH_3C(NO_2)_2CH_2CH(NO_2)CH_3$	93.2	107–108 (0.8); n^{20}_D 1.4699	172
$CH_3CH(NO_2)_2$	$CH_2=CHCOCH_3$	$CH_3C(NO_2)_2CH_2CH_2COCH_3$	95	109–110 (1.3); n^{20}_D 1.4607	172
$CH_3CH(NO_2)_2$	$CH_2=CHCHO$	$CH_3C(NO_2)_2CH_2CH_2CHO$	74.3	97–97.5 (0.8); n^{20}_D 1.4650	172
$CH_3CH(NO_2)_2$	$CH_2=CHSO_2CH_3$	$CH_3C(NO_2)_2CH_2CH_2SO_2CH_3$	23	76–78	172
$CH_3CH(NO_2)_2$	$C_6H_5CH=CHCOCH_3$	$CH_3C(NO_2)_2CH(C_6H_5)CH_2COCH_3$	—	103	140
$CH_3CH(NO_2)_2$	$C_6H_5COCH=CH_2$	$C_6H_5COCH_2CH_2C(NO_2)_2CH_3$	64	101–102	143
$CH_3CH(NO_2)_2$	$[CH_3CH_2C(NO_2)=CH_2]^b$	$CH_3CH_2CH(NO_2)CH_2C(NO_2)_2CH_3$	65	90–92 (0.2); 29–29.5	40
$CH_3CH(NO_2)_2$	$CH_2=CHNO_2$	$CH_3C(NO_2)_2CH_2CH_2NO_2$	50.7	114–115 (1); n^{20}_D 1.4765	141
$CH_3CH(NO_2)_2$	$CH_3CH=CHNO_2$	$CH_3C(NO_2)_2CH(CH_3)CH_2NO_2$	86.3	130–131 (1); n^{20}_D 1.4738	141
$HC_3CH(NO_2)_2$	$CH_3CH_2CH=CHNO_2$	$CH_3C(NO_2)_2CH(C_2H_5)CH_2NO_2$	93.2	128 (0.5); n^{20}_D 1.4775	141
$HC_3CH(NO_2)_2$	$CH_3CH_2CH_2CH=CHNO_2$	$CH_3C(NO_2)_2CH(C_3H_7)CH_2NO_2$	—	124–125 (0.5); n^{20}_D 1.4762	141
$HC(NO_2)_2CN\cdot 4H_2O$	$CH_2=CHCOOMe$	$(O_2N)_2C(CN)CH_2CH_2COOMe$	21	78–80 (0.12)	156
$HC(NO_2)_2CN$	$CH_2=CHCONH_2$	$(O_2N)_2C(CN)CH_2CH_2CONH_2$	29	62–63	156
$HC(NO_2)_2CN\cdot 4H_2O$	$CH_2=CHCOOH(H_2O)$	$(O_2N)_2C(CN)CH_2CH_2COOH^+$	13	73–74	156
		$(O_2N)_2C(CONH_2)CH_2CH_2COOH$	60	115–117	
$HC(NO_2)_2CN\cdot 4H_2O$	$CH_2=CHCOOH(t\text{-}BuOH)$	$(O_2N)_2C(CONH_2)CH_2CH_2COOH$	69	111–113	156
$HC(NO_2)_2CN$	$CH_2=CHCOOH(EtOAc)$		34	146–147	156
$HC(NO_2)_2CN\cdot 4H_2O$	$CH_2=CHCHO$	$(O_2N)_2C(CN)CH_2CH_2CHO$	57	80–81 (0.4)^c	156
$HC(NO_2)_2CN\cdot 4H_2O$	$(CH_2=CHCONH)_2CH_2$	$[(O_2N)_2C(CN)CH_2CH_2CONH]_2CH_2$	51	133–134	156
$HC(NO_2)_2CN\cdot 4H_2O$	$CH_2=CHCOCH_3$	$(O_2N)_2C(CN)CH_2CH_2COCH_3$	68	75 (0.2)^d	156
$HC(NO_2)_2CN\cdot 4H_2O$		Tris adduct	26	140–141	156
$HC(NO_2)_2CONH_2$	$CH_2=CHCOOH$	$H_2NCOC(NO_2)_2CH_2CH_2COOH$	63.4	115–117	153

$HC(NO_2)_2CONH_2$	$CH_2{=}CHCONH_2$	$H_2NCOC(NO_2)_2CH_2CH_2CONH_2$	61.3	110–111	153
$KO_2N{=}C(NO_2)CH_2OH^a$	$CH_2{=}CHNO_2$	$KO_2N{=}C(NO_2)CH_2CH_2NO_2$	13	118–119 dec.	89
$KO_2N{=}C(NO_2)CH_2OH$	$[CH_2{=}C(NO_2)_2]^f$	$KO_2N{=}C(NO_2)CH_2C(NO_2)_2CH_2OH$	70	110 dec.	107
$KO_2N{=}C(NO_2)CH_2OH^e$	$2CH_2{=}CHCOOMe$ (pH 7.7)	$(O_2N)_2C(CH_2CH_2COOMe)_2$	58	44.5–45	81
$KO_2N{=}C(NO_2)CH_2OH$	$CH_2{=}CHCOOMe$ (pH 5–6)	$HOCH_2C(NO_2)_2CH_2CH_2COOMe$	20.1	Oil; n^{24}_D 1.4738	101
C_3					
$CH_3CH_2CH(NO_2)_2$	$[CH_2{=}C(NO_2)CH_2CH_2C(NO_2){=}CH_2]^g$	$[CH_3CH_2C(NO_2)_2CH_2CH(NO_2)CH_2]_2$	94	*h*	40
$KO_2N{=}C(NO_2)CH_2C(NO_2){=}NO_2K$	$CH_2{=}CHCOOMe$	$KO_2N{=}C(NO_2)CH_2C(NO_2)_2CH_2CH_2COOMe$	49	140 dec.	107
C_4					
$O_2N{-}(CH_2)_4{-}NO_2$	$2CH_2{=}CHCOCH_3$	$[CH_3COCH_2CH_2CH(NO_2){-}CH_2]_2$	83	*h*	32
$O_2N{-}(CH_2)_4{-}NO_2$	$4CH_2{=}CHCOCH_3$		86	*h*	32
$O_2N{-}(CH_2)_4{-}NO_2$	$2CH_2{=}CHCOOMe$	$[MeOOCCH_2CH_2CH(NO_2)CH_2]_2$	66	65–75^h	32
$O_2N{-}(CH_2)_4{-}NO_2$	$4CH_2{=}CHCOOMe$	$[(MeOOCCH_2CH_2)_2C(NO_2)CH_2]_2$	93	122.5–123.5	32
$O_2N{-}(CH_2)_4{-}NO_2$	$4CH_2{=}CHCN$	$[(NCCH_2CH_2)_2C(NO_2)CH_2]_2$	68	162–164	32
$(O_2N)_2CHCH_2CH_2CH(NO_2)_2$	$CH_2{=}CHCOCH_3$	$[CH_3COCH_2CH_2C(NO_2)_2CH_2]_2$	82	152–153	37
$(O_2N)_2CHCH_2CH_2CH(NO_2)_2$	$CH_2{=}CHCHO$	$[OHCCH_2CH_2C(NO_2)_2CH_2]_2$	—	Oil	37
$(O_2N)_2CHCH_2CH_2CH(NO_2)_2$	$CH_2{=}CHNO_2$	$[NO_2CH_2CH_2C(NO_2)_2CH_2]_2$	58	147–150	37
C_5					
$O_2N{-}(CH_2)_5NO_2$	$CH_2{=}CHCOCH_3$	$[CH_3COCH_2CH_2CH(NO_2)CH_2]_2CH_2$	34	77.5–78.5	27
$NaO_2N{=}C(NO_2)CH_2CH_2COOCH_3$	$CH_2{=}CHCOOCH_3$	$(O_2N)_2C(CH_2CH_2COOCH_3)_2$	40	45.5–46	156
$NaO_2N{=}C(NO_2)CH_2CH_2COOCH_3$	$CH_2{=}CHCOOH$	$HOOCCH_2CH_2C(NO_2)_2CH_2CH_2COOCH_3$	63.1	92–93	65
$NaO_2N{=}C(NO_2)CH_2CH_2COOCH_3$	$CH_2{=}CHCN$	$NCCH_2CH_2C(NO_2)_2CH_2CH_2COOCH_3$	—	50	101
C_6					
$[HOCH_2C(NO_2)_2CH_2]_2^e$	$CH_2{=}CHCN$	$[NCCH_2CH_2C(NO_2)_2CH_2]_2$	48	148–149	37
$[HOCH_2C(NO_2)_2CH_2]_2^e$	$CH_2{=}CHCOOH$	$[HOOCCH_2CH_2C(NO_2)_2CH_2]_2$	60	188	37
$[HOCH_2C(NO_2)_2CH_2]_2^e$	$CH_2{=}CHCOOCH_3$	$[CH_3OOCCH_2CH_2C(NO_2)_2CH_2]_2$	68	157–157.5	37
$[HC(NO_2)_2CH_2CH_2]_2$	$CH_2{=}CHSO_2CH_3$	$[CH_3SO_2CH_2CH_2C(NO_2)_2{-}CH_2CH_2]_2$	47	169.5–170	37
$[HC(NO_2)_2CH_2CH_2]_2$	$CH_2{=}CHCN$	$[NCCH_2CH_2C(NO_2)_2CH_2CH_2]_2$	54	130–131	37
$[HC(NO_2)_2CH_2CH_2]_2$	$CH_2{=}CHCOOCH_3$	$[CH_3OOCCH_2CH_2C(NO_2)_2CH_2CH_2]_2$	83	102.5–103	37
$[HC(NO_2)_2CH_2CH_2]_2$	$CH_2{=}CHCOCH_3$	$[CH_3COCH_2CH_2C(NO_2)_2CH_2CH_2]_2$	98	128	37
$[KO_2N{=}C(CN)CH_2]_2$	$CH_2{=}CHCOCH_3$	 $[CH_3COCH_2CH_2\underset{\displaystyle CN}{\underset{\vert}{C}}(NO_2)CH_2]_2$	51	163–164	44
C_7					
$[HOCH_2C(NO_2)_2CH_2]_2CH_2^e$	$CH_2{=}CHCN$	$[NCCH_2CH_2C(NO_2)_2CH_2CH_2]_2CH_2$	33	91	37
$[HOCH_2C(NO_2)_2CH_2]_2CH_2^e$	$CH_2{=}CHCOOCH_3$	$[CH_3OOCCH_2CH_2C(NO_2)_2CH_2CH_2]_2CH_2$	65	64.5	37
Others					
	$CH_2{=}CHCOOCH_3$		48.4	113–115	50

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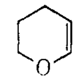
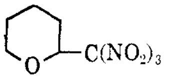
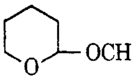
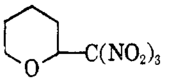
[a] Probably generated *in situ* from the Hg salt-catalyzed hydration of the corresponding acetylenes. [b] Generated *in situ* by the base-catalyzed elimination of acetic acid from 2-nitrobutyl acetate. [c] Crude aldehyde treated directly with methyl orthoformate; yield and boiling point as dimethyl acetal. [d] Boiling point in falling film still. [e] Base-catalyzed demethylolation occurs under the reaction conditions. [f] Postulated intermediate from the dehydration of 2,2-dinitroethanol. [g] Generated *in situ* from 1,6-diacetoxy-2,5-dinitroheptane. [h] Mixture of epimers.

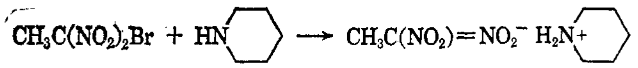
TABLE XV

1,2-ADDITION REACTIONS

Nitro compound	Olefin	Product	Yield, %	B.p. (mm.), °C., and/or n^t_D	Ref.
$HC(NO_2)_3$	$CH_3CH_2OCH{=}CH_2$	$CH_3CH_2OCH(CH_3)C(NO_2)_3$	68	63–64.5 (0.6); n^{20}_D 1.4386	168
$HC(NO_2)_3$	$(CH_3)_2CHOCH{=}CH_2$	$(CH_3)_2CHOCH(CH_3)C(NO_2)_3$	73	65 (0.4); n^{20}_D 1.4390	168
$HC(NO_2)_3$	$(CH_3)_2CHCH_2OCH{=}CH_2$	$(CH_3)_2CHCH_2OCH(CH_3)C(NO_2)_3$	75	65 (0.7); n^{20}_D 1.4389	168
$HC(NO_2)_3$	$CH_3OCH_2CH_2OCH{=}CH_2$	$CH_3OCH_2CH_2OCH(CH_3)C(NO_2)_3$	50	102–103 (1.5); n^{20}_D 1.4468	168
$HC(NO_2)_3$			81	103 (1.0); n^{20}_D 1.4708	168
$HC(NO_2)_3$	$CH_3OCH{=}CH_2$	$CH_3OCH(CH_3)C(NO_2)_3$	—	63–64 (2.0); n^{20}_D 1.4420	189
$HC(NO_2)_3$	$CH_2{=}CHOCOCH_3$	$(O_2N)_3CCH(CH_3)OOCCH_3$	48	62–4 (2.0); n^{19}_D 1.4432	190
$BrC(NO_2)_3$	$(CH_3)_2CHOCH{=}CH_2$	$(CH_3)_2CHOCH(CH_2Br)C(NO_2)_3$ [a]	36	86–88 (2.0); n^{20}_D 1.475	1
$BrC(NO_2)_3$	$CH_3COCH{=}CH_2$	$CH_3COCH(CH_2Br)C(NO_2)_3$	63	107.5 (3.0); n^{20}_D 1.4987	2
$HC(NO_2)_3$	$CH_3CH_2CH_2CH(OC_2H_5)_2$	$CH_3CH_2CH_2CH(OC_2H_5)C(NO_2)_3$	87	69 (0.8); n^{25}_D 1.4424	165
$HC(NO_2)_3$	$CH_3CH_2CH_2CH(OPr\text{-}i)_2$	$CH_3CH_2CH_2CH(OPr\text{-}i)C(NO_2)_3$	66	70 (0.3)	165
$HC(NO_2)_3$			85	70 (0.2); n^{25}_D 1.4705	165

[a] Structure not proven; nitroform–acetal reaction.

the case of 1,1,1-trinitroethane (see section IIIA2), giving salts of 1,1-dinitroethane as products.



The structure of the salt was confirmed when 1,1-dinitroethane was treated with piperidine to give an identical salt, piperidinium 1,1-dinitroethane.

The reaction of 1-bromo-1,1-dinitroethane with sodium diethyl malonate took place by displacement and positive bromine transfer, rather than by an initial elimination–addition process, as evidenced by the products formed with various amounts of base used. A reasonable mechanistic path, which adequately explains the results, can be written as follows.

$$CH_3C(NO_2)_2Br + NaCH(COOEt)_2 \rightarrow CH_3C(NO_2){=}NO_2^-Na^+ + BrCH(COOEt)_2$$

$$Na^+\bar{C}H(COOEt)_2 + BrCH(COOEt)_2 \rightarrow NaBr + (EtOOC)_2CHCH(COOEt)_2$$

$$(EtOOC)_2CHCH(COOEt)_2 + Na^+\bar{C}H(COOEt)_2 \rightarrow (EtOOC)_2CH\bar{C}(COOEt)_2\overset{+}{Na} + CH_2(COOEt)_2$$

$$(EtOOC)_2CH\bar{C}(COOEt)_2\overset{+}{Na} + BrC(NO_2)_2CH_3 \rightarrow (EtOOC)_2CHCBr(COOEt)_2 + \overset{+}{Na}\bar{O}_2N{=}C(NO_2)CH_3$$

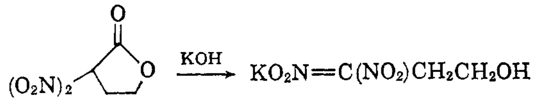
$$(EtOOC)_2CHCBr(COOEt)_2 + \overset{+}{Na}\bar{O}_2N{=}C(NO_2)CH_3 \rightarrow (EtOOC)_2C{=}C(COOEt)_2 + NaBr + HC(NO_2)_2CH_3$$

Nielsen (122–124) studied the reactions of the isomeric dinitrocyclohexanes with base. The 1,2-dinitrocyclohexanes undergo the expected elimination of a nitro group, giving 1-nitrocyclohexene. The 1,3-dinitrocyclohexane rapidly forms a dinitronate ion in base, which slowly ring-opens to give 2-nitro-2,4-hexadiene; the 1,4-dinitrocyclohexane forms a stable dinitronate ion.

Parker and co-workers (154, 156) reported, in a series of articles on cyanodinitromethane, some interesting reactions in base.

$$\begin{tikzcd} & {[NCC(NO_2)_2]^-C_6H_5\overset{+}{N}H_3} \\ NCC(NO_2)_2COOEt \arrow[ur, "C_6H_5NH_2"] \arrow[dr, "NaI", "\text{or } HBr,\ KOH"'] & \\ & NaO_2N{=}C(CN)COOEt \end{tikzcd}$$

$$CH_3OOCCH_2CH_2C(NO_2)_2CN \xrightarrow{KOH} CH_3OOCCH_2CH_2C(NO_2){=}NO_2K$$



Because of the sensitive, unstable nature of nitronitronate salts in general, they are usually handled as their halo derivatives. The halogen derivatives are generally prepared by adding the halogen to an aqueous solution or suspension of the nitronate salts, or occasionally the halogenations are effected in an ether suspension of the nitronate salts.

Feuer and Savides (45) described some interesting reactions centering around dipotassium dinitroadiponitrile and bromo derivatives.

$$\begin{tikzcd} KO_2N{=}C(CN)CH_2CH_2C(CN){=}NO_2K \arrow[r, "Br_2"] \arrow[d, "{Br_2,\ KOH,\ \Delta}"'] \arrow[dr, "{Br_2,\ KOH,\ 0°}"] & NCCBr(NO_2)CH_2CH_2CBr(NO_2)CN \arrow[d, "{1.\ KOH,\ -5°\quad 2.\ H^+}"] \arrow[dl, "{KOH,\ 70°}"'] \\ O_2NC(Br)_2CH_2CH_2C(Br)_2NO_2 & O_2NCHBrCH_2CH_2CBr(NO_2)CONH_2 \arrow[l, "KOH"'] \end{tikzcd}$$

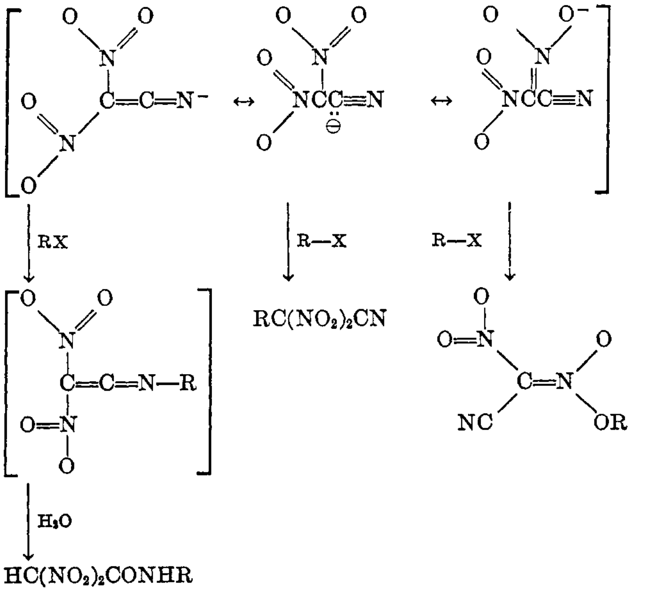
Glowiak (64) reported the preparation of diazonium nitroformate from diazonium chloride and nitroform. The colorless crystalline product is hygroscopic and light sensitive.

Table XVI lists nitronitronate salts and their halogen derivatives. In many cases, no physical properties of the salts are given.

b. Reactions of Nitro Salts

Alkylation Reactions.—Early work indicated that alkylation of silver nitroform with alkyl halides would be of limited synthetic value. Methyl iodide (203) and certain substituted benzyl iodides (161) gave good yields of C-alkylated products. Recently Hammond and co-workers (73) reported a detailed study of this reaction. The kinetics of the reaction of methyl iodide with silver nitroform shows close agreement with over-all third-order kinetics. It was definitely shown that nitroform anion must be involved in the rate-determining step in acetonitrile solution. However, the reaction is faster and more complex in acetone solution. It was found that only simple primary alkyl halides produced C-alkylated trinitromethyl derivatives; however, the solvent system employed determines to a great extent the success of the reaction. Hammond and co-workers (73) reported that attempted alkylation of 1,4-dibromo-2-butyne with silver nitroform in acetonitrile gave a poorly characterized mixture of products, whereas Tawney (188) reported that the same reactants gave a 72% yield of the expected C-alkylated product 1,1,1,6,6,6-hexanitro-3-hexyne in such solvents as dioxane, acetone, and methyl formate.

Parker and co-workers (156) reported attempted alkylation reactions of the cyanodinitromethide ion. Of the organic halides studied, only methyl, allyl, and *t*-butyl halides gave stable, isolable products. Methyl iodide gave only O-alkylated product; allyl bromide gave C-alkylated product (35%); and *t*-butyl bromide gave 17% C-alkylated product and 18% N-alkylated product. Thus, products which represent covalent bond formation derived from all three possible resonance structures of the cyanodinitromethide ion have been isolated.



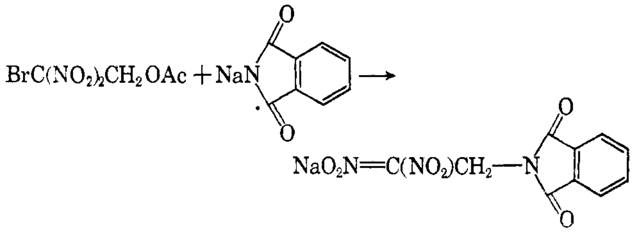
Hammond and co-workers (73) also studied the alkylation of the cyanodinitromethide ion, and their results were in agreement with the work of Parker (156).

Frankel (50) found that treating 2-bromo-2,2-dinitroethyl acetate with potassium iodide did not yield the expected product, potassium 2,2-dinitroethyl acetate. Instead, the product was identified as potassium 2,2,4,4-tetranitrobutyl acetate.

$$\mathrm{BrC(NO_2)_2CH_2OAc + KI \rightarrow KO_2N{=}C(NO_2)CH_2C(NO_2)_2CH_2OAc}$$

Similar reactions occurred when sodium 1,1-dinitroethane or sodium phthalimide was treated with 2-bromo-2,2-dinitroethyl acetate.

$$\mathrm{BrC(NO_2)_2CH_2OAc + NaO_2N{=}C(NO_2)CH_3 \rightarrow NaO_2N{=}C(NO_2)CH_2C(NO_2)_2CH_3}$$



Frankel suggested that the reaction proceeds through the reactive transitory intermediate 1,1-dinitroethylene, formed by the elimination of acetate ion from sodium 2,2-dinitroethyl acetate, which then undergoes a Michael addition with a nucleophilic species present in solution. In studies of nitrogen and oxygen base displacements on 2-bromo-2,2-dinitroethyl acetate, Winters and McEwen (200) have reported experimental evidence substantiating Frankel's proposed mechanistic path. Disodium ethylenedinitramine and sodium phthalimide also effectively displace the acetate group.

$$\mathrm{BrC(NO_2)_2CH_2OAc + NaN(NO_2)CH_2CH_2N(NO_2)Na \rightarrow [BrC(NO_2)_2CH_2N(NO_2)CH_2]_2\ 72\%}$$

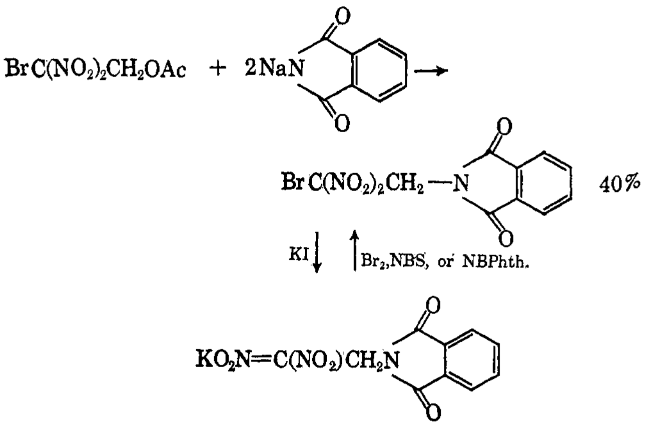


TABLE XVI
SALTS OF POLYNITRO COMPOUNDS AND HALOGEN DERIVATIVES

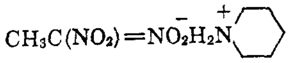
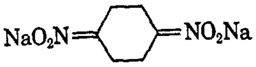
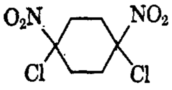
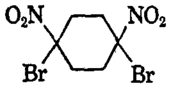
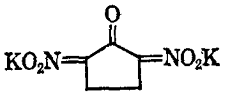
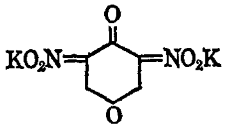
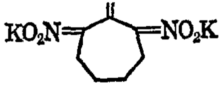
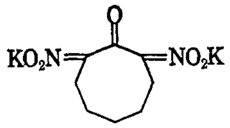
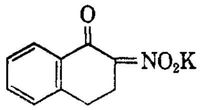
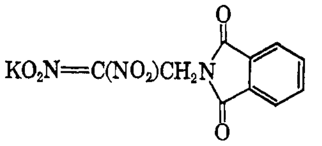
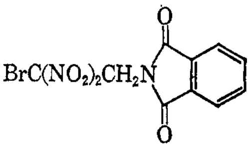
Nitronate salt	M.p., °C.	Halogen derivatives	B.p. (mm.) or m.p., °C.	Ref.
C_1				
$NaO_2N{=}CH(NO_2)$	211–213 dec.			153
$KO_2N{=}CH(NO_2)$	205 dec.			153
$AgO_2N{=}CH(NO_2)$	135 dec.			153
$(O_2N)_2C{=}NO_2{}^-C_6H_5N^+{\equiv}N$				64
C_2				
$Na^+[C(NO_2)_2CN]^-$	224–226 dec.	$BrC(NO_2)_2CN$	35–36 (4); n^{23}_D 1.4860	155
$K^+[C(NO_2)_2CN]^-$	262–264 dec.	$ClC(NO_2)_2CN$	38 (14); n^{20}_D 1.4509	155
$Ag^+[C(NO_2)_2CN]^-$	196 dec.			155
$Na^+[C(NO_2)_2CONH_2]^-$	167 dec.			153
$K^+[C(NO_2)_2CONH_2]^-$	159 dec.			153
$Ag^+[C(NO_2)_2CONH_2]^-$	130 dec.			153
$C_6H_5NH_3{}^+[C(NO_2)_2CN]^-$	152–153 dec.			154
${}^-O_2N{=}C(NO_2)CH_2NH_3{}^+$		$BrC(NO_2)_2CH_2NH_3{}^+Br^-$	129–129.5	88
	113.5–114.5			203
$2K^+[C(NO_2)_2C(NO_2)_2]^{-2}$	293–294 dec.	$ClC(NO_2)_2C(NO_2)_2Cl$	104–105 dec.	127
$KO_2N{=}C(NO_2)CH_2OH$	137–140 dec.	$BrC(NO_2)_2CH_2OH$	88–93 (2);	50
$KO_2N{=}C(NO_2)CH_3$	189–190 dec.	$ClC(NO_2)_2CH_3$	59–61 (22); n^{20}_D 1.4439	203, 127
		$BrC(NO_2)_2CH_3$	49–50 (47); n^{20}_D 1.4757	203, 127
C_3				
$KO_2N{=}C(NO_2)C(CHO){=}NO_2K$		$BrC(NO_2)_2CBr_2NO_2$	119.5–120.5	129
$KO_2N{=}C(NO_2)CH_2C(NO_2){=}NO_2K$	236–270 dec.	$BrC(NO_2)_2CH_2CBr(NO_2)_2$	66–67.5	88, 89, 107, 132, 133
$KO_2N{=}C(NO_2)CH_2OCH_3$		$ClC(NO_2)_2CH_2CCl(NO_2)_2$	35–35.5	107
$NaC(NO_2)_2COOCH_3$	212 dec.			153
$KC(NO_2)_2COOCH_3$	213–214 dec.			153
$AgC(NO_2)_2COOCH_3$	168–170 dec.			153
C_4				
$NaO_2N{=}C(NO_2)CH_2CH_2COONa$	197 dec.	$BrC(NO_2)_2CH_2CH_2COOH$	88–89	101
$KO_2N{=}C(NO_2)CH_2C(NO_2)_2CH_3$	137–138			50
$[KO_2N{=}C(NO_2)CH_2]_2NH$		$[BrC(NO_2)_2CH_2]_2NH$	68–70	88, 104
$[KO_2N{=}C(NO_2)CH_2]_2NNO_2$		$[(O_2N)_2C(Cl)CH_2]_2NNO_2$	147	104
$[KO_2N{=}C(NO_2)CH_2]_2NNO$		$[(O_2N)_2C(Br)CH_2]_2NNO$	117–118	104
$[KO_2N{=}C(NO_2)CH_2]_2NCN$		$[(O_2N)_2C(CN)CH_2]_2NCN$	158	104
Other compounds				
Esters				
$NaO_2N{=}C(NO_2)CH_2CH_2COOCH_3$		$BrC(NO_2)_2CH_2CH_2COOCH_3$	110–120 (2)	101
$KO_2N{=}C(NO_2)CH_2C(NO_2)_2CH_2CH_2COOCH_3$	140 dec.			
$KO_2N{=}C(NO_2)CH(OH)COOC_2H_5$		$ClC(NO_2)_2CH(OH)COOC_2H_5$	70 (0.2)	96
Hydrocarbons				
$NaO_2N{=}CH{-}(CH_2)_4{-}CH{=}NO_2Na$		$O_2NCHI(CH_2)_4CHINO_2$	68.5–69.5	184
			125–188[a]	124
			155–201[a]	124
$NaO_2N{=}C(C_2H_5)CH_2C(C_2H_5){=}NO_2Na$-*n*		$C_2H_5CBr(NO_2)CH_2CBr(NO_2)C_2H_5$	75	6
n-$C_3H_7C({=}NO_2Na)CH_2C({=}NO_2Na)C_3H_7$-*n*		*n*-$C_3H_7CBr(NO_2)CH_2CBr(NO_2)C_3H_7$-*n*	105–106	6
i-$C_3H_7C({=}NO_2Na)CH_2C({=}NO_2Na)C_3H_7$-*i*		*i*-$C_3H_7CBr(NO_2)CH_2CBr(NO_2)C_3H_7$-*i*	127	6
n-$C_6H_{13}C({=}NO_2Na)CH_2C({=}NO_2Na)C_6H_{13}$-*n*		*n*-$C_6H_{13}CBr(NO_2)CH_2CBr(NO_2)C_6H_{13}$-*n*	84	6
Alcohols				
$[HOCH_2C({=}NO_2Na)CH_2]_2$		$[HOCH_2CBr(NO_2)CH_2]_2$	111–112	42
Ketones				
$CH_3CH_2C({=}NO_2K)COC({=}NO_2K)CH_2CH_3$		$CH_3CH_2CBr(NO_2)COCBr(NO_2)CH_2CH_3$	100–101 (0.5); n^{20}_D 1.5151	44
$[CH_3COCH_2CH_2C({=}NO_2Na)CH_2]_2$		$[CH_3COCH_2CH_2CBr(NO_2)CH_2]_2$	121–122	32
$[CH_3COCH_2CH_2C({=}NO_2Na)CH_2]_2CH_2$		$[CH_3COCH_2CH_2CH_2CBr(NO_2)CH_2]_2CH_2$	65.5–66.5	27
		$O_2NCBr_2CH_2CH_2CBr_2NO_2$	100–101	103, 105
		$O_2NCBr_2CH_2CH_2CH_2CBr_2NO_2$	40–41	46, 103
		$O_2NCBr_2CH_2CH_2CH_2CH_2CBr_2NO_2$	85–86	46

TABLE XVI (*Continued*)

Nitronate salt	M.p., °C.	Halogen derivatives	B.p.(mm.) or m.p., °C.	Ref.
		$O_2NCBr_2CH_2CH_2CH_2CH_2CH_2CBr_2NO_2$	85–86	46
		$HOOCC_6H_4CH_2CH_2CBr_2NO_2$-*o*	127–128	46
Nitriles				
$[NCC(=NO_2K)CH_2]_2$		$O_2NCBr_2CH_2CH_2CBr_2NO_2$	98–100	45
$[NCC(=NO_2K)CH_2]_2$		$O_2NCBr(CN)CH_2CH_2CBr(CN)NO_2$	130–131	44
$[NCC(=NO_2K)CH_2]_2CH_2$		$O_2NCBr(CN)CH_2CH_2CH_2CBr(CN)NO_2$	70–71.5	44
$[NCC(=NO_2K)CH_2CH_2]_2$		$[O_2NCBr(CN)CH_2CH_2]_2$	98–99	44
$[NCC(=NO_2K)CH_2CH_2CH_2]_2$		$[O_2NCBr(CN)CH_2CH_2CH_2]_2$	77–77.5	44
$NaO_2N=C(NO_2)CH_2N(NO_2)CH_2COOC_2H_5$	87–88 dec.	$(O_2N)_2CBrCH_2N(NO_2)COOC_2H_5$	57–58	30
$[KO_2N=C(NO_2)CH_2N(NO_2)CH_2]_2$	167 dec.	$[BrC(NO_2)_2CH_2N(NO_2)CH_2]_2$	176–178 dec.	200
	239 exp.		117–118	200

[a] Mixture of isomers.

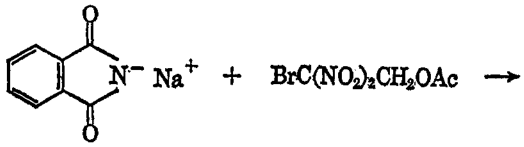
In the reaction with sodium phthalimide, if the molar ratio is reduced to 1:1 the yield of the N-(2-bromo-2,2-dinitroethyl)phthalimide is reduced to 10%, an important fact in the mechanism proposed. The methanolysis of 2-bromo-2,2-dinitroethyl acetate was studied conductometrically and found to be pseudo first order, $k = 0.144$ hr.$^{-1}$ at 35.22° with $C_0 = 0.224\ M$.

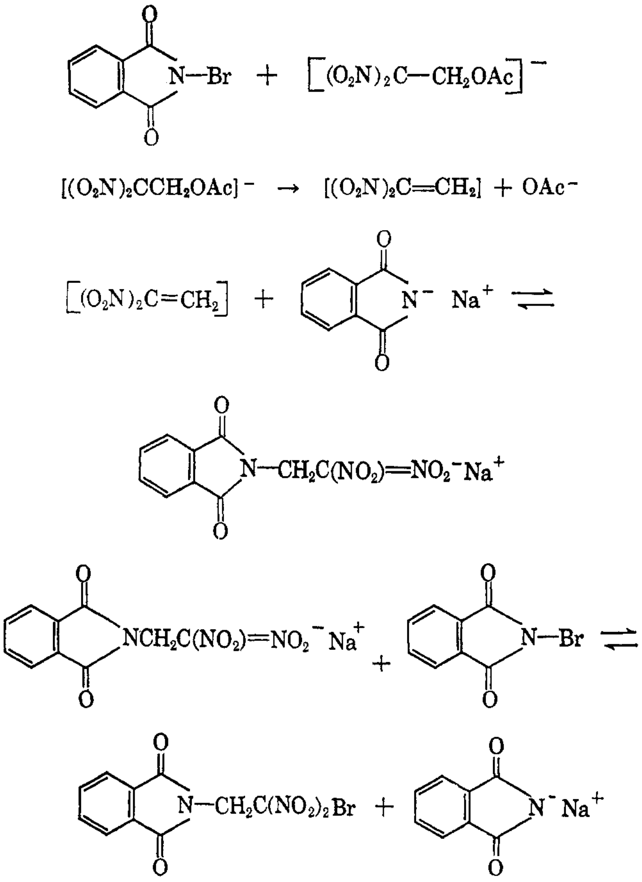
$$BrC(NO_2)_2CH_2OAc + MeOH \rightarrow BrC(NO_2)_2CH_2OCH_3\ (72\%) + BrC(NO_2)_2CH_2OH\ (12\%)$$

The reaction of 2-bromo-2,2-dinitroethanol with methanol giving 2-bromo-2,2-dinitroethyl methyl ether was also studied conductometrically and found to be pseudo first order, $k = 0.0664$ hr.$^{-1}$ at 66.1° with $C_0 = 0.447$ M.

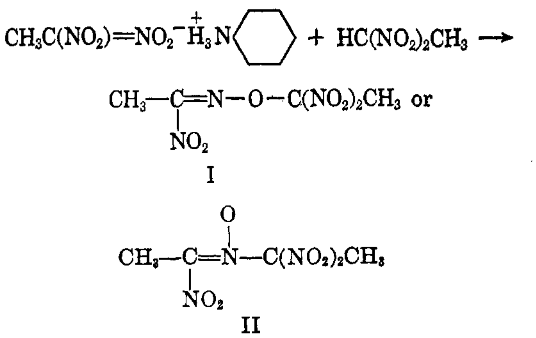
Feuer and co-workers (37) reported that the reaction of 2-bromo-2,2-dinitroethyl acetate with 1 mole-equivalent of disodium 1,1,4,4-tetranitrohexane led to the formation of 1,1,3,3,8,8,10,10-octanitrodecane and 1,6-dibromo-1,1,6,6-tetranitrohexane.

All the data indicate that the mechanism of the reaction of 2-bromo-2,2-dinitroethyl acetate with bases (C, N, or O) proceeds as proposed by Frankel (50) with the modification that the anion formed by addition of the base to the intermediate 1,1-dinitroethylene regains a bromine from the appropriate source of "positive bromine" in the reaction mixture. The complete mechanistic path may be depicted as follows.



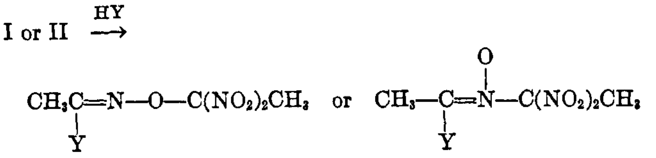


Belew and co-workers (13) found that 1,1-dinitroethane reacted with its nitrogen base salts to give a coupled product of unresolved structure. Analytical data and reactions of the product indicate its structure is either I or II.


I

II

The product has one easily replaceable nitro group.



where Y = –Cl, –OEt, $-OC_6H_5$, or $-NH_2$.

Ungnade and Kissinger (197) reported that 2,2-dinitropropiohydroxamoyl chloride is condensed to a furoxan by sodium bicarbonate.

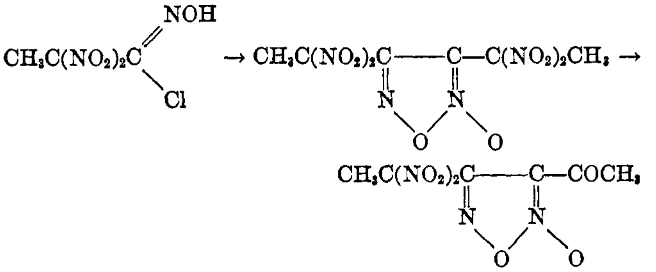
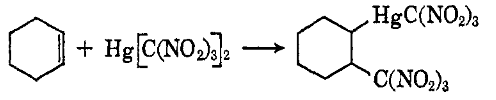


Table XVII lists the reactions and products for the various alkylation reactions reported in the literature.

Reactions of Mercury Nitroform.—Early work on reactions of mercury nitroform (110) has recently been extended by Novikov and his co-workers (136–138, 149, 150). The elements of mercury nitroform added readily to double bonds (150, 187). For example

$$CH_2{=}CH_2 + Hg[C(NO_2)_3]_2 \rightarrow (NO_2)_3CCH_2CH_2HgC(NO_2)_3$$

$$(NO_2)_3CCH_2CH_2HgC(NO_2)_3 + CH_2{=}CH_2 \rightarrow Hg[CH_2CH_2C(NO_2)_3]_2$$



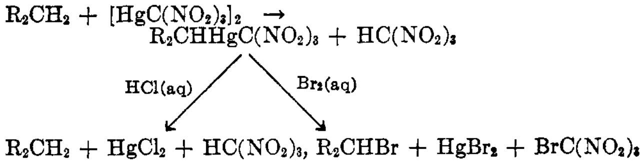
$$CH_2{=}CHCH_2OH + Hg[C(NO_2)_3]_2 \rightarrow (NO_2)_3CHgCH_2CH(C(NO_2)_3)CH_2OH$$

Propylene, styrene, and 2-buten-4-ol provide further examples of this general reaction. It is interesting to note that phenyl mercury nitroform adds readily to ethylene, but the unsymmetrical product apparently undergoes disproportionation leading to the formation of bisdiphenylmercury and bis-3,3,3-trinitropropylmercury, which are isolated. Isobutylene fails to react.

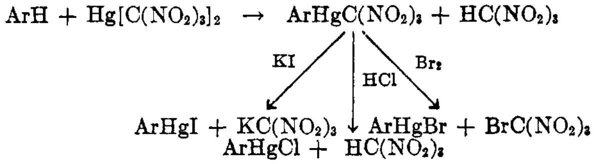
These addition products may be converted to the halogenated mercury compound by treatment with aqueous HCl, Br_2, or KI.

$$(NO_2)_3CCH_2CH_2HgC(NO_2)_3 \xrightarrow{HCl} (NO_2)_3CCH_2CH_2HgCl + HC(NO_2)_3$$

Compounds having active hydrogen are readily mercurated, with the reactions carried out at room temperature in aqueous solution (137). In the following example, such compounds as malonic ester, acetoacetic ester, nitroacetic ester, acetylacetonate, acetone, and cyclohexanone have been employed.



The mercuration of certain aromatic and heterocyclic compounds may also be effected by mercury nitroform (136).



The aromatic nitro compounds apparently do not react in this manner, but rather form complexes which are isolable solid products. These complexes may be decomposed with base.

If the addition reaction is carried out in alcohol as the solvent, the alcohol moiety is incorporated in the product (149).

$$R'{-}CH{=}C{-}R'' + Hg[C(NO_2)_3]_2 \xrightarrow{ROH} R'CH(OR)CH(R'')HgC(NO_2)_3$$

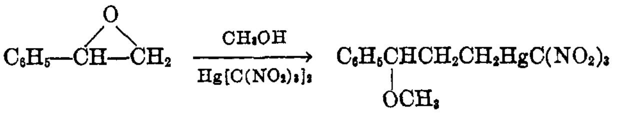


Table XVIII lists the reactants and products for various mercuration reactions in the literature.

4. *Miscellaneous Reactions*

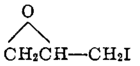
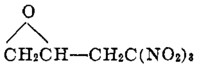
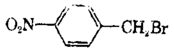
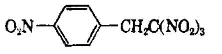
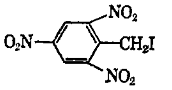
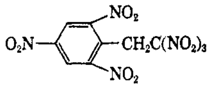
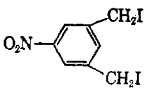
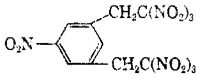
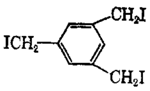
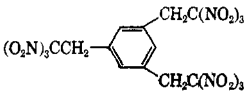
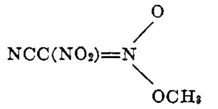
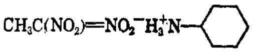
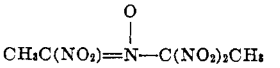
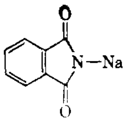
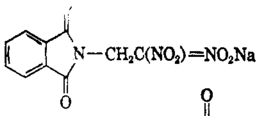
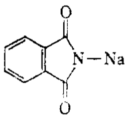
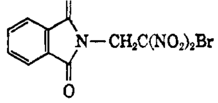
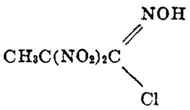
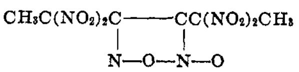
It has been found, through the efforts of many workers in the field of polynitro chemistry, that many interconversions of functional groups, normal to aliphatic chemistry, can also be effected with polynitro-substituted aliphatic compounds. The main categories of the various derivatives will be presented, with a description of the general techniques used. Tables XVIV–XXII list most of the derivatives for each category.

a. Polynitro Alcohol Derivatives

The esterification of polynitro alcohols can generally be effected by direct treatment of the alcohol with an

TABLE XVII

ALKYLATION REACTIONS

Nitro compound	Reactant	Product	Yield, %	B.p. (mm.) or m.p., °C., and/or $n^t\mathrm{D}$	Ref.
$AgC(NO_2)_3$	CH_3I	$CH_3C(NO_2)_3$	52	55–56	73
	CH_3CH_2I	$CH_3CH_2C(NO_2)_3$	52	74 (13.3); $n^{20}\mathrm{D}$ 1.4442	
	$CH_3CH_2CH_2I$	$CH_3CH_2CH_2C(NO_2)_3$	33	68 (6.0); $n^{20}\mathrm{D}$ 1.4432	
	$CH_3(CH_2)_3I$	$CH_3(CH_2)_3C(NO_2)_3$	32	82 (5.0); $n^{20}\mathrm{D}$ 1.4459	
	$CH_3(CH_2)_4I$	$CH_3(CH_2)_4C(NO_2)_3$	29	84 (3.0); $n^{20}\mathrm{D}$ 1.4474	
	$CH_3(CH_2)_5I$	$CH_3(CH_2)_5C(NO_2)_3$	24	80 (0.6); $n^{20}\mathrm{D}$ 1.4482	
	$CH_3(CH_2)_6I$	$CH_3(CH_2)_6C(NO_2)_3$	26	74 (0.1); $n^{20}\mathrm{D}$ 1.4507	
	$CH_3(CH_2)_7I$	$CH_3(CH_2)_7C(NO_2)_3$	20	90 (0.2); $n^{20}\mathrm{D}$ 1.4493	
	$CH_2{=}CHCH_2I$	$CH_2{=}CHCH_2C(NO_2)_3$	64	55–56 (2.6); $n^{20}\mathrm{D}$ 1.4588	
	$CH_2{=}CHCH_2Br$	$CH_2{=}CHCH_2C(NO_2)_3$	47	60–62 (4); $n^{20}\mathrm{D}$ 1.4587	
			19	80 (0.7); $n^{20}\mathrm{D}$ 1.4715	
	$CH_2{=}C(CH_3)CH_2Br$	$CH_2{=}C(CH_3)CH_2C(NO_2)_3$	28	57 (0.35); $n^{20}\mathrm{D}$ 1.4635	73
	$BrCH_2C{\equiv}CCH_2Br$	$(O_2N)_3CCH_2C{\equiv}CCH_2C(NO_2)_3$	72	129.4–129.7	188
			45	135	161
			64	153–154	161
			Low	170–171.5	161
$AgC(NO_2)_3$			Low	205–206	161
$AgC(NO_2)_2CN$	$CH_2{=}CHCH_2Br$	$CH_2{=}CHCH_2C(CN)(NO_2)_2$	35	38–40 (0.4); $n^{20}\mathrm{D}$ 1.4552	73, 156
$AgC(NO_2)_2CN$	CH_3I		58.3	62–64	73, 156
$AgC(NO_2)_2CN$	$CH_3C(CH_3)_2Br$	$NCC(NO_2)_2C(CH_3)_2CH_3$	13.6	132–133 dec.	73, 156
	$HC(NO_2)_2CH_3$	$CH_3C(NO_2){=}N{-}OC(NO_2)_2CH_3$ or  $CH_3C(NO_2){=}\overset{\overset{\displaystyle O}{\vert}}{N}{-}C(NO_2)_2CH_3$	36	119–120	13
$BrC(NO_2)_2CH_2OAc$	KI $[KO_2N{=}C(NO_2)CH_2OAc]$	$KO_2N{=}C(NO_2)CH_2C(NO_2)_2CH_2OAc$	64.5	174 exp.	50
	$NaO_2N{=}(CNO_2)CH_3$	$KO_2N{=}C(NO_2)CH_2C(NO_2)_2CH_3$	—	137–138 dec.	50
$BrC(NO_2)_2CH_2OAc$			64.3	238, exp.	50
$BrC(NO_2)_2CH_2OAc$			40	117–118	200
$BrC(NO_2)_2CH_2OAc$	HOMe	$BrC(NO_2)_2CH_2{-}O{-}Me$	72	84 (7); $n^{25}\mathrm{D}$ 1.4728	200
	$[NaO_2N{=}C(NO_2)CH_2CH_2]_2$	$[HC(NO_2)_2CH_2C(NO_2)_2CH_2CH_2]_2$ and $[BrC(NO_2)_2CH_2CH_2]_2$	27	130–131 dec.	37
	$NaHCO_3$		85.9	109 dec.	197

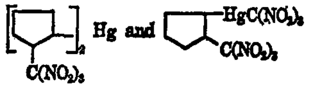
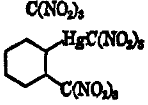
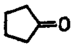
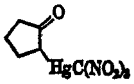
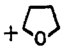
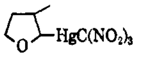
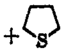
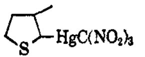
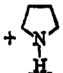
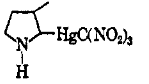
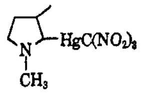
acid chloride. In many cases, this reaction requires the use of a catalyst such as aluminum chloride in a procedure developed by Hill (83) for the esterification of polyfluoroalcohols. A paper by Gold and Klager (67) gives a summary of the standard methods employed to effect esterifications. They found that polyphosphoric acid was an effective condensing agent for the esterification of polynitro alcohols with polynitrocarboxylic acids. Kissinger and co-workers (97) also reported the use of polyphosphoric acid, and also trifluoroacetic anhydride, as a condensing agent. Novikov and co-workers (147) reported the addition of polynitroalcohols to ethoxyacetylene to give good yields of the corresponding acetates.

$$(O_2N)_3CCH_2OH + HC{\equiv}C{-}OEt \rightarrow (O_2N_3)CCH_2OAc$$

Mixed acetals have been prepared by the addition of polynitro alcohols to vinyl ethers (145). A review by

TABLE XVIII

REACTIONS OF MERCURY NITROFORM

Reactant	Solvent	Product	Yield, %	M.p., °C. Product	M.p., °C. Derivatives RHgCl	M.p., °C. Derivatives RHgBr	Ref.
$Hg[C(NO_2)_3]_2 + CH_2{=}CH_2$	Aq.	$(O_2N)_3CCH_2CH_2HgC(NO_2)_3$	93	167 dec.	142	128–129	187
$ClHgC(NO_2)_3 + CH_2{=}CH_2$	Aq.	$(O_2N)_3CCH_2CH_2HgCl$	80	142			187
$Hg[C(NO_2)_3]_2 + 2CH_2{=}CH_2$	EtOH	$Hg[CH_2CH_2C(NO_2)_3]_2$	84	155 dec.			187
$C_6H_5Hg{-}C(NO_2)_3 + CH_2{=}CH_2$	EtOH	$[(O_2N)_3CCH_2CH_2]_2Hg + C_6H_5{-}Hg{-}C_6H_5$	80.5	155 dec.			187
$(NO_2)_3CCH_2CH_2HgC(NO_2)_3 + CH_2{=}CH_2$	EtOH	$[(O_2N)_3CCH_2CH_2]_2Hg$	65.5	155 dec.			187
$Hg[C(NO_2)_3]_2 + CH_3{-}CH{=}CH_2$	Aq.	$(NO_2)_3C\underset{\substack{\mid\\ CH_3}}{C}H{-}CH_2HgC(NO_2)_3$	97	133–134 dec.	119	117–118	187
$Hg[C(NO_2)_3]_2 + 2CH_3{-}CH{=}CH_2$	Aq.	$[(NO_2)_3C\underset{\substack{\mid\\ CH_3}}{C}H{-}CH_2]_2Hg$	79	124–125 dec.			187
$Hg[C(NO_2)_3]_2 + C_6H_5{-}CH{=}CH_2$	Aq.	$(NO_2)_3CCH(C_6H_5)CH_2HgC(NO_2)_3$	80	129 dec.	147		187
$ClHgC(NO_2)_3 + C_6H_5CH{=}CH_2$	Aq.	$(NO_2)_3CCH(C_6H_5)CH_2HgCl$	61	147			187
$Hg[C(NO_2)_3]_2$ + 	Aq.		Major Minor	89–90 dec. 111–112		129.5	187
$Hg[C(NO_2)_3]_2$ + 	Aq.		55	95	152	144	187
$Hg[C(NO_2)_3]_2 + CH_2{=}CHCH_2OH$	Aq.	$(NO_2)_3CHgCH_2CH(C(NO_2)_3)CH_2OH$	54	150	150	89–90	150
$Hg[C(NO_2)_3]_2 + 2CH_2{=}CH{-}CH_2OH$	Aq.	$[HOCH_2CH(C(NO_2)_3)CH_2]_2Hg$	80	108			150
$Hg[C(NO_2)_3]_2 + CH_2{=}CHCH_2CH_2OH$	Aq.	$(O_2N)_3CHgCH_2CH(C(NO_2)_3)CH_2CH_2OH$	75	140–141			150
$Hg[C(NO_2)_3]_2 + CH_2{=}CHCH_2CH_2CH_2OH$	Aq.		100	115–116			150
$Hg[C(NO_2)_3]_2 + CH_2{=}CHCH_2CH_2CH_2OH$	CH_3NO_2	$[HOCH_2CH_2CH_2CH(C(NO_2)_3)CH_2]_2Hg$	86	Oil			150
$Hg[C(NO_2)_3]_2 + CH_2{=}CHCH_2CH_2CH_2OAc$	Aq.	$(NO_2)_3CHgCH_2CH[C(NO_2)_3]CH_2CH_2CH_2OAc$	100	106		104	150
$Hg[C(NO_2)_3]_2 + CH_2(COOEt)_2$		$(EtOOC)_2CH{-}HgC(NO_2)_3$	35	250 dec.			137
$Hg[C(NO_2)_3]_2 + CH_3COCH_2COOEt$		$CH_3COCH[HgC(NO_2)_3]COOEt$	62	159 dec.			137
$Hg[C(NO_2)_3]_2 + (CH_3CO)_2CH_2$		$(CH_3CO)_2CHHgC(NO_2)_3$	95	158 dec.			137
$Hg[C(NO_2)_3]_2 + CH_3COCH_3$		$CH_3COCH_2Hg(NO_3)_3$	100	153 dec.			137
$Hg[C(NO_2)_3]_2$ + 			100	140 dec.			137
$Hg[C(NO_2)_3]_2 + O_2N{-}CH_2COOEt$		$(O_2N)_3CHgCH(NO_2)COOEt$	100	134–135			137
$Hg[C(NO_2)_3]_2 + C_6H_6$		$C_6H_5HgC(NO_2)_3$	58.5	146			136
$Hg[C(NO_2)_3]_2 + C_6H_5CH_3$		$CH_3C_6H_4HgC(NO_2)_3$-*o* and -*p*	51.5	149 *para* 126 *ortho*			136
$Hg[C(NO_2)_3]_2 + C_6H_5OCH_3$		$CH_3OC_6H_4HgC(NO_2)_3$-*o* and -*p*	41	114 *ortho* 101 *para*			136
$Hg[C(NO_2)_3]_2 + C_6H_5NH_2$		$C_6H_5NHHgC(N_2O)_3$	59	117 dec.			136
$Hg[C(NO_2)_3]_2 + C_6H_5N(CH_3)_2$		$(CH_3)_2NC_6H_4HgC(NO_2)_3$-*p*	—	110 dec.			136
$Hg[C(NO_2)_3]_2$ + 			25	120 dec.			136
$Hg[C(NO_2)_3]_2$ + 			28	115 dec.			136
$Hg[C(NO_2)_3]_2$ + 			—	122 dec.			136
$Hg[C(NO_2)_3]_2$ + 			—	117 dec.			136

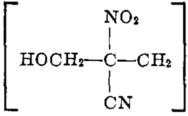
Shvekhgeimer and co-workers (174) on the preparation and properties of nitro alcohols surveys the literature through 1957.

Table XIX lists the ester and mixed acetal derivatives of polynitro alcohols. Table XX lists carbamate derivatives of isocyanates and alcohols.

b. Polynitrocarboxylic Acids and Derivatives

Polynitrocarboxylic acids are generally obtained by the acid hydrolysis of their esters. The esters can be obtained from Michael or Mannich-type reactions of nitro paraffins. The polynitrocarboxylic acids are generally converted in good yield to the corresponding acid chloride on treatment with thionyl chloride. The acid chlorides can be treated with sodium azide to effect conversion to the intermediate acid azides, which, upon warming, are smoothly rearranged to the polynitro-substituted isocyanates. Generally, the acid chlorides and acid azides are not purified. The isocyanates thus obtained can generally be converted to all the normal derivatives: carbamates, ureas, and

TABLE XIX
POLYNITROALCOHOL ESTERS

Alcohol	Ester	B.p. (mm.) or m.p., °C., and/or n^{t}_{D}	Ref.
$(NO_2)_3CCH_2OH$	Acetate	118 (4)	116
	Propionate	125 (6)	116
	Acrylate	80 (2)	33
	Methacrylate	26	33
	Crotonate	97 (5)	33
	Fumarate	150	33
	Itaconate	97	33
	4,7-Dinitrazadecanedioate	128	52
	4,4,6,6,8,8-Hexanitroundecanedioate	117–118	52
	4,4-Dinitroheptanedioate	170–171	52
	4-Nitrazaheptanedioate	110–111	52
	3,5,5-Trinitro-3-azahexanoate	121	52
	4-Nitrazapentanoate	58.5–59	67
	4,4-Dinitropentanoate	93.5–94.5	67
	4-Nitro-4-methylpentanoate	68.5–69	67
$BrC(NO_2)_2CH_2OH$	Acetate	70 (0.35); n^{25}_{D} 1.4728	50
$CH_3C(NO_2)_2CH_2OH$	Formate	65 (0.5); n^{25}_{D} 1.4505	97
	Acetate	75 (0.5); n^{25}_{D} 1.4413	97
	Trifluoroacetate	47 (0.07); n^{25}_{D} 1.3961	97
	Acrylate	71 (0.4); n^{25}_{D} 1.4610	67
	Methacrylate	71 (0.03); n^{25}_{D} 1.4593	97
	2-Trifluoromethylacrylate	38–39	97
	Malonate	37–39	97
	Oxalate	109–110	97
	Maleate	62–63	97
	Pentanedioate	45–46	97
	Hexanedioate	66–67	97
	4-Methyl-4-nitroheptanedioate	118–121	97
	4(2-Carbethoxyethyl)-4-nitroheptanedioate	62–64	97
	α-Bromopropionate	90 (0.5); n^{25}_{D} 1.4793	97
	4-Nitro-4-azahexanoate	180 (0.04)	97
	Phosphate	146–147	97
	4-Nitropentanoate	39–40	67
	4,4-Dinitropentanoate	100	67
	4-Nitro-4-methylpentanoate	73.5–74	67
$NCC(NO_2)_2CH_2OH$	Acetate	73–75 (1.25); n^{20}_{D} 1.4439	156
	Acrylate	56–60 (0.1)	156
	Methacrylate	53–58 (0.07)	156
	Nitrate	46–55 (0.1)	156
	Trifluoroacetate	39 (0.15); n^{20}_{D} 1.4045	156
$H_2NCOC(NO_2)_2CH_2OH$	Acetate	60–62	153
$HOCH_2C(NO_2)_2CH_2OH$	Diacetate	113–115 (1)	29
$CH_3C(NO_2)_2CH(OH)COOH$	Acetate	128	96
	Trifluoroacetate	131	96
$(NO_2)_2CHCH(OH)COOEt$	Acetate	54	96
$ClC(NO_2)_2CH(OH)COOEt$	Acetate	67–69 (0.01)	96
$HC(NO_2)_2CH_2C(NO_2)_2CH_2OH$	Acetate	58–59	107
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$	Nitrate	108–111	68
	Acetate	56–57	68
$(NO_2)_2C(CH_2CH_2CH_2OH)_2$	Dinitrate	27–28	52
$O_2NCH[CH_2C(NO_2)_2CH_2CH_2CH_2OH]_2$	Dinitrate	73–75	52
$(O_2N)_2C[CH_2C(NO_2)_2CH_2CH_2CH_2OH]_2$	Dinitrate	100–101	52
$O_2N—N[CH_2C(NO_2)_2CH_2CH_2CH_2OH]_2$	Dinitrate	106–108	52
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$	Nitrate	59–60	52
 $\left[HOCH_2-\overset{NO_2}{\underset{CN}{C}}-CH_2\right]_2$	Diacetate	181–182	44
$O_2NCH_2CH(OH)CH(OH)CH_2NO_2$	Diacetate	80.5–81	144
$[(HOCH_2)_2C(NO_2)CH_2]_2$	Tetraacetate	122–123	43
$HOCH_2—CH(NO_2)CH_2CH_2CH_2NO_2$	α-Naphthylurethane	121–123	43
$[HOCH_2CH(NO_2)CH_2]_2$	Diacetate	105–107 (mixture of epimers)	43
$HOCH_2CH(NO_2)CH_2CH_2CH_2CH_2NO_2$	α-Naphthylurethane	99–100	43

MIXED ACETAL DERIVATIVES OF POLYNITROALCOHOL

	Vinyl ether		
$(NO_2)_3CCH_2OH$	$CH_2=CHOEt$	84–86 (3); n^{20}_{D} 1.4435	145
$CH_3C(NO_2)_2CH_2OH$	$CH_2=CHOEt$	96–99 (4); n^{20}_{D} 1.4405	145
	$CH_2=CHOCH(CH_3)_2$	99–102 (4); n^{20}_{D} 1.4335	145
	$CH_2=CHOCH_2CH_2CH_3$	116–120 (5); n^{20}_{D} 1.4367	145

amine hydrochlorides. Table XXI lists examples and references for the polynitrocarboxylic acids and derivatives.

$$CH_3C(NO_2)_2CH_2CH_2COOH + SOCl_2 \rightarrow [CH_3C(NO_2)_2CH_2CH_2COCl] \xrightarrow{NaN_3} [CH_3C(NO_2)_2CH_2CH_2CON_3] \xrightarrow{\Delta} CH_3C(NO_2)_2CH_2CH_2NCO$$

TABLE XX

CARBAMATES AND N-NITRO CARBAMATES

Isocyanate	Alcohol	M.p., °C. Carbamate	M.p., °C. N-Nitro deriv.	Ref
CH_3NCO	$(NO_2)_3CCH_2OH$	Oil	39–40	51
C_2H_5NCO	$(NO_2)_3CCH_2OH$	Oil	50–51	51
$C_2H_5OOCCH_2NCO$	$(NO_2)_3CCH_2OH$	71–72	46–47	51
$CH_3N(NO_2)CH_2CH_2NCO$	$(NO_2)_3CCH_2OH$	98–99	103–104	51
$CH_3N(NO_2)CH_2CH_2NCO$	$C(NO_2)_2(CH_2OH)_2$	128–129	117–118	51
$CH_3C(NO_2)_2CH_2CH_2NCO$	$CH_3C(NO_2)_2CH_2OH$	Oil	70–72	51
$CH_3C(NO_2)_2CH_2CH_2NCO$	$(NO_2)_3CCH_2OH$	Oil	107–108	51
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2NCO$	$(NO_2)_3CCH_2OH$	Oil	140–141	51
$(NO_2)_3CCH_2CH_2NCO$	C_2H_5OH	65–66	94–95	51
$(NO_2)_3CCH_2CH_2NCO$	cyclo-$C_6H_{11}OH$	96–97	56–58	51
$(NO_2)_3CCH_2CH_2NCO$	C_6H_5OH	102–103	127–129	51
$(NO_2)_3CCH_2CH_2NCO$	$CH_3C(NO_2)_2CH_2OH$	103–104	71–72	51
$(NO_2)_3CCH_2CH_2NCO$	$(NO_2)_3CCH_2OH$	91–92	96–97	51
$(NO_2)_3CCH_2CH_2NCO$	$C(NO_2)_2(CH_2OH)_2$	Oil	94–96	51
$(NO_2)_3CCH_2CH_2NCO$	$HOCH_2C{\equiv}CCH_2OH$	Oil	115–116	51
$CH_2(NCO)_2$	$(NO_2)_3CCH_2OH$	125–126	103–104 (mono) 95–96/112–113 (di)[a]	51
$C(NO_2)_2(CH_2CH_2NCO)_2$	$(NO_2)_3CCH_2OH$	96–97	151–152	51
$N(NO_2)(CH_2NCO)_2$	$(NO_2)_3CCH_2OH$	Oil	185–186	51
$OCNCH_2N(NO_2)CH_2CH_2NCO$	$(NO_2)_3CCH_2OH$	65–67	113–114	51
$N(NO_2)(CH_2CH_2NCO)_2$	$(NO_2)_3CCH_2OH$	130–131	120–122	51
$[CH_3N(NO_2)CH_2CH_2NCO]_2$	$(NO_2)_3CCH_2OH$	156–158	127–128	51
$N(NO_2)[CH_2C(NO_2)_2CH_2CH_2NCO]_2$	$(NO_2)_3CCH_2OH$	157–159	150–151	51
C_2H_5NCO	$CH_3C(NO_2)_2CH_2OH$	[b]	34–36	97

[a] Polymorphs. [b] B.p. 80° (0.02 mm.).

Table XX lists the polynitroisocyanates and derivatives.

$$CH_3C(NO_2)_2CH_2CH_2NCO \left\{ \begin{array}{l} \xrightarrow{HCl} CH_3C(NO_2)_2CH_2CH_2NH_2{\cdot}HCl \\ \xrightarrow{ROH} CH_3C(NO_2)_2CH_2CH_2NHCOOR \\ \xrightarrow{H_2O} [CH_3C(NO_2)_2CH_2CH_2]_2CO \end{array} \right.$$

Feuer, Bachman, and May (30) reported that methyl 3,5,5-trinitro-3-azapentanoate (III) could not be hydrolyzed to the corresponding acid; instead, total decomposition of the compound took place.

$HC(NO_2)_2CH_2N(NO_2)CH_2COOMe$

III

$CH_3C(NO_2)_2CH_2N(NO_2)CH_2COOMe$

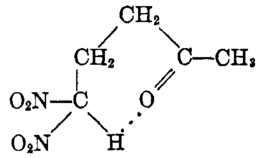
IV

However, Frankel and Klager (56) showed that, by replacing the acidic proton by a methyl group, methyl 3,5,5-trinitro-3-azahexanoate (IV) could readily be hydrolyzed to the corresponding acid and then converted to all the normal acid derivatives except the amine hydrochloride. Parker (153) reported the facile conversion of sodium cyanodinitromethide to dinitroacetamide with anhydrous hydrochloric acid.

c. Selective Reductions

It is well known that nitro groups are easily reduced to a variety of products, even under such extremely mild conditions as zinc dust and water. Therefore, most reduction reactions on functional groups other than the nitro groups might be expected to attack the nitro group as well. However, Shechter and co-workers (171) showed that polynitro-substituted aldehydes and ketones could be reduced to the corresponding alcohols by aluminum isopropoxide (Meerwein–Ponndorf–Verley reduction) or by acidic sodium borohydride in good yield. The reduction of 5,5-dinitro-2-pentanone was slow and incomplete after extremely long reaction times, probably because of its existence in a cyclic hydrogen-bonded structure.

$(O_2N)_2CHCH_2CH_2COCH_3 \rightleftharpoons$



Feuer and Kucera (34) reported the selective reduction of polynitro esters to the corresponding alcohols with lithium aluminum hydride at −50 to −60°. Gold and Klager (67) reported the use of sodium borohydride for the selective reduction of polynitro- and nitraza-substituted acid chlorides to the corresponding alcohols and for the reduction of polynitro-substituted keto alcohols to the diols. Klager (103, 106) selectively debrominated α,ω-dinitro-α,α,ω,ω-tetrabromoalkanes using sodium borohydride.

$$O_2NCBr_2CH_2CH_2CBr_2NO_2 \xrightarrow{NaBH_4} O_2NCH_2CH_2CH_2CH_2NO_2$$

Prior to the development of the selective reduction techniques, alcohols having the hydroxyl group more than one carbon removed from the nitro group were very difficult to obtain. Techniques used were the amine nitrosation reaction and the acetolysis of halides (82).

Table XXII lists the various selective reductions of polynitro-substituted compounds.

d. Polynitro Halides

Very little work has been reported on the synthesis of polynitro halides having the halogen substituent one or

TABLE XXI

POLYNITROCARBOXYLIC ACIDS AND DERIVATIVES

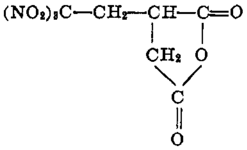
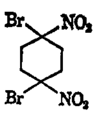
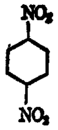
Compound	B.p. (mm.) or m.p., °C.	Ref.
$(NO_2)_2C(CH_2CH_2COOH)_2$	139–140	203
$(NO_2)_2C(CH_2CH_2COCl)_2$	57	81
$(NO_2)_2C(CH_2CH_2COOCH_3)_2$	43.5–44.5	81
$(NO_2)_2C(CH_2CH_2CON_3)_2$	68–69 dec.	81
$(NO_2)_2C(CH_2CH_2NCO)_2$	37–38	81
$(NO_2)_2C(CH_2CH_2NHCO_2CH_3)_2$	114	81
$(NO_2)_2C(CH_2CH_2NH_2 \cdot HCl)_2$	225–230	81
$CH_3C(NO_2)_2CH_2CH_2COOH$	97.4–99.2	172
$CH_3C(NO_2)_2CH_2CH_2COOCH_3$	94–97 (0.06)	172
$CH_3C(NO_2)_2CH(OOCCH_3)COOCH_3$	89–91 (0.3)	96
$CH_3C(NO_2)_2CH(OOCCH_3)COOCH_2CH_3$	106–107 (0.05)	96
$(NO_2)_2CHCH(OCH_3)COOCH_3$	60–61	96
$ClC(NO_2)_2COOCH_3$	40 (4)	99
$[(HOOCCH_2CH_2)_2C(NO_2)CH_2]_2$	219.5	32
$[(CH_3OOCCH_2CH_2)_2C(NO_2CH_2]_2$	122.5–123.5	32
$(NO_2)_3CCH_2CH(COOH)CH_2COOH$	41–42	48
	86–87	48
$(NO_2)_3CCH_2CH_2COCl$	65–66 (0.5)	65
$[(NO_2)_3CCH_2CH_2CO]_2O$	109.5–110	65
$(NO_2)_3CCH_2CH_2NCO$	73–75 (1 μ)	65
$[(NO_2)_3CCH_2CH_2NH]_2CO$	170–171	65
$(NO_2)_3CCH_2CH_2NHCO_2CH_2CH_3$	65.5–66	65
$(NO_2)_3CCH_2CH_2NH_2 \cdot HCl$	161–163	65
$CH_3C(NO_2)_2CH_2CH_2NCO$	106–110 (1 μ)	65
$[CH_3C(NO_2)_2CH_2CH_2NH]_2CO$	120–121	65
$CH_3C(NO_2)_2CH_2CH_2NHCO_2CH_3$	48–49	65
$CH_3C(NO_2)_2CH_2CH_2NH_2 \cdot HCl$	220–230	65
$CH_3OOCCH_2CH_2C(NO_2)_2CH_2CH_2NCO$	140–150 (1 μ)	65
$[CH_3OOCCH_2CH_2C(NO_2)_2CH_2CH_2NH]_2CO$	159–160	65
$CH_3OOCCH_2CH_2C(NO_2)_2CH_2CH_2NHCO_2CH_3$	74–75	65
$CH_3OOCCH_2CH_2C(NO_2)_2CH_2CH_2NH_2 \cdot HCl$	180–182	65
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2COOH$	133–136	56
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2COCl$	87–88	56
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2COOCH_3$	80–81	54
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2NCO$	97–100	56
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2NHCO_2CH_3$	100–102	56
$HOOCCH_2CH_2C(NO_2)_2(CH_2)_2C(NO_2)_2CH_2CH_2COOH$	182–184	37
$MeOOCCH_2CH_2C(NO_2)_2(CH_2)_2C(NO_2)_2CH_2CH_2COOMe$	157–157.5	37
$ClCOCH_2CH_2C(NO_2)_2(CH_2)_2C(NO_2)_2CH_2CH_2COCl$	143–144	37
$OCNCH_2CH_2C(NO_2)_2(CH_2)_2C(NO_2)_2CH_2CH_2NCO$	161–163	37
$H_2NCH_2CH_2C(NO_2)_2(CH_2)_2C(NO_2)_2CH_2CH_2NH_2 \cdot 2HCl$	215 dec.	37
$H_2NCOCH_2CH_2C(NO_2)_2(CH_2)_2C(NO_2)_2CH_2CH_2CONH_2$	195	37
$CH_3CO_2NHCH_2CH_2C(NO_2)_2(CH_2)_2C(NO_2)_2CH_2CH_2NHCO_2CH_3$	161–163	37
$HOOCCH_2CH_2C(NO_2)_2(CH_2)_3C(NO_2)_2CH_2CH_2COOH$	174.4–174.7	37
$MeOOCCH_2CH_2C(NO_2)_2(CH_2)_3C(NO_2)_2CH_2CH_2COOMe$	64.5	37
$ClCOCH_2CH_2C(NO_2)_2(CH_2)_3C(NO_2)_2CH_2CH_2COCl$	64.5–67.5	37
$OCNCH_2CH_2C(NO_2)_2(CH_2)_3C(NO_2)_2CH_2CH_2NCO$	Oil	37
$H_2NCH_2CH_2C(NO_2)_2(CH_2)_3C(NO_2)_2CH_2CH_2NH_2 \cdot 2HCl$	223	37
$H_2NCOCH_2CH_2C(NO_2)_2(CH_2)_3C(NO_2)_2CH_2CH_2CONH_2$	127–128	37
$CH_3CO_2NHCH_2C(NO_2)_2(CH_2)_3C(NO_2)_2CH_2CH_2NHCO_2CH_3$	93–94	37
$HOOCCH_2CH_2C(NO_2)_2(CH_2)_4C(NO_2)_2CH_2CH_2COOH$	182–183	37
$MeOOCCH_2CH_2C(NO_2)_2(CH_2)_4C(NO_2)_2CH_2CH_2COOMe$	102–104	37

TABLE XXII

SELECTIVE REDUCTION

Polynitro compound	Product	Yield, %	B.p. (mm.) or m.p., °C., and/or n^t_D	Ref.
$CH_3C(NO_2)_2CH_2CH_2COCH_3$	$CH_3C(NO_2)_2CH_2CH_2CH(OH)CH_3$	87.9[a] 78.2[b]	104–104.5 (0.6); n^{20}_D 1.4636	171
$CH_3C(NO_2)_2CH_2CH_2CHO$	$CH_3C(NO_2)_2CH_2CH_2CH_2OH$	62.8[a] 67.6[b]	109–110 (0.8); n^{20}_D 1.4469	171
$(O_2N)_2CHCH_2CH_2COCH_3$	$(O_2N)_2CHCH_2CH_2CH(OH)CH_3$	48.5[b]	115.5–116.5 (1); n^{20}_D 1.4628	171
$CH_3C(NO_2)_2CH_2CH_2COOCH_3$	$CH_3C(NO_2)_2CH_2CH_2CH_2OH$	53[c]	109–110 (0.8)	34
$(O_2N)_2C(CH_2CH_2COOCH_3)_2$	$(O_2N)_2C(CH_2CH_2CH_2OH)_2$	56[c]	74.5–75	34
$O_2NCBr_2CH_2CH_2CBr_2NO_2$	$O_2NCH_2(CH_2)_2CH_2NO_2$	[b]	30–33	103, 106
		63[b]	110–145[d]	122

[a] Aluminum isopropoxide reducing agent. [b] Sodium borohydride reducing agent. [c] Lithium aluminum hydride reducing agent. [d] Product is a mixture of epimers.

more carbon atoms removed from the polynitro substituent. The Hunsdiecker silver salt degradation has been used for the preparation of certain polynitrobromoalkanes (172, 182).

$$CH_3C(NO_2)_2CH_2CH_2COOAg \xrightarrow[CCl_4]{Br_2} CH_3C(NO_2)_2CH_2CH_2Br$$

$$(O_2N)_2C(CH_2CH_2COOAg)_2 \xrightarrow[CCl_4]{Br_2} (O_2N)_2C(CH_2CH_2Br)_2$$

Novikov and co-workers (131, 146) have reported two methods for the conversion of polynitro alcohols to the corresponding chlorides in fair yield.

$$CH_3CH(OEt)OCH_2C(NO_2)_2CH_3 \xrightarrow{PCl_5} ClCH_2C(NO_2)_2CH_3$$

$$CH_3CH(OEt)OCH_2C(NO_2)_3 \xrightarrow{PCl_5} (O_2N)_3CCH_2Cl$$

$$(O_2N)_2C(CH_2OH)_2 \xrightarrow[pyr.]{SOCl_2} (O_2N)_2C(CH_2Cl)_2$$

e. Polynitroolefins

Only a few polynitro-substituted olefins have been reported (144, 160, 189). They were prepared by dehydrohalogenation or by acetate elimination.

$$CH_3C(NO_2)_2CH_2CH_2Br \xrightarrow{CH_3ONa} CH_3C(NO_2)_2CH{=}CH_2$$

$$[AcOCH_2CH(NO_2)CH_2]_2 \xrightarrow{\Delta} [CH_2{=}C(NO_2)CH_2]_2$$

$$O_2NCH_2CH(OAc)CH(OAc)CH_2NO_2 \xrightarrow[HCCl_3]{KHCO_3} O_2NCH{=}CH{-}CH{=}CHNO_2$$

f. Polynitro Polymers

Fischer (49) reported rate studies of nitropolyurethane formation from 3,3-dinitropentamethylene diisocyanate with 2,2-dinitro-1,3-propanediol, 3,3-dinitro-1,5-pentanediol, and 1,3-propanediol. A profound retarding effect of nitro groups upon the reactivity of the primary hydroxyl groups was found, with the greatest influence effected by nitro groups adjacent to the hydroxyl. Boron trifluoride increases the rate of nitrourethane formation initially but rapidly loses its effectiveness. Metal acetylacetonates are effective catalysts for the polymerizations (except that the lead and copper compounds promote diisocyanate homopolymer formation as well), with ferric acetylacetonate by far the most effective.

The polymerization of methyl methacrylate in the presence of a variety of nitro compounds was studied by Fukuto and Kispersky (59). The chain-transfer constants were found to increase with increasing numbers of nitro groups, with tetranitromethane inhibiting the polymerization. Polynitro compounds were found to inhibit the polymerization of styrene and of vinyl acetate. The polymerization of trinitroethyl methacrylate was found to give a constant molecular weight homopolymer over a wide variation of initiator concentration and polymerization rate.

Feuer and co-workers (33) reported the thermal polymerization of trinitroethyl acrylate, trinitroethyl methacrylate, and a mixture of trinitroethyl methacrylate and trinitroethyl fumarate.

IV. PHYSICAL PROPERTIES

A. ULTRAVIOLET SPECTRA

The ultraviolet absorption spectra of a considerable number of polynitroalkanes have been reported in the literature (Tables XXIII and XXIV). They are characterized by a high-intensity band near 210 mμ (π_2–π_3^* transition) and a band of lower intensity near 280 mμ ($n_a \rightarrow \pi_3^*$ forbidden transition). In a number of cases, the 280-mμ maximum appears as only a shoulder on the higher intensity band. It has been observed

TABLE XXIII

ULTRAVIOLET ABSORPTION SPECTRA OF POLYNITROALKANES

Compound	λ_{max}	ϵ_{max}	Solvent	Ref.
Tetranitromethane	280	135	CH_2Cl_2	178
1,1-Dinitroethane	281	52	Hexane	179
	280	53.5	CH_2Cl_2	179
Trinitromethane	280	110	Isooctane	178
1,2-Dinitroethane	282	44	CH_2Cl_2	178
	278	96.0	Isooctane	179
1,1,1-Trinitroethane	279	96.2	CH_2Cl_2	179
1,1-Dinitropropane	281	50.5	Hexane	179
2,2-Dinitropropane	280	60	Isooctane	179
	278	38.8	C_4F_9N	198
	280	55	Cyclohexane	198
	280	53.5	CCl_4	198
1,3-Dinitropropane	275	46	95% EtOH	184
	275	60	Dioxane	184
1,1-Dinitro-2-methylpropane	280	65.4	CH_2Cl_2	179
	281	63.5	Hexane	179
1,3-Dinitro-2,2-dimethylpropane	280	68	Isooctane	178
	280	91	Isooctane	179
1,1,1-Trinitropropane	280	106	CH_2Cl_2	179
1,1,1,3-Tetranitropropane	275	145	Isooctane	178
1,4-Dinitrobutane	277	47	95% EtOH	184
	275	57	Dioxane	184
1,1-Dinitrobutane	280	57.8	Hexane	179
1,4-Dinitro-2-methylbutane	280	62.0	Hexane	179
1,4-Dinitrobutane	278	47	CH_2Cl_2	178
2,3-Dinitro-2,3-dimethylbutane	283	65	CH_2Cl_2	178
	281	61.9	EtOH	194
1,1,1-Trinitrobutane	279	100	Isooctane	179
2,2,3-Trinitrobutane	282	108	Isooctane	178
1,1,3-Trinitro-2-ethylbutane	280	110	Isooctane	178
	280	106	CH_2Cl_2	178
2,2,3,3-Tetranitrobutane	280	135	CH_2Cl_2	178
	277	144	Isooctane	178
1,1,1,3-Tetranitrobutane	277	147	Isooctane	178
	280	138	CH_2Cl_2	178
1,5-Dinitropentane	277	48	95% EtOH	184
	277	58	Dioxane	184
1,1-Dinitropentane	281	61.0	Hexane	179
	278	61.5	CH_2Cl_2	179
1,1,1-Trinitropentane	280	102	Isooctane	179
1,1,1,3-Tetranitropentane	278	145	Isooctane	178
	281	142	CH_2Cl_2	178
1,1,1,3-Tetranitro-4-methylpentane	275	140	Isooctane	178
1,6-Dinitrohexane	277	48	95% EtOH	184
	277	58	Dioxane	184
2,5-Dinitrohexane	280	49	95% EtOH	184
	282	56	Dioxane	184
1,1,1-Trinitrohexane	279	105.0	Isooctane	179
	280	106.5	CH_2Cl_2	179
1,1,1,3-Tetranitrohexane	274	140	Isooctane	178
1,1,-Dinitrohexane	280	58.1	Hexane	179
	281	67.8	CH_2Cl_2	179
1,1-Dinitrooctane	279	60.5	Hexane	179
1,1-Dinitrononane	279	60.5	Hexane	179
1,1-Dinitrodecane	280	64.0	Hexane	179

TABLE XXIV
ULTRAVIOLET SPECTRA OF HALOGEN-SUBSTITUTED POLYNITROALKANES[a]

Compound	λ_{max}	ϵ_{max}
1-Chloro-1,1-dinitroethane	281	75
1-Chloro-1,1-dinitropropane	280	78
1-Chloro-1,1-dinitrobutane	280	84
1-Chloro-1,1-dinitropentane	279	81
Chlorotrinitromethane	277	129
1-Chloro-1,1,3,3-tetranitrobutane	280	160
1-Chloro-1,1,3,3-tetranitropentane	279	160
1,2-Dichloro-1,1,2,2-tetranitroethane	(269)	215
1,3-Dichloro-1,1,3,3-tetranitropropane	277	194
1-Bromo-1,1-dinitroethane	280	108
1-Bromo-1,1-dinitropropane	289	106
1-Bromo-1,1-dinitrobutane	277	125
1-Bromo-1,1-dinitropentane	279	112
1-Bromo-1,1-dinitrohexane	277	113
Bromotrinitromethane	(278)	180
1-Bromo-1,1,3,3-tetranitrobutane	275	185
1-Bromo-1,1,3,3-tetranitropentane	277	185
1,3-Dibromo-1,1,3,3-tetranitropropane	(274)	235

[a] Solvent, isooctane (ref. 175).

that the dinitroparaffins have molar absorptivities about double those of the corresponding mononitroalkanes, regardless of whether the groups are geminal or vicinal. The nitro groups absorb independently, and there is apparently very little if any interaction between them. This observation may be extended to additional groups in the molecule and the value of the molar absorptivity used as a means of estimating the number present (178, 179).

Compound	280 mμ (hexane)
Mononitroalkane	24.7 ± 1.7
Dinitroalkane	58 ± 6
Trinitroalkane	98 ± 7
Tetranitroalkane	141 ± 6

The effects of solvents on the absorption spectra of some polynitro compounds have been investigated (25, 194, 196, 198). The observed intensity increases are believed to be due to an electron donor–acceptor interaction between solvent and solute. The magnitude of the effects in N-containing solvents parallels the basic strengths which would be predicted from inductive effects alone. In the case of tetranitromethane in cyclohexane, the long wave-length absorption which is not found in the vapor phase is attributed to charge-transfer transitions (25).

Kamlet and Glover (90, 91) have observed that the ultraviolet absorption spectra of polynitroalkane anions (Table XXV) are a better method of identification than the melting points or decomposition points of these explosive salts. They have correlated the λ_{max} in the charge-resonance spectra of 1,1-dinitroalkane anions with substituents.

$$\lambda_{max} = (381.6 - 15.25\sigma^* - 8.5\gamma) \pm 0.5 \text{ m}\mu$$

σ^* = Taft's σ^*

γ = 0 or 1, depending on the absence or presence of non-bonded electrons on the β-atom

The application of this correlation to the elucidation of the structure of potassium 1,1,3-trinitro-2-propene (89) is an example of its utility.

TABLE XXV
ULTRAVIOLET SPECTRA OF POLYNITROALKANE ANIONS[a]

Compound	λ_{max}	Log ϵ_{max}	Ref.
$(CH_3)_3CC(NO_2)_2^-$	384		90, 91
$CH_3CH_2CH(CH_3)C(NO_2)_2^-$	384		90, 91
$CH_3CH_2CH_2CH_2C(NO_2)_2^-$	382 (384)		90, 91
$CH_3CH_2C(NO_2)_2^-$	382 (383)		90, 91
$CH_3C(NO_2)_2^-$	381.5 (381)	4.21	63, 90, 91, 203
$(CH_3)_2NCH_2C(NO_2)_2^-$	369.5		90, 91
$O_2NCH_2CH_2C(NO_2)_2^-$	374		90, 91
$CH_3CH_2OCH_2C(NO_2)_2^-$	365		90, 91
$HOCH_2C(NO_2)_2^-$	365		90, 91
$C_6H_5C(NO_2)_2^-$	373		90, 91
$NC{-}CH_2C(NO_2)_2^-$	362.5		90, 91
$(CH_3)_3\overset{+}{N}CH_2C(NO_2)_2^-$	352		90, 91
$^-O_2NCHCH_2CHNO_2^-$	234	3.89	121
$^-O_2NCHCH_2CH_2CHNO_2^-$	240	4.27	121
$^-O_2NCHCH_2CH_2CH_2CHNO_2^-$	235	4.28	121
$^-O_2NCHCH_2CH_2CH_2CH_2CHNO_2^-$	234	4.31	121
2,2-Dinitroethylamine	362	4.19	88
N,N-Dimethyl-2,2-dinitroethylamine	357	4.25	88
Potassium N,N-dimethyl-2,2-dinitroethylamine	357	4.23	88
	369.5	4.20	88
2-Guanidino-1,1-dinitroethane	364	4.21	203
2-Piperidino-1,1-dinitroethane	357	4.05	203
	369	4.14	203
Trimethylammonium-N-(2-nitroethyl-2-nitronate)	352	4.17	203
Dipotassium bis(2,2-dinitroethyl)-amine	367	4.46	88
Dipotassium 1,1,3,3-tetranitropropane	367	4.41	88
Potassium 1,1,3-trinitropropane	373.5	4.24	63, 89
Potassium 1,1,3-trinitro-2-propene	394	4.32	89
$CH_3OOCCH_2CH_2C(NO_2)_2^-$	379	4.23	63, 90, 91
$C_6H_5COCH_2CH_2C(NO_2)_2^-$	379	4.21	63
$CH_3COCH_2CH_2C(NO_2)_2^-$	379	4.22	63, 90, 91
$H_2NCOCH_2CH_2C(NO_2)_2^-$	379	4.21	63
$NC{-}C(NO_2)_2^-$	345		156

[a] Solvent, dilute alkali or water.

B. INFRARED SPECTRA

Grabiel, Bisgrove, and Clapp (69) have proposed a method for determining the number of nitro groups in aliphatic polynitro compounds based on the value of the absorbance in the 1580-cm.$^{-1}$ region of the infrared. For some compounds reported, they found that the ϵ_{max} per nitro group was 400 to 550. Some general observations based on the difference $\Delta\nu$ between the symmetric and asymmetric stretching frequencies of the nitro group may also be made. The *gem*-dinitroalkanes show a $\Delta\nu$ of about 250 cm.$^{-1}$, and the trinitroalkanes about 300 cm.$^{-1}$ (179). This value is changed by structure and halogen substitution in such a way that the method is of limited application. The infrared spectra of the ammonium salts of the *gem*-dinitroalkane are given in Table XXVI; the infrared spectra of the polynitroalkanes are summarized in Table XXVII.

TABLE XXVI
INFRARED SPECTRA OF AMMONIUM SALTS OF *gem*-DINITROALKANES, KBr PELLETS (100)

Ammonium salt	Bands attributed to absorption of the anions, μ		
1,1-Dinitroethane[a]	6.75 m	8.11 s	8.90 s
1,1-Dinitropropane	6.77 m	8.25 s	8.95 s
1,1-Dinitrobutane	6.81 m	8.32 s	8.88 s
1,1-Dinitropentane	6.78 m	8.38 s	8.99 s

[a] Bands at 8.05 and 8.69 μ are reported (18) for the potassium salt.

TABLE XXVII

THE INFRARED SPECTRA OF POLYNITROALKANES

Compound	NO_2 stretching, cm.$^{-1}$ Asym.	NO_2 stretching, cm.$^{-1}$ Sym.	Solvent[a]	$\Delta\nu$, cm.$^{-1}$	Ref.
1,1-Dinitroethane	1587	1337		250	18
	1582	1331		251	130, 179
1,1-Dinitropropane	1582	1330		252	18
	1582	1330		252	130, 179
2,2-Dinitropropane	1572	1330	$CHCl_3$	242	18
	1572	1325	$CHCl_3$	247	198, 196
	1575	1330		245	130, 179, 196
1,1-Dinitro-2-methylpropane	1575	1330		245	130, 179
1,3-Dinitropropane	1550	1385		165	184
1,3-Dinitro-2,2-dimethylpropane	1550	1375		175	18
1,4-Dinitrobutane	1550	1379		171	184
1,1-Dinitrobutane	1577	1330		247	130, 179
1,2-Dinitrobutane	1567	1383		184	18
2,3-Dinitro-2-methylbutane	1550	1344		206	18
1,1-Dinitro-3-butanol	1575	1332		243	18
4,4-Dinitro-2-methylbutane	1575	1330		245	130, 179
2,2-Dinitropropionitrile	1600	1304		296	100
2,2-Dinitrobutyronitrile	1597	1299		298	100
2,2-Dinitrovaleronitrile	1597	1299		298	100
1,5-Dinitropentane	1550	1383		167	184
1,1-Dinitropentane	1577	1330		247	130, 179
1,6-Dinitrohexane	1550	1385		165	184
2,5-Dinitrohexane	1538	1389		149	184
1,1-Dinitrohexane	1575	1327		248	179
1,1-Dinitrocyclohexane	1572	1323	$CHCl_3$	249	18
3,4-Dinitro-3-hexene (*trans*)	1546	1351		195	18
1,1-Dinitroheptane	1577	1330		247	179
1,1-Dinitrooctane	1577	1330		247	179
1,1-Dinitrononane	1582	1330		252	179
1,1-Dinitrodecane	1577	1327		250	179
1,1-Dinitro-3-octanol	1582	1333		249	18
Bis(1-nitro-2-methyl-2-propyl) ether	1548	1374		174	18
Trinitromethane	1597	1307	Fusion	290	179, 196
Deuteriotrinitromethane	1605	1310		295	212
Tetranitromethane	1618	1266		352	114
1,1,1-Trinitroethane	1603	1298	C_2Cl_4	305	179
1,1,1-Trinitropropane	1603	1303		300	179
1,1,1-Trinitrobutane	1603	1305		298	179
1,1,1-Trinitropentane	1603	1305		298	179
1,1,1-Trinitrohexane	1603	1303		300	179
1-Bromo-1,1-dinitroethane	1587	1315		272	175
1-Chloro-1,1-dinitroethane	1589	1314		275	175
1-Bromo-1,1-dinitropropane	1588	1309		279	175
1-Chloro-1,1-dinitropropane	1587	1312		275	175
1-Bromo-1,1-dinitrobutane	1586	1312		274	175
1-Chloro-1,1-dinitrobutane	1589	1314		275	175
1-Bromo-1,1-dinitropentane	1585	1313		272	175
1-Chloro-1,1-dinitropentane	1590	1315		275	175
1-Bromo-1,1-dinitrohexane	1586	1311		275	175
Bromotrinitromethane	1609	1293		316	175
	1616	1290		320	173
Chlorotrinitromethane	1617	1281		336	175
	1630	1293		337	173
Iodonitromethane	1613	1298		315	173

[a] Neat unless otherwise stated.

A detailed study of several polynitro alcohols indicates little or no hydrogen bonding (196); possible reasons for this anomaly are discussed.

C. ACIDITY AND TAUTOMERISM

Belew and Hepler (14) have discussed the acid dissociation of the 1,1-dinitroparaffins.

$$\begin{tikzcd}
\text{nitro-form} \arrow[rr, leftrightharpoons, "\text{slow}"] \arrow[dr, leftrightharpoons, "\text{slow}"'] & & \textit{aci}\text{-form} \arrow[dl, leftrightharpoons, "\text{fast}"] \\
& H^+ + A^- &
\end{tikzcd}$$

$$K_i = \frac{[\textit{aci}\text{-form}]}{[\text{nitro-form}]},\ K_n = \frac{[H^+][A^-]}{[\text{nitro-form}]},\ K_{aci} = \frac{[H^+][[A^-]}{[\textit{aci}\text{-form}]}$$

$$K_n = K_iK_{aci},\ K_{\text{apparent}} = \frac{[H^+][A^-]}{[\textit{aci}\text{-form}] + [\text{nitro-form}]} = \frac{K_n}{1 + K_i}$$

From the values of K_i obtained, they concluded that approximately 4% *aci*-form exists in tautomeric mixtures, an amount considerably larger than that found for the mononitroalkanes (193). Inasmuch as K_i is small compared with unity, the values of K_{app} can be used in discussing relative acidity in terms of pK_a. Selected values of some equilibrium constants for nitroparaffins are given in Table XXVIII.

From determinations of the dissociation constants at various temperatures, the enthalpy and entropy of dissociation for a number of polynitroalkanes were determined (176) (Table XXIX).

A study of the Na and K salts of dinitrocyanomethane (155, 156) showed that they are completely ionized in aqueous solution. Neither salt could be titrated potentiometrically with $HClO_4$ in acetic acid, indicating that dinitroacetonitrile is a stronger acid than nitric acid.

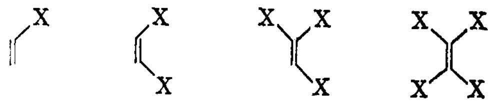
The acidities of the nitroalcohols have been discussed in the literature (116, 162), and values of the dissociation constants determined by Hall (71) are given in Table XXX. Hall states that a dilute solution of trinitroethanol in 0.1 *N* NaOH has the spectrum and molar extinction coefficient of trinitromethyl anion, showing that it is completely ionized

$$(NO_2)_3CCH_2OH \rightleftarrows (NO_2)_3C^- + CH_2(OH)_2 + H^+$$

and suggests that the reason the preparation of 1-substituted trinitroethanols from nitroform and acetaldehyde, cyclobutanone, or acetone has not been successful is that these alcohols are too highly dissociated in aqueous solution.

D. COMPLEXES OF POLYNITRO COMPOUNDS

Heilbronner (77) has described a test for the classification of olefins using the ultraviolet absorption spectrum of the π-complex formed between tetranitromethane and the olefin. The variation of the ultraviolet spectra of the complexes divides the olefins into four groups, depending upon the degree of substitution of the carbon–carbon double bond.



The ultraviolet spectra of some charge-transfer complexes of tetranitromethane and aromatic compounds

TABLE XXVIII

EQUILIBRIUM CONSTANTS FOR NITROPARAFFINS

Compound	pK_a	K_{app}	K_i	K_{aci}	K_n	Ref.
Nitromethane	10.2	6.1×10^{-11}	1.1×10^{-7}	5.6×10^{-4}	6.1×10^{-11}	193
	11					157
Dinitromethane	3.6^a	2.5×10^{-4}				176
	4					157
Trinitromethane	~0					157
	0.2^a	6.8×10^{-1}				176
Nitroethane	8.5	3.5×10^{-9}	8.9×10^{-5}	3.9×10^{-5}	3.5×10^{-9}	193
1,1-Dinitroethane	5.2^a	6.2×10^{-6}				176
	5.3	5.2×10^{-6}	4×10^{-2}	1×10^{-4}	5.4×10^{-6}	5
	5.4					130
Nitropropane	9.0	1.0×10^{-9}				193
2-Nitropropane	7.7	2.1×10^{-8}	2.75×10^{-3}	7.7×10^{-6}	2.1×10^{-8}	193
1,1-Dinitropropane	5.7	2.2×10^{-6}	5×10^{-2}	8×10^{-5}	2.3×10^{-6}	5
	5.7					130
	5.5^a	3×10^{-6}				176
1,1-Dinitrobutane	5.4^a	4.0×10^{-6}				176, 148
	(5.2)					130
1,1-Dinitropentane	5.5					130
	5.4^a					176
1,1-Dinitrohexane	5.5					130
1,1-Dinitroheptane	5.5					130
1,1-Dinitrooctane	5.5					130
1,1-Dinitrononane	5.5					130
1,1-Dinitrodecane	5.5					130
	5.5^a					176
2-Methyl-1,1-dinitropropane	6.7					130
2-Methyl-1,1-dinitrobutane	5.4					130
1,1,3,3-Tetranitropropane[a]	$pK_1 = 1.1$; $pK_2 = 5.0$					176
1,1,3,3-Tetranitrobutane[a]	1.4					176

[a] Value determined at 20°.

TABLE XXIX

ENTHALPY AND ENTROPY OF DISSOCIATION

Compound	$\Delta H°$, kcal./mole	$\Delta S°$, cal./mole deg.
$CH(NO_2)_3$	+1.59	+5.64
$CH_2(NO_2)_2$	+2.22	−9.22
$CH_3CH(NO_2)_2$	+3.54	−11.82
$CH_3CH_2CH(NO_2)_2$	+3.68	−12.83
$CH_3(CH_2)_2CH(NO_2)_2$	+3.62	−12.33
$CH_3(CH_2)_3CH(NO_2)_2$	+3.86	−11.44
$CH_3(CH_2)_4CH(NO_2)_2$	+4.02	−11.08
$CH_3(CH_2)_8CH(NO_2)_2$	+2.50	−16.46

TABLE XXX

DISSOCIATION CONSTANTS OF NITROALCOHOLS

	pK_a
$(NO_2)_3CCH_2OH$	6.1
$(NO_2)_3CCH(CH_3)OH$	3.6
$(NO_2)_3CC(CH_3)_2OH$	2.2

TABLE XXXI

TETRANITROMETHANE COMPLEXES OF AROMATIC HYDROCARBONS

	λ_{max}, mμ	$h\nu$,[a] e.u.	Ionization potential,[b] e.v.
Naphthalene	359	3.46	8.30
Anthracene	407	3.05	7.74
Phenanthrene	390	3.18	8.27
Chrysene	397	3.13	8.04
Pyrene	388	3.20	7.82
Triphenylene	397	3.28	8.48
Biphenyl	330	3.76	8.53
Stilbene	405	3.07	7.99
Fluoranthene	416	2.98	8.30

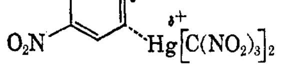
[a] Energy in e.u. corresponding to λ_{max}. [b] Ionization potential in e.v. calculated by molecular orbital method.

have been determined (21) (Table XXXI). The extinction coefficient was found to be time dependent indicating that nitration of the aromatic nucleus also occurs. Tetranitromethane (TNM) in heptane exhibited a spectrum similar to that of cyclohexane–TNM, attributed by Evans (25) to charge-transfer complexes.

Buck and co-workers (19) have reported that charge-transfer complexes between tetranitromethane and 4,4′-diaminodiphenyl, and also 4,4′-bisdimethylaminodiphenyl, show an electron spin resonance signal. The electrical conductivity of the benzidine–TNM complex was determined at room temperature (86) to be 5×10^{-6} ohm^{-1} cm.$^{-1}$.

Mercury nitroform, which has been found to react with a number of substrates, was found (138) to form a complex with nitrobenzene instead of yielding mercuriated derivatives (Table XXXII).

A σ-type structure is suggested for the complexes



since no complex was formed with compounds having the positions *meta* to nitro group substituted, such as

TABLE XXXII

MERCURY NITROFORM COMPLEXES OF NITROAROMATICS

Compound	Complex, m.p., °C.	Yield, %
Nitrobenzene	116	55
m-Dinitrobenzene	147	60
o-Nitrotoluene	75	55.5
o-Nitroanisole	109	51

3,5-dinitrotoluene, 3,5-dinitroanisole, and 1,3,5-trinitrobenzene.

A molecular complex of nitroform and dioxane, having the formula $C_4H_8O_2 \cdot 2HC(NO_2)_3$, was found to be a stable source of nitroform (168). The complex (m.p. 44–44.5°) may be distilled [b.p. 61–62° (9 mm.)] without decomposition.

E. MISCELLANEOUS

Hine (84) has reported substituent constants (σ_{para} and σ^*) for some polynitroaliphatic groups (Table XXXIII) and noted that the values for the trinitromethyl group appear to be the largest that have been measured for any electrically neutral group.

TABLE XXXIII

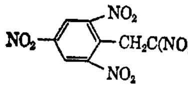
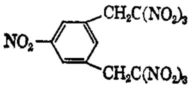
SUBSTITUENT CONSTANTS

Group	σ_{para}	σ^*
Trinitromethyl	0.820	4.54
1,1-Dinitroethyl	0.609	
2-Nitro-2-propyl	0.200	
1,1-Dinitropropyl	0.642	
3,3,3-Trinitropropyl		0.579
3,3-Dinitrobutyl		0.352
3,3-Dinitropentyl		0.377
2,2,2-Trinitroethyl		1.62

The dipole moments of some polynitroalkanes have been determined in benzene (5,207) and are summarized in Table XXXIV.

TABLE XXXIV

DIPOLE MOMENTS

Compound	μ, Debyes
$(NO_2)_3CH$	2.61
$(NO_2)_3CCH_3$	3.33
$NO_2C_6H_4CH_2C(NO_2)_3$-*p*	3.45
	3.35
	3.77
$CCl(NO_2)_3$	2.17
$CBr(NO_2)_3$	2.56
$CI(NO_2)_3$	3.79
$CH_3C(NO_2)_3$	3.17
$CH_3CH(NO_2)_2$	3.47
$CH_3CBr(NO_2)_2$	3.26
$CH_3CCl(NO_2)_2$	3.00
$CH_3CHBr(NO_2)$	2.94

Holder and Klein (87) have determined n.m.r. chemical shifts of N^{14} for tetranitromethane and hexanitroethane as 3.00 gauss relative to NO_2^- as zero. The shifts are positive and are normalized to 10,000 gauss.

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