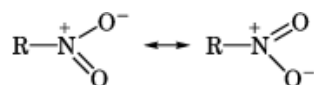


## NITROPARAFFINS

Nitroparaffins (or nitroalkanes) are derivatives of the alkanes in which one hydrogen or more is replaced by the electronegative nitro group, which is attached to carbon through nitrogen. The nitroparaffins are isomeric with alkyl nitrites,  $\text{RONO}$ , which are esters of nitrous acid. The nitro group in a nitroparaffin has been shown to be symmetrical about the  $\text{R-N}$  bond axis, and may be represented as a resonance hybrid:



Nitroparaffins are classed as primary,  $\text{RCH}_2\text{NO}_2$ , secondary,  $\text{R}_2\text{CHNO}_2$ , and tertiary,  $\text{R}_3\text{CNO}_2$ , by the same convention used for alcohols. Primary and secondary nitroparaffins exist in tautomeric equilibrium with the enolic or aci forms.

The nitroparaffins are named as derivatives of the corresponding hydrocarbons by using the prefix “nitro” to designate the  $\text{NO}_2$  group (1), eg, 1,1-dinitroethane,  $\text{CH}_3\text{CH}(\text{NO}_2)_2$ . The salts obtained from nitroparaffins and the so-called nitronic acids are identical and may be named as derivatives of either, eg, sodium salt of *aci*-nitromethane, or sodium methanenitronate [25854-38-0].

Nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane are produced by a vapor-phase process developed in the 1930s (2).

### 1. Physical Properties

The physical constants of the lower mononitroparaffins and of a number of polynitroparaffins are listed in Tables 1–>3. Most polynitroparaffins are colorless crystalline or wax-like solids at or near room temperature. They are insoluble in water and alkanes but soluble in most other organic solvents. The lower mononitroparaffins are colorless, dense liquids with mild odors. The boiling points of the mononitroparaffins are much higher than those of the isomeric nitrates; for example, the normal boiling point of nitromethane is  $101.2^\circ\text{C}$ , whereas that of methyl nitrate is  $-12^\circ\text{C}$ . This phenomenon may be attributed in large part to intermolecular hydrogen bonding. Accurate vapor-pressure determinations (3) for the lower nitroparaffins have been made and adapted to an Antoine equation (see Tables 1 and 2). A nomograph was constructed from these data (4). The properties of azeotropes of nitroparaffins with water or with organic liquids (5) and critical solution temperature data of nitroparaffins in binary (6) and ternary (7) systems have been described.

The molecular configuration of the  $\text{C-NO}_2$  group in nitromethane has been determined by electron-diffraction methods (8). These data indicate that the nitrogen atom and atoms attached to it lie in the same plane, and that the  $\text{O-N-O}$  bond angle ( $127 \pm 3^\circ$ ) is greater than the  $\text{C-N-O}$  bond angles ( $116 \pm 3^\circ$ ). The spreading of the  $\text{O-N-O}$  bond angle beyond  $120^\circ$  is attributed to the repulsion of the negatively charged

## 2 NITROPARAFFINS

**Table 1. Physical Properties of the Lower Mononitroparaffins**

Property	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane
CAS Registry Number	[75-52-5]	[79-24-3]	[108-03-2]	[79-46-9]
molecular weight	61.041	75.068	89.095	89.095
boiling point at 101.3 kPa, <sup>a</sup> °C	101.20	114.07	131.18	120.25
vapor pressure, <sup>b</sup> kPa <sup>a</sup>	3.64	2.11	1.01	1.73
freezing point, °C	-28.55	-89.52	-103.99	-91.32
density, <sup>b</sup> g/mL	1.138	1.051	1.001	0.988
coefficient of expansion per °C	0.00122	0.00112	0.00101	0.00104
refractive index, $n_D^{20}$	1.38188	1.39193	1.40160	1.39439
surface tension, <sup>b</sup> mN/m( =dyn/cm)	37.48	32.66	30.64	29.87
viscosity, <sup>b</sup> mPas( = cP)	0.647	0.677	0.844	0.770
heat of combustion (liq) at 25°C kJ/mol <sup>c</sup>	-708.4	-1362	-2016	-2000
heat of vaporization, kJ/mol <sup>c</sup> (liq) at 25°C	38.27	41.6	43.39	41.34
at bp	34.4	38.0	38.5	36.8
heat of formation (liq) at 25°C, kJ/mol <sup>c</sup>	-113.1	-141.8	-168.0	-180.7
specific heat at 25°C J/(mol·°C) <sup>c</sup>	106.0	138.5	175.6	175.2
J/(g·°C) <sup>c</sup>	1.74	1.85	1.97	1.97
dielectric constant at 30°C	35.87	28.06	23.24	25.52
dipole moment, $\times 10^{-30}$ °C·m <sup>d</sup> gas	11.68	11.94	12.41	12.44
liquid	10.58	10.64		
aqueous azeotrope bp, °C	83.59	87.22	91.63	88.55
wt % nitroparaffin	76.4	71.0	63.5	70.6
pH of 0.01 M aqueous solution of 25°C	6.4	6.0	6.0	6.2
solubility in water, wt % at 20°C	10.5	4.6	1.5	1.7
at 70°C	19.3	6.6	2.2	2.3
solubility <sup>b</sup> of water in nitroparaffin, wt %	1.8	0.9	0.6	0.5
at 70°C	7.6	3.0	1.7	1.6
Antoine's constant <sup>e</sup> A	6.399073	6.300057	6.252442	6.208143
B	1441.610	1435.402	1474.299	1422.898
C	226.939	220.184	215.986	218.341
critical temperature, °C	315	388	402	344

<sup>a</sup>To convert kPa to mm Hg, multiply by 7.5.

<sup>b</sup>At 20°C.

<sup>c</sup>To convert J to cal, divide by 4.184.

<sup>d</sup>To convert C<sub>m</sub> to debye, divide by  $3.336 \times 10^{-30}$ .

<sup>e</sup> $\log p_{\text{kPa}} = A - B/(t + C)$ .

oxygen atoms of the highly polar system. Infrared (9) and mass spectra (10) for this group have also been discussed.

Most organic compounds, including aromatic hydrocarbons, alcohols, esters, ketones, ethers, and carboxylic acids are miscible with nitroparaffins, whereas alkanes and cycloalkanes have limited solubility. The lower nitroparaffins are excellent solvents for coating materials, waxes, resins, gums, and dyes.

**Table 2. Physical Constants of C-4 and Higher Mononitroparaffins**

Property	1-Nitro-butane	2-Nitro-butane	1-Nitro-2-methyl-propane	2-Nitro-2-methyl-propane	Nitro-cyclohexane
CAS Registry Number	[627-05-4]	[600-24-8]	[625-74-1]	[594-70-7]	[1122-60-7]
freezing point, °C	−81.33	glass	−76.85	26.23	−34
boiling point, °C	152.77	139.50	141.72	127.16	205.5–206
Antoine's con-stant <sup>a</sup>					
<i>A</i>	6.220403	6.202795	6.199044	6.112625	
<i>B</i>	1523.797	1494.318	1483.643	1396.948	
<i>C</i>	208.778	216.542	212.905	212.989	
vapor pressure at 20°C, kPa <sup>b</sup>	0.36	0.77	0.64	<i>solid</i>	
density at 25°C, g/mL	0.96848	0.96036	0.95848	<i>solid</i>	1.0680 <sup>19</sup>
refractive in-dex, <i>n</i> <sub>D</sub> <sup>20</sup>	1.41019	1.40407	1.40642	1.39175 <sup>30</sup>	1.4608

<sup>a</sup> $\log p_{\text{kPa}} = A - B/(t + C)$ .<sup>b</sup>To convert kPa to mm Hg, multiply by 7.5.**Table 3. Physical Constants of Polynitro Compounds**

Compound	CAS Registry Number	Mp, °C	Boiling point		Sp gr	Refractive index, <i>n</i> <sub>D</sub> <sup>t</sup>	Water solubility <sup>a</sup>
			°C	at kPa <sup>b</sup>			
dinitro-methane	[625-76-3]		39–40	0.266	1.524	1.4480 <sup>20</sup>	
trinitro-methane	[517-25-9]	14.3 (dec)	45–47	2.933	1.5967 <sup>24</sup> <sub>4</sub>	1.445511 <sup>24</sup> <sub>He</sub>	sol
tetranitro-methane	[509-14-8]	13.8	125.7		1.6377 <sup>21</sup> <sub>4</sub>	1.43416 <sup>21</sup>	insol
1,1-dinitro-ethane	[600-40-8]		185–186		1.3503 <sup>23</sup> <sub>23</sub>	1.4346 <sup>20</sup>	sl sol
1,2-dinitro-ethane	[7570-26-5]	39–40	135	0.800	1.4597 <sup>20</sup> <sub>4</sub>	1.4488 <sup>20</sup>	sl sol
1,1,1-trinitroethane	[595-86-8]	57	68	2.266	1.4223 <sup>77</sup> <sub>4</sub>	1.4171 <sup>77</sup> <sub>α</sub>	insol
2,2-dinitro-propane	[595-49-3]	54	185				insol
1,1-dinitro-cyclohex-ane	[4028-15-3]	36	142–143	4.666	1.2452 <sup>21</sup> <sub>4</sub>	1.4732 <sup>21</sup>	insol

<sup>a</sup>All named compounds are soluble in ethanol and in ethyl ether.<sup>b</sup>At 101.3 kPa (=1 atm) if not indicated. To convert kPa to mm Hg, multiply by 7.5.

The thermal characteristics of higher nitroparaffins are quite different from those of nitromethane. The nitropropanes provide nearly twice as much heat as does nitromethane when burned in air or oxygen. When the only source of oxygen is that contained within the molecule, nitropropanes yield only 20% as much energy as nitromethane on burning.

## 2. Chemical Properties

The chemical reactions of the nitroparaffins have been discussed in depth (11–19), and their utility for the synthesis of heterocyclic and other compounds has been noted (20, 21).

## 4 NITROPARAFFINS

**Table 4. Ionization Constants of Lower Mononitroparaffins**

Compound	$K_{\text{nitro}}$	$K_{\text{aci}}$
nitromethane	$6.1 \times 10^{-11}$	$5.6 \times 10^{-4}$
nitroethane	$3.5 \times 10^{-9}$	$3.9 \times 10^{-5}$
2-nitropropane	$2.1 \times 10^{-8}$	$7.7 \times 10^{-6}$
1-nitropropane		$2.0 \times 10^{-5}$

### 2.1. Tautomerism

Primary and secondary mononitroparaffins are acidic substances which exist in tautomeric equilibria with their nitronic acids.



The nitro isomer is weakly acidic; the nitronic acid isomer (aci form) is much more acidic. A comparison of the ionization constants of the two forms in water at 25°C is given in Table 4.

An equilibrium mixture of the isomers usually contains a much higher proportion of the true nitro compound. The equilibrium for each isomeric system is influenced by the dielectric strength and the hydrogen-acceptor characteristics of the solvent medium. The aci form is dissolved and neutralized rapidly by strong bases, and gives characteristic color reactions with ferric chloride.

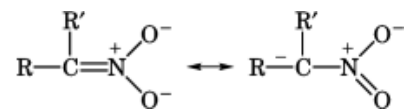
Polynitroparaffins are stronger acids than the corresponding mononitroparaffins. Thus 1,1-dinitroethane has an ionization constant of  $5.6 \times 10^{-6}$  in water at 20°C; trinitromethane is a typical strong acid with an ionization constant in the range of  $10^{-2}$  to  $10^{-3}$ . Neutralization of these substances occurs rapidly, and they may be titrated readily.

In addition to neutralization, prolonged action of alkaline reagents can effect oxidation-reduction and extensive decomposition. 1,1-Dinitroparaffins and trinitromethane are more stable than are mononitro compounds during neutralization and subsequent regeneration, and therefore more rigorous experimental conditions are permissible.

Acidification of mononitroparaffin salts immediately gives the nitronic acid. Many nitronic acids have been isolated and stored as crystalline solids. In solution, a nitronic acid either isomerizes slowly into its more stable nitro form or undergoes some irreversible transformation. The isomerization occurs sufficiently slowly that it can be measured by conductometric or halometric methods.

### 2.2. Salts

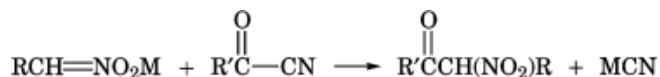
Nitroparaffins dissociate to form ambidentate anions, which are capable of alkylation at either the carbon or oxygen atom (22).



Reactions of alkyl, allylic, and benzylic halides with these salts usually give carbonyl compounds, presumably through the nitronic ester (O-alkylation) as an intermediate. With certain benzyl halides substituted in the para or ortho position with nitro groups, the reaction gives almost exclusively C-alkylation. For example, sodium 2-propanenitronate [12384-98-4] reacts with *p*-nitrobenzyl chloride (23) or with *p*-nitrobenzyltrimethylammonium iodide (24) to form 2-methyl-2-nitro-1-(*p*-nitrophenyl)propane [5440-67-5].

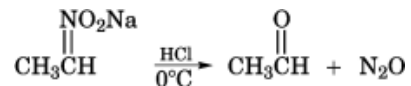
This reaction depends on the nature of the leaving group (22) and is inhibited by powerful electron acceptors (25). It has been considered a radical-anion (25) or chain process (26).

Alkali salts of primary nitroparaffins, but not of secondary nitroparaffins, react with acyl cyanides to yield  $\alpha$ -nitroketones by C-acylation (27).

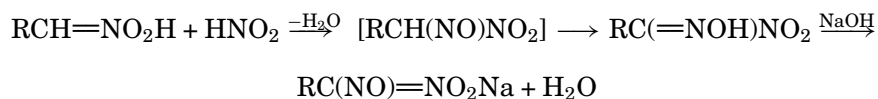


Most other acylating agents act on salts of either primary or secondary nitroparaffins by O-acylation, giving first the nitronic anhydrides which rearrange to give, eg, nitrosoacyloxy compounds (28).

Alkaline solutions of mononitroparaffins undergo many different reactions when stored for long periods, acidified, or heated. Acidification of solutions of mononitro salts is best effected slowly at 0°C or lower with weak acids or buffered acidic mixtures, such as acetic acid-urea, carbon dioxide, or hydroxylammonium chloride. If mineral acids are used under mild conditions, eg, dilute HCl at 0°C, decomposition yields a carbonyl compound and nitrous oxide (Nef reaction).



Reaction with nitrous acid can be used to differentiate primary, secondary, and tertiary mononitroparaffins. Primary nitroparaffins give nitrolic acids, which dissolve in alkali to form bright red salts.



Secondary nitroparaffins give alkali-insoluble nitroso derivatives known as pseudonitroles. As monomers in the liquid state, pseudonitroles have a characteristic blue color; as solids they exist as white crystalline dimers. Tertiary nitroparaffins do not react with nitrous acid and no color develops.

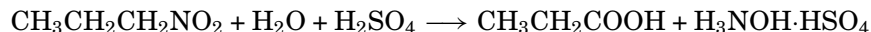


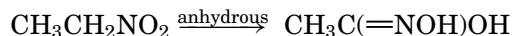
With sodium azide, salts of secondary nitroparaffins rearrange to N-substituted amides (29). With SO<sub>2</sub>, primary or secondary nitroparaffins give imidodisulfonic acid salts (30). Potassium nitroform reacts quantitatively with nitril chloride in ether to form tetranitromethane (31).

Sodium methanenitronate reacts with phenyl isocyanate in benzene to give the readily separable sodium salts of nitroacetanilide and nitromalondianilide. Except as the salt, nitromethane is unreactive with phenyl isocyanate at temperatures up to 100°C; the higher homologues do not give condensation products that can be isolated.

### 2.3. Acid Hydrolysis

With hot concentrated mineral acids, primary nitroparaffins yield a fatty acid and a hydroxylamine salt. If anhydrous acid and lower temperatures are used, the intermediate hydroxamic acid can be recovered.





## 2.4. Halogenation

In the presence of alkali, chlorine replaces the hydrogen atoms on the carbon atom holding the nitro group. If more than one hydrogen atom is present, the hydrogen atoms can be replaced in stages; exhaustive chlorination of nitromethane yields chloropicrin, ie, trichloronitromethane [76-06-2]. The chlorination can be stopped at intermediate stages. Bromination or iodination takes a similar course, but bromopicrin [464-10-8] and iodopicrin [39247-25-1] tend to be less stable.

Halonitroparaffins can be prepared in which the halogen and nitro groups are not on the same carbon atom. The direct chlorination of nitroparaffins to give nongeminal substitution is promoted by irradiation in anhydrous media (32, 33). For example, nitroethane yields 2-chloro-1-nitroethane [625-47-8], and 1-nitropropane yields both 2- [503-76-4] and 3-chloro-1-nitropropane [13021-02-8] on treatment with alkalies (34). Replacement of the hydroxy group in nitro alcohols (qv) with halogen yields vicinal halonitroparaffins. Action of phosphorus tribromide on nitro alcohols in dimethylformamide gives *vic*-bromonitroparaffins (35).

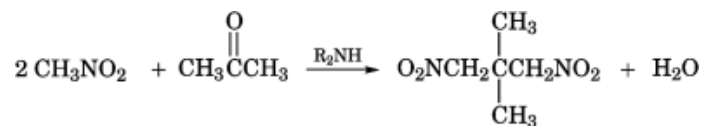
The acid chloride of *aci*-nitromethane,  $\text{CH}_2=\text{N}(\text{Cl})\text{O}$  (mp  $-43^\circ\text{C}$ , bp  $2-3^\circ\text{C}$ ), is formed by fusion of nitromethane and picrylpyridinium chloride (36). It is hydrolyzed to nitrosomethane, reduces potassium permanganate strongly, and exhibits no reactions characteristic of hydroxamic acids.

## 2.5. Reaction With Carbonyl Compounds

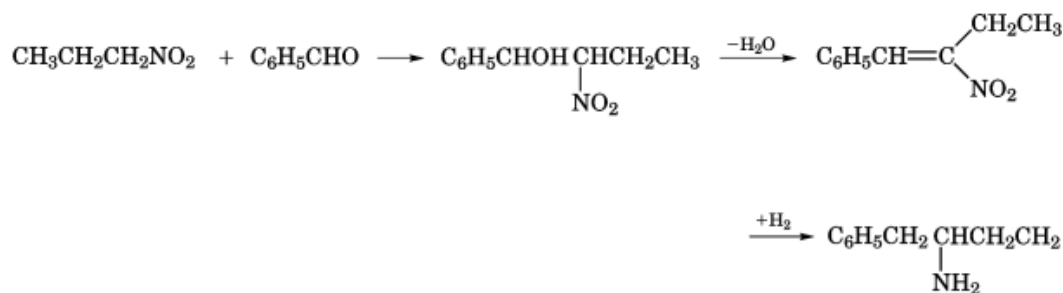
Primary and secondary nitroparaffins undergo aldol-type reactions with a variety of aldehydes and ketones to give nitro alcohols (11). Those derived from the lower nitroparaffins and formaldehyde are available commercially (see Nitro alcohols). Nitro alcohols can be reduced to the corresponding amino alcohols.

These reversible reactions are catalyzed by bases or acids, such as zinc chloride and aluminum isopropoxide, or by anion-exchange resins. Ultrasonic vibrations improve the reaction rate and yield. Reaction of aromatic aldehydes or ketones with nitroparaffins yields either the nitro alcohol or the nitro olefin, depending on the catalyst. Conjugated unsaturated aldehydes or ketones and nitroparaffins (Michael addition) yield nitro-substituted carbonyl compounds rather than nitro alcohols. Condensation with keto esters gives the substituted nitro alcohols (37); keto aldehydes react preferentially at the aldehyde function.

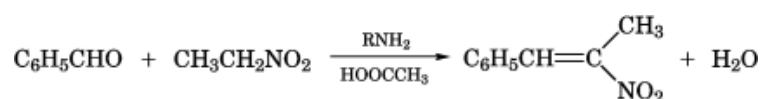
Most nitroparaffins do not react with ketones, but in the presence of alkoxide catalysts, nitromethane and lower aliphatic ketones give nitro alcohols; in the presence of amine catalysts dinitro compounds are obtained.



Nitro olefins can be made in some cases by dehydration of the aromatic nitrohydroxy derivatives. Subsequent reduction yields the aromatic amine. The following three-step reaction yielding 2-amino-1-phenylbutane illustrates the synthesis of this class of valuable pharmaceutical compounds.

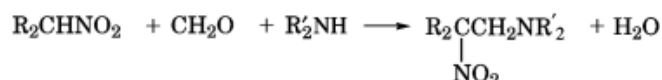


In the presence of amine salts of weak acids, the nitro olefin is formed directly.



## 2.6. Mannich-Type Reactions

Secondary nitroparaffins, formaldehyde (qv), and primary or secondary amines can react in one step to yield Mannich bases.



Primary nitroparaffins react with two moles of formaldehyde and two moles of amines to yield 2-nitro-1,3-propanediamines. With excess formaldehyde, Mannich bases from primary nitroparaffins and primary amines can react further to give nitro-substituted cyclic derivatives, such as tetrahydro-1,3-oxazines or hexahydropyrimidines (38, 39). Pyrolysis of salts of Mannich bases, particularly of the boron trifluoride complex (40), yields nitro olefins by loss of the amine moiety. Closely related to the Mannich reaction is the formation of sodium 2-nitrobutane-1-sulfonate [76794-27-9] by warming 1-nitropropane with formaldehyde and sodium sulfite (41).

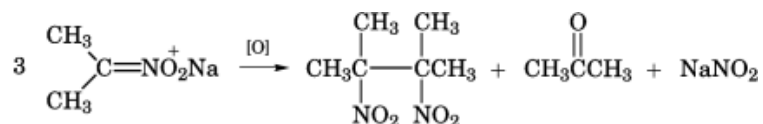
## 2.7. Reduction

The lower nitroparaffins are reduced readily to the corresponding primary amines with a number of reducing agents. Partial reduction yields aldoximes, ketoximes, or N-substituted hydroxylamines. Suitable reduction methods range from iron and hydrochloric acid to high pressure hydrogenation over Raney nickel or noble-metal catalysts. Reaction conditions have been developed also for the reduction of olefinic or carbonyl groups with or without reduction of the nitro group present, and for the reduction of the nitro group leaving the other groups untouched (42). Some of the products obtained are useful as pharmaceuticals.

## 2.8. Oxidation

Nitroparaffins are resistant to oxidation. At ordinary temperatures, they are attacked only very slowly by strong oxidizing agents such as potassium permanganate, manganese dioxide, or lead peroxide. Nitronate salts, however, are oxidized more easily. The salt of 2-nitropropane is converted to 2,3-dimethyl-2,3-dinitrobutane [3964-18-9], acetone, and nitrite ion by persulfates or electrolytic oxidation. With potassium permanganate, only acetone is recovered.

## 8 NITROPARAFFINS



$\alpha$ -Nitroacetaldehyde [5007-21-6] is formed in low yield by the oxidation of nitroethane with selenium dioxide. This product is easily oxidized in air to nitroacetic acid [625-75-2], which spontaneously decarboxylates to nitromethane.

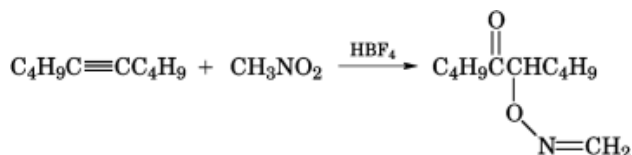
### 2.9. Addition to Multiple Bonds

Mono- or polynitroparaffins with a hydrogen on the carbon atom carrying the nitro group add to activated double bonds under the influence of basic catalysts (43–45). Thus nitromethane forms tris( $\beta$ -cyanoethyl)nitromethane [1466-48-4] with acrylonitrile and 2-nitropropane yields 4-methyl-4-nitrovaleronitrile [16507-00-9]. These Michael-type condensations with acrylic compounds take place in liquid ammonia without catalyst (46). In the presence of dehydrating agents, such as phenyl isocyanate or phosphorus oxychloride, nitroparaffins add to activated olefins, such as methyl acrylate, to give oxazines (47).

Nitroparaffins add 1,4 to conjugated systems; methyl vinyl ketones, for example, yield the corresponding  $\gamma$ -nitro ketone, which can be reduced to a  $\gamma$ -nitro alcohol (48). More than one vinyl group may react with primary nitroparaffins (49).

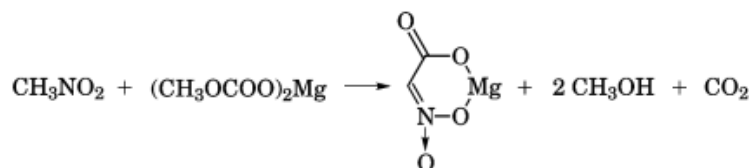
Conjugated nitro olefins can function as the acceptor to which nitroparaffins may add to form polynitro derivatives (50, 51). Nitro olefins also undergo Diels-Alder condensations with compounds such as maleic anhydride or anthracene (52).

Nitroparaffins and  $\text{HBF}_4$  react with alkynes through conjugate addition of a proton and the nitronate ion at the triple bond as illustrated by nitromethane and 5-decyne (53).



### 2.10. Other Reactions

$\alpha$ -Nitroalkanoic acids or their esters can be prepared (54–56) by treating nitroparaffins with magnesium methyl carbonate, or with triisopropylaluminum and carbon dioxide. These products are reduced readily to  $\alpha$ -amino acids.



1,1,1-Trinitroparaffins can be prepared from 1,1-dinitroparaffins by electrolytic nitration, ie, electrolysis in aqueous caustic sodium nitrate solution (57). Secondary nitroparaffins dimerize on electrolytic oxidation (58); for example, 2-nitropropane yields 2,3-dimethyl-2,3-dinitrobutane, as well as some 2,2-dinitropropane. Addition of sodium nitrate to the anolyte favors formation of the former. The oxidation of salts of *aci*-2-nitropropane with



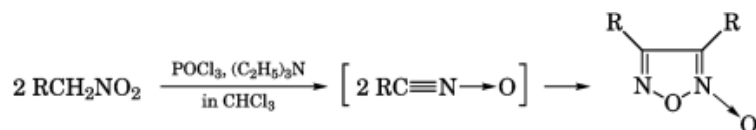
**Table 5. Effect of Temperature on the Nitration of Propane with Nitric Acid**

Product	Nitration temperature		Type of substitution
	505–510°C	790–795°C	
nitromethane, mol %	22.0	32.3	alkyl cleavage
nitroethane, mol %	16.6	24.2	alkyl cleavage
1-nitropropane, mol %	13.2	24.2	primary
2-nitropropane, mol %	48.2	19.3	secondary
ratio of cleavage products to substitution products	0.628	1.30	

either cationic or anionic oxidants generally gives both 2,2-dinitropropane and acetone (59); with ammonium peroxydisulfate, for example, these products are formed in 53 and 14% yields, respectively. Ozone oxidation of nitroso groups gives nitro compounds; 2-nitroso-2-nitropropane [5275-46-7] (propylpseudonitrole), for example, yields 2,2-dinitropropane (60).

*O*-Acylation of 2-nitropropane occurs on reaction with either ketene or acetic anhydride (61) in the presence of dry sodium acetate at 70–80°C. Ketovinylation of 2-nitropropane at the 1-position occurs on treatment of sodium 2-propanenitronate with a chlorovinyl ketone (62).

Furoxans are formed by the dehydration of two moles of a nitroparaffin (63).



### 3. Preparation and Manufacture

Synthetic methods suitable for preparation of a wide variety of nitroparaffins have been reviewed (64–67).

A general one-step method for preparation of primary and secondary nitroparaffins from amines by oxidation with *m*-chloroperbenzoic acid in 1,2-dichloroethane has been reported (68). This method is particularly useful for laboratory quantities of a wide variety of nitroparaffins because a large number of amines are readily available from ketones by oxime reduction and because the reaction is highly specific for nitroparaffins.

Higher nitroalkanes are prepared from lower primary nitroalkanes by a one-pot synthesis (69). Successive condensations with aldehydes and acylating agents are followed by reduction with sodium borohydride. Overall conversions in the 75–80% range are reported.

The only method utilized commercially is vapor-phase nitration of propane, although methane (70), ethane, and butane also can be nitrated quite readily. The data in Table 5 show the typical distribution of nitroparaffins obtained from the nitration of propane with nitric acid at different temperatures (71). Nitrogen dioxide can be used for nitration, but its low boiling point (21°C) limits its effectiveness, except at increased pressure. Nitrogen pentoxide is a powerful nitrating agent for *n*-alkanes; however, it is expensive and often gives polynitrated products.

Nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane are made on a large scale at the Sterling, Louisiana, plant of ANGUS Chemical Company. In the manufacturing process (11, 72–74), nitric acid (qv) reacts with excess propane at 370–450°C and 0.81–1.2 MPa (8–12 atm). Stainless steel is the preferred material of construction. The reaction products are cooled and the nitroparaffins and associated by-products, such as aldehydes and ketones, condense. Propane and nitric oxide remain in the gas stream. The propane

## 10 NITROPARAFFINS

**Table 6. Typical Properties of Commercial-Grade Nitroparaffins**

Property	Nitromethane	Nitroethane <sup>a</sup>	1-Nitropropane <sup>a</sup>	2-Nitropropane
distillation range at 101.3 kPa <sup>b</sup> (90% min), °C	100–103	112–116	129–133	119–122
vapor density (air = 1)	2.11	2.58	3.06	3.06
change of density with temperature, 0–50°C, g/mL per °C	0.0014	0.0012	0.0011	0.0011
weight per L at 20°C, kg	1.13	1.05	1.00	0.9
flash point, °C				
Tag open cup	44.4	41.1	48.9	37.8
Tag closed cup	35.6	30.6	35.6	27.8
lower limit of flam-mability, vol %	7.3 <sup>c</sup>	3.4 <sup>d</sup>	2.2 <sup>e</sup>	2.5 <sup>f</sup>
ignition temperature, °C	418	414	420	428
evaporation rate <sup>g</sup>	139	121	88	110
evaporation number <sup>h</sup>	9	11	16	10
hydrogen bonding pa-rameter, $\gamma$	2.5	2.5	2.5	2.5
solubility parame-ter, $\delta$	12.7	11.1	10.7	10.7

<sup>a</sup>A mixture of 1-nitropropane and nitroethane is marketed as NiPar640.

<sup>b</sup>To convert kPa to mm Hg, multiply by 7.5.

<sup>c</sup>At 33°C.

<sup>d</sup>At 30°C.

<sup>e</sup>At 34°C.

<sup>f</sup>At 27°C.

<sup>g</sup>*n* – Butyl acetate = 100.

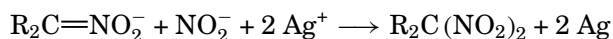
<sup>h</sup>Diethyl ether = 1.

is separated and recycled to the reactor. The nitric oxide is converted to nitric acid, which, mixed with fresh acid, is fed to the reactor. The crude nitroparaffins are washed to remove oxygenated impurities, and then are fractionated to commercial-grade nitroparaffins (Table 6). The ANGUS Chemical plant has a production capacity of 41,000 t of nitroparaffins. The single-drum prices for 1994 were as follows: nitromethane, \$6.05/kg; nitroethane, \$6.16/kg; 1-nitropropane, \$5.94/kg; and 2-nitropropane, \$5.65.

The only other nitroparaffin manufactured on a large scale was nitrocyclohexane [1122-60-7], made by liquid-phase nitration of cyclohexane. Nitrocyclohexane was the starting material for  $\epsilon$ -caprolactam via reduction to cyclohexanone oxime. This process has been superseded by other, more efficient processes (see Caprolactam). Nitrocyclohexane is not being produced in large quantities for either captive use or sale.

The preparation of polynitroparaffins has been reviewed (75). 2,2-Dinitropropane has been produced in pilot-plant quantities by liquid-phase nitration starting from either propane or 2-nitropropane (76, 77) (see Nitration).

*gem*-Dinitroparaffins are made conveniently from primary or secondary mononitroparaffins by the oxidative nitration of mononitroparaffins in alkaline solution using silver ion as the oxidizing agent (Shechter-Kaplan reaction) (78–80). This reaction has been used to prepare 1,1-dinitroethane on a tonnage scale.



### 4. Shipment and Storage

The four commercial nitroparaffins are available in drums; they are also available in bulk except for nitromethane, for which shipment in tank cars or trucks is prohibited.

**Table 7. Specifications of Commercially Available Nitroparaffins**

Assay	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane
purity, <sup>a</sup> min wt %	98.0	98.0	98.5	96.0
total nitroparaffins, min wt %	99.0	99.0	99.0	99.0
specific gravity at 25/25°C	1.124–1.135			
acidity as acetic acid, max wt %	0.1		0.2	0.1
water, max wt %	0.1	0.2	0.1	0.1
color, max APHA	20	20	20	20

<sup>a</sup>Determined by gas chromatography.

Safety factors have been of prime consideration in the development of recommendations (81, 82) for the storage and safe handling of nitromethane during recovery operations and transfer in piping systems. Bulk shipments of specified mixtures containing nitromethane and a diluent are permitted under a Department of Transportation (DOT) exemption. Nitromethane preferably should be stored in the 208-L (55-gal) drums in which it is shipped. These containers are of lightweight construction and there is little possibility that they might develop sufficiently high internal pressure either to ignite the nitromethane or to allow it to burn as a monopropellant. Bulk-storage tanks should be isolated, buried, or barricaded to protect them from projectile impacts should an explosion occur in nearby equipment or facilities. It is recommended that nitromethane be diluted with another suitable liquid prior to bulk storage. Despite the fact that nitromethane may be detonated under certain conditions, it is not classified as an explosive for shipping purposes.

Commercial-grade nitroparaffins are shipped and stored in ordinary carbon steel. However, wet nitroparaffins containing more than 0.1–0.2% water may become discolored when stored in steel for long periods, even though corrosion is not excessive. Aluminum and stainless steel are completely resistant to corrosion by wet nitroparaffins. Storage in contact with lead (qv), copper, or alloys containing these metals should be avoided. Polymeric materials for gaskets, hoses, and connections should be tested for their suitability before exposure to nitroparaffins.

Because of their flash points, nitroparaffins are classified as flammable liquids under DOT regulations (hazard class 3, PG III). Nitromethane and nitroethane fires can be extinguished with water, CO<sub>2</sub>, foam, or class ABC dry chemical extinguishers. Nitroparaffins should not be exposed to dry caustic soda, lye, or similar alkaline materials.

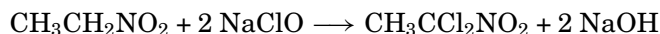
## 5. Specifications

The specifications of the four commercial nitroparaffins are given in Table 7.

## 6. Analytical Methods

The nitroparaffins have been determined by procedures such as fractionation, titration, colorimetry, infrared spectroscopy, mass spectrometry, and gas chromatography. The early analytical methods and uses of polynitroparaffins as analytical reagents have been reviewed (11). More recent qualitative and quantitative methods have also been reviewed (83).

A titration method for primary and secondary nitroparaffins using hypochlorite gives good accuracy ( $\pm 0.1\%$ ) (84). It is based on the following equation:



## 12 NITROPARAFFINS

**Table 8. Oral Toxicity<sup>a</sup> and Threshold Limit Values<sup>b</sup> of Nitroparaffins**

Nitroparaffin	LD <sub>50</sub> , mg/kg	TLV, ppm	TLV, mg/m <sup>3</sup>
nitromethane	1210 ± 322	20	50
nitroethane	1625 ± 193	100	307
1-nitropropane	455 ± 75	25	91
2-nitropropane	725 ± 160	10	36

<sup>a</sup>In rat.

<sup>b</sup>Ref. 99.

A number of colorimetric methods are available (83); however, spectroscopic methods are generally preferred.

Data on infrared curves for many nitroparaffins and their sodium salts have been reported (10, 85–89). References (87, 90) and 91 give uv spectra. Accurate analysis and positive identification of the components of a mixture of several nitroparaffins can be obtained by mass spectrometry (qv) (92).

Gas chromatography is probably the most versatile method for analyzing nitroparaffins (93–95), eg, in the presence of nitric acid esters (96).

High performance liquid chromatography (hplc) may be used to determine nitroparaffins by utilizing a standard uv detector at 254 nm. This method is particularly applicable to small amounts of nitroparaffins present, eg, in nitro alcohols (qv), which cannot be analyzed easily by gas chromatography. Suitable methods for monitoring and determination of airborne nitromethane, nitroethane, and 2-nitropropane have been published by the National Institute of Occupational Safety and Health (NIOSH) (97). Ordinary sorbant tubes containing charcoal are unsatisfactory, because the nitroparaffins decompose on it unless the tubes are held in dry ice and analyzed as soon after collection as possible.

## 7. Health and Safety Factors

### 7.1. Toxicology

The nitroparaffins have minimal effects by way of actual contact. There were neither systemic effects nor irritation in dermal studies in rabbits. Human exposure of a prolonged or often-repeated nature has led to low grade irritation attributable to removal of oil from the skin, an effect produced by most organic solvents. Eye irritation potential of all four nitroparaffins has been determined in rabbits. Other than a transient slight redness and some lachrymation, no effects were noted. The average Draize score was 0.0. The acute oral toxicity, LD<sub>50</sub>, of all four nitroparaffins has been determined in the rat (Table 8).

Inhalation is the chief route of worker exposure. Comparative data from acute or subchronic inhalation exposures with rats (98) indicate that nitromethane and nitroethane are the least toxic of the nitroparaffins by this route and do not induce methemoglobin formation. The nitropropanes are less well tolerated; 2-nitropropane is more toxic than 1-nitropropane and is more likely to cause methemoglobinemia.

The 1994–1995 threshold limit values as recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) are given in Table 8. These time-weighted average values are those levels to which nearly all workers may be exposed for an 8-h workday and a 40-h work week without adverse effect (99).

A comprehensive study of the tolerance of laboratory animals to vapors of 2-nitropropane was reported in 1952 (100). In a study published in 1979, rabbits and rats survived exposure to nitromethane for six months at 750 and 100 ppm, respectively, with no unexpected findings (101). Similarly, no compound-related effects were found for rabbits exposed to 2-nitropropane at 200 ppm or for rabbits or rats exposed at 27 ppm. Liver damage was extensive in male rats exposed at 207 ppm for six months, and hepatocellular carcinomas were observed.

Subsequently, the International Agency for Research on Cancer (IARC) found that there is “sufficient evidence” to conclude that 2-nitropropane causes cancer in rats but that epidemiologic data are inadequate to reinforce the conclusion in humans (102). The National Toxicology Program also concluded that it “may reasonably be anticipated to be a carcinogen” (103).

Because of these findings with 2-nitropropane, lifetime inhalation studies have been conducted in rats at 200 ppm with nitromethane and nitroethane (104), and at 100 ppm with 1-nitropropane (105). In no instance was cancer found in any exposed rats. This difference was confirmed by an independent study in which oral administration of 2-nitropropane caused liver tumors, whereas 1-nitropropane administration did not (106). Also, mutagenicity testing has provided clear evidence that the primary nitroparaffins are not genotoxic or mutagenic. 2-Nitropropane, in contrast, is mutagenic in the Ames test. Many studies have compared the genotoxicity of the primary nitroparaffins to that of 2-nitropropane (107); possible mechanisms of carcinogenicity and the fact that tumors developed only in rats at 2-nitropropane levels and lengths of exposure sufficient to cause hepatotoxicity also have been discussed. An excellent review of the toxicity of 2-nitropropane has been published by the World Health Organization (108).

## 7.2. Safe Handling

Any work area where nitroparaffins are present should be ventilated adequately so as to maintain concentration levels below the accepted exposure limit. Fresh-air masks should be supplied to workers entering confined spaces, eg, storage tanks, containing a high concentration of nitroparaffin vapors. Nitroparaffins have high heats of adsorption on respirator canisters containing Hopcalite, a mixture of copper, cobalt, manganese, and silver present in some canisters for converting carbon monoxide to carbon dioxide; the use of respirator masks containing these substances may lead to fire in the presence high concentrations of the nitroparaffins.

The ignition temperature of the lower homologues are relatively high for organic solvents. When ignited, nitromethane burns with a lazy flame that often dies spontaneously, and in any case is extinguished readily with water which floats on the heavier nitromethane. Nitropropanes burn more vigorously, but less so than gasoline.

Some dry-chemical fire extinguishers contain sodium or potassium bicarbonate; these should not be used on nitromethane or nitroethane fires. Dry chemical extinguishers can be used on nitropropane fires.

Three conditions have been identified under which nitromethane can be detonated: (1) nitromethane can explode if subjected to a severe shock such as that of a high explosive with more power than a No. 8 blasting cap; (2) it can be initiated by a rapid compression under adiabatic conditions; and (3) nitromethane can be detonated by heating it under confinement to near the critical temperature (315°C). These conditions combining high pressure with high temperature are the same as those under which nitromethane burns as a monopropellant. Certain compounds, eg, amines or strong oxidizing agents, when present in admixture with nitromethane, can sensitize it to decomposition by strong shock. The addition of such sensitizers should be avoided unless the nitromethane is intended for use as an explosive.

In designing facilities for handling and processing nitromethane, it is recommended that nitromethane not be processed in high pressure equipment. All vessels for nitromethane service should be protected to prevent adiabatic compression. Detonation traps should be installed at each end of transfer lines and in every 61 m (200 feet) of continuous line. Nitromethane lines should be located underground or in channels wherever possible. Pressure relief devices (rated ~690 kPa = 100 psig) should be installed between closed valves (81).

The insensitivity of nitromethane to detonation by shock under normal conditions of handling has been demonstrated by a number of full-scale tests. Sensitivity to shock increases with temperature; at 60°C, nitromethane can be detonated by a No. 8 blasting cap. Nitroethane can be initiated only when heated near its boiling point under heavy confinement; neither it or the nitropropanes can be detonated in unconfined conditions.

## 14 NITROPARAFFINS

### 7.3. Environmental Concerns

Few data on the environmental effects of the nitroparaffins are available. However, they are known to be of low toxicity to the fathead minnow (109). Based on their uv spectra, the nitroparaffins would be expected to undergo photolysis in the atmosphere. The estimated half-life of 2-nitropropane in the atmosphere is 3.36 h (110). Various values have been determined for the half-life of nitromethane, but it is similar to 2-nitropropane in persistence (111). Reviews of the available data on the environmental effects of nitromethane and 2-nitropropane have been published by the U.S. Environmental Protection Agency (112, 113).

When disposed of, all the nitroparaffins are considered to be hazardous waste. All have the characteristic of ignitability; however, 2-nitropropane also is a listed hazardous waste (U171) because of its toxicity. The preferred method of disposal is by incineration. Generally, the nitroparaffins must be blended with other flammable liquids to ensure compliance with NO<sub>x</sub> emission standards.

## 8. Uses

The nitroparaffins have been utilized for many applications (114). Some of these uses have been discontinued because of economic and environmental considerations. For instance, significant quantities of 1-nitropropane once were used for the production of hydroxylammonium sulfate and propionic acid by hydrolysis. The need to dispose of an acid waste stream from this process made it uneconomical, so it was discontinued.

This article limits discussion to the current uses of each of the nitroparaffins and omits uses that are either no longer of commercial interest or that have not yet become of commercial importance.

### 8.1. Nitromethane

The nitroparaffins are used widely as raw materials for synthesis. Nitromethane is used to produce the nitro alcohol (qv) 2-(hydroxymethyl)-2-nitro-1,3-propanediol, which is a registered biocide useful for control of bacteria in a number of industrial processes. This nitro alcohol also serves as the raw material for the production of the alkanolamine (qv) 2-amino-2-(hydroxymethyl)-1,3-propanediol, which is an important buffering agent useful in a number of pharmaceutical applications.

Halogenation of nitromethane is utilized to produce two economically important pesticides, chloropicrin [76-06-2], a soil fumigant, and bronopol, a biocide useful for control of microbial growth in cosmetics and industrial applications.

Nitromethane also is used in the synthesis of the antiulcer drug, ranitidine [66357-35-5]. A two-step process utilizing nitromethane, carbon disulfide, potassium hydroxide, and dimethyl sulfate yields 1,1-bis(methylthio)-2-nitroethene [13623-94-4], which reacts further to produce ranitidine.

Significant quantities of nitromethane find use as fuel in drag racing and as a hobby fuel. In addition, nitromethane is used in explosive applications, particularly in shaped charges for specialized applications. It has the advantage of not in itself being classified as an explosive, but it can be made cap-sensitive on-site, thus simplifying the transport of the explosive system to remote locations.

Only small amounts of nitromethane are used as solvent, but it is used in specialized applications such as the solubilization of  $\alpha$ -cyanoacrylate glue and acrylic polymers. Also, nitromethane is useful as solvent for single-phase Friedel-Crafts reactions (115).

Finally, nitromethane has been used in large quantities as a stabilizer for 1,1,1-trichloroethane. The use of this degreasing solvent is expected to decline and disappear under the provisions of the Montreal Protocol (116), which bans ozone-depleting substances, of which this is one.

## 8.2. Nitroethane

The principal use of nitroethane is as a raw material for synthesis in two applications. It is used to manufacture  $\alpha$ -methyl dopa, a hypertensive agent. Also, the insecticide *S*-methyl-*N*-[(methylcarbamoyl)oxy]thioacetimidate [16752-77-5], can be produced by a synthesis route using nitroethane as a raw material. The first step of this process involves the reaction of the potassium salt of nitroethane, methyl mercaptan, and methanol to form methyl methylacetohydroxamate. Solvent use of nitroethane is limited but significant. Generally, it is used in a blend with 1-nitropropane.

## 8.3. 1-Nitropropane

The alkanolamines (qv), 2-amino-2-ethyl-1,3-propanediol and 2-amino-1-butanol, are produced by the two-step process described previously.

Though less important economically, solvent usage consumes a larger portion of the 1-nitropropane production than is consumed of the other nitroparaffins for this use. In particular, a blend of nitroethane and 1-nitropropane has been developed which is useful as an additive for improved coatings performance (116).

## 8.4. 2-Nitropropane

As much as 9100 t of 2-nitropropane once were consumed for use in coatings annually. Concern about toxicity and a general movement to low volatile organic compound (VOC) coatings have resulted in almost the complete disappearance of this use for 2-nitropropane. However, derivatives such as 2-methyl-2-nitro-1-propanol (used in tire cord adhesive) and 2-amino-2-methyl-1-propanol (a pigment dispersant and buffer), have served as an outlet for 2-nitropropane production.

## BIBLIOGRAPHY

"Nitroparaffins" in *ECT* 1st ed., Vol. 9, pp. 428–455, by H. Shechter, Ohio State University, and R. B. Kaplan, E. I. du Pont de Nemours & Co., Inc.; in *ECT* 2nd ed., Vol. 13, pp. 864–888, by J. L. Martin and P. J. Baker, Jr., Commercial Solvents Corp.; in *ECT* 3rd ed., Vol. 15, pp. 969–987, P. J. Baker, Jr., and A. F. Bollmeier, Jr., International Minerals & Chemical Corp.

### Cited Publications

1. *IUPAC Nomenclature of Organic Chemistry*, Pergamon Press, New York, 1979, p. 275.
2. U.S. Pat. 1,967,667 (July 24, 1934), H. B. Hass, E. B. Hodge, and B. M. Vanderbilt (to Purdue Research Foundation); *Ind. Eng. Chem.* **28**, 339 (1936).
3. E. E. Toops, Jr., *J. Phys. Chem.* **60**, 304 (1956).
4. B. Fader, *Chem. Process. (Chicago)* **19**(8), 174 (1956).
5. L. H. Horsley, *Adv. Chem. Ser.* **6**, (1952); L. H. Horsley and W. S. Tamplin, *Adv. Chem. Ser.* **35**, (1962); L. H. Horsley, *Adv. Chem. Ser.* **116**, (1973).
6. A. W. Francis, *Adv. Chem. Ser.* **31**, (1961).
7. A. W. Francis, *Liquid-Liquid Equilibriums*, John Wiley & Sons, Inc., New York, 1963, pp. 174, 214; A. W. Francis, *J. Chem. Eng. Data* **11**, 234 (1966).
8. L. O. Brockway, J. Y. Beach, and L. Pauling, *J. Am. Chem. Soc.* **57**, 2693 (1935).
9. G. Geiseler and H. Kessler, in T. Urbanski, ed., *Nitro Compounds: Proceedings of an International Symposium, Warsaw, Poland, 1963*, Pergamon Press Ltd., Oxford, U.K., 1964, 187–194.
10. R. T. Aplin, M. Fischer, D. Becher, H. Budzikiewicz, and C. Djerassi, *J. Amer. Chem. Soc.* **87**, 4888 (1965); N. M. M. Nibbering, Th. J. de Boer, and H. J. Hofman, *Rec. Trav. Chim.* **84**, 481 (1965); A. V. Iogansen and G. D. Litovchenko,

- Zh. Prikl. Spektroskopii, Akad. Nauk Belorussk. SSR* **21**(3), 243 (1965); *Ibid.* **3**(6), 538 (1965).
11. H. B. Hass and E. F. Riley, *Chem. Rev.* **32**, 373 (1943).
  12. N. Levy and J. D. Rose, *Q. Rev. (London)* **1**, 358 (1947).
  13. P. A. S. Smith, *The Chemistry of the Open-Chain Organic Nitrogen Compounds*, Vol. **II**, W. A. Benjamin, Inc., New York, 1966, 391–454.
  14. H. H. Baer and L. Urbas, in H. Feuer, ed., *The Chemistry of the Nitro and Nitroso Groups*, Pt. 2, Wiley-Interscience, New York, 1970, 75–200.
  15. D. Seebach, E. W. Colvin, F. Lehr, and T. Weller, *Chimia* **33**, 1 (1979).
  16. H. Fuer, ed., *Tetrahedron* **19**(Suppl. 1), (1963).
  17. T. Urbanski, ed., *Nitro Compounds: Proceedings of an International Symposium, Warsaw, Poland, 1963*, Pergamon Press Ltd., Oxford, U.K., 1964.
  18. N. Ono and A. Kaji, *Synth. Org. Chem. Japan* **38**, 115 (1980).
  19. H. Feuer and A. T. Nielsen, eds., *Nitro Compounds, Recent Advances in Synthesis and Chemistry*, VCH Publishers, Inc., New York, 1990.
  20. T. Urbanski, *Synthesis*, 613 (1974).
  21. M. T. Shipchandler, *Synthesis*, 666 (1979).
  22. N. Kornblum and P. Pink, in Ref. 16, 17–22.
  23. H. B. Hass, E. J. Berry, and M. L. Bender, *J. Am. Chem. Soc.* **71**, 2290 (1949).
  24. H. Shechter and R. B. Kaplan, *J. Am. Chem. Soc.* **73**, 1883 (1951).
  25. R. C. Kerber, G. W. Urrey, and N. Kornblum, *J. Am. Chem. Soc.* **87**, 4520 (1965).
  26. G. A. Russell and W. C. Danen, *J. Am. Chem. Soc.* **88**, 5663 (1966).
  27. G. B. Bachman and T. Hokama, *J. Am. Chem. Soc.* **81**, 4882 (1959).
  28. E. H. White and W. J. Considine, *J. Am. Chem. Soc.* **80**, 626 (1958).
  29. L. G. Donaruma and M. L. Huber, *J. Org. Chem.* **21**, 965 (1958).
  30. H. L. Wehrmeister, *J. Org. Chem.* **25**, 2132 (1960).
  31. T. Urbanski, Z. Novak, and E. Morag, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **11**(2), 77 (1963).
  32. U.S. Pat. 2,337,912 (Dec. 28, 1943), E. T. McBee and E. F. Riley (to Purdue Research Foundation).
  33. U.S. Pat. 3,099,612 (July 30, 1963), L. A. Wilson (to Commercial Solvents Corp.).
  34. U.S. Pat. 3,100,806 (Aug. 13, 1963), P. Bay (to Abbott Laboratories).
  35. U.S. Pat. 3,054,829 (Sept. 18, 1962), G. B. Bachman and R. O. Downs (to Purdue Research Foundation).
  36. K. Okon and G. Aluchna, *Bull. Acad. Polon. Sci., Ser. Sci. Chim. Geol. Geograph.* **7**, 83 (1959).
  37. N. J. Leonard and A. B. Simon, *J. Org. Chem.* **17**, 1262 (1952).
  38. M. Senkus, *J. Am. Chem. Soc.* **68**, 1611 (1946); **72**, 2967 (1950).
  39. T. Urbanski and co-workers, in Ref. 17, 195–218.
  40. W. D. Emmons, W. N. Cannon, J. W. Dawson, and R. M. Ross, *J. Am. Chem. Soc.* **75**, 1993 (1953).
  41. U.S. Pat. 2,477,870 (Aug. 2, 1949), M. H. Gold and L. J. Draker (to The Visking Corp.).
  42. S. L. Ioffe, V. A. Tartakovskii, and S. S. Novikov, *Russ. Chem. Rev.* **35**, 19 (1966).
  43. S. S. Novikov, I. S. Korsakova, and K. K. Babievskii, *Usp. Khim.* **26**, 1109 (1957).
  44. E. E. Hamel in Ref. 16, 85–95.
  45. M. B. Frankel in Ref. 16, 213–217.
  46. S. Wakamatsu and K. Shimo, *J. Org. Chem.* **27**, 1609 (1962).
  47. E. Profft, *Chem. Tech. (Berlin)* **8**, 705 (1956).
  48. H. Shechter, D. L. Ley, and L. Zeldin, *J. Am. Chem. Soc.* **74**, 3664 (1952).
  49. H. Feuer and R. Harmetz, *J. Org. Chem.* **26**, 1061 (1961).
  50. V. V. Perekalin, in Ref. 17, 135–157.
  51. V. V. Perekalin, *Unsaturated Nitro Compounds*, Gosudarst. Nauch.-Tekh. Izdatel. Khim. Lit., Leningrad, USSR, 1961; in Israel Program for Scientific Translation, Jerusalem, Israel, 1963.
  52. M. H. Gold and K. Klager, in Ref. 16, 77–84.
  53. G. V. Roitburd and co-workers, *Tetrahedron Lett.* **48**, 4935 (1972).
  54. U.S. Pat. 3,055,936 (Sept. 25, 1962), M. Stiles and H. L. Finkbeiner (to Research Corp.).
  55. H. L. Finkbeiner and M. Stiles, *J. Amer. Chem. Soc.* **85**, 616 (1963).
  56. H. L. Finkbeiner and G. W. Wagner, *J. Org. Chem.* **28**, 215 (1963).



57. A. P. Hardt, F. G. Borgardt, W. L. Reed, and P. Noble, Jr., *Electrochem. Technol.* **1**, 375 (1963).
58. C. T. Bahner, *Ind. Eng. Chem.* **44**, 317 (1952).
59. H. Shechter and R. B. Kaplan, *J. Amer. Chem. Soc.* **75**, 3980 (1953).
60. U.S. Pat. 3,267,158 (Aug. 16, 1966), A. J. Havlik (to Aerojet-General Corp.).
61. T. Urbanski and W. Gurzynska, *Rocz. Chem.* **25**, 213 (1951).
62. V. F. Belyaev and R. I. Shamanovskaya, *Zh. Org. Khim.* **1**, 1388 (1965).
63. T. Mukaiyama and T. Hoshino, *J. Amer. Chem. Soc.* **82**, 5339 (1960).
64. A. V. Topchiev, *Nitration of Hydrocarbons and Other Organic Compounds*, Pergamon Press Ltd., Oxford, U.K., 1959.
65. N. Kornblum, in A. C. Cope, ed., *Organic Reactions*, Vol. **12**, John Wiley & Sons, Inc., New York, 1962, 101–156.
66. H. O. Larson, in Ref. 14, Part 1, 1969, 301–348.
67. R. F. Purcell, in J. J. McKetta ed., *Encyclopedia of Chemical Processes and Design*, Vol. **31**, Marcel Dekker, Inc., New York, 1990, 267–281.
68. K. E. Gilbert and W. T. Borden, *J. Org. Chem.* **44**, 659 (1979).
69. G. B. Bachman and R. J. Maleski, *J. Org. Chem.* **37**, 2810 (1972).
70. U.S. Pat. 4,329,523 (May 11, 1982), R. James and R. Egly (to International Minerals & Chemical Corp.).
71. H. B. Hass and H. Shechter, *Ind. Eng. Chem.* **39**, 817 (1947).
72. F. A. Lowenheim and M. K. Moran, eds., *Faith, Keyes, and Clark's Industrial Chemicals*, 4th ed., John Wiley & Sons, Inc., New York, 1975.
73. R. N. Shreve, *The Chemical Process Industries*, McGraw-Hill Book Co., Inc., New York, 1956, p. 933.
74. J. C. Reidel, *Oil & Gas J.* **54**(36), 110 (1956).
75. P. Noble, Jr., F. G. Borgardt, and W. L. Reed, *Chem. Rev.* **64**, 7 (1964).
76. U.S. Pat. 2,489,320 (Nov. 29, 1949), E. M. Nygaard and W. I. Denton (to Socony-Vacuum Oil Co.).
77. W. I. Denton, R. B. Bishop, E. M. Nygaard, and T. T. Noland, *Ind. Eng. Chem.* **40**, 381 (1948).
78. R. B. Kaplan and H. Shechter, *J. Amer. Chem. Soc.* **83**, 3535 (1961).
79. U.S. Pat. 2,997,504 (Aug. 22, 1961), H. Shechter and R. B. Kaplan (to Ohio State Research Foundation).
80. U.S. Pat. 3,000,966 (Sept. 19, 1961), K. Klager (to Aerojet-General Corp.).
81. *Nitromethane: Storage and Handling Guidelines, Technical Data Sheet No. 2*, ANGUS Chemical Company, Buffalo Grove, Ill., Aug. 1993.
82. *Nitroparaffins and Their Hazards*, Research Report No. 12, Committee on Fire Prevention and Engineering Standards, National Board of Fire Underwriters, New York, 1959.
83. C. J. Wassink and J. T. Allen, in F. D. Snell and L. S. Ettre, eds., *Encyclopedia of Industrial Chemical Analysis*, Vol. **16**, John Wiley & Sons, Inc., 1972, 412–448.
84. L. R. Jones and J. A. Riddick, *Anal. Chem.* **28**, 1137 (1956).
85. C. Frejacques and M. Leclercq, *Mem. Poudres* **39**, 57 (1957).
86. J. R. Nielsen and D. C. Smith, *Ind. Eng. Chem., Anal. Ed.* **15**, 609 (1943).
87. R. N. Hazeldine, *J. Chem. Soc.*, 2525 (1953).
88. N. Kornblum, H. E. Ungnade, and R. A. Smiley, *J. Org. Chem.* **21**, 377 (1956).
89. Z. Buczkowski and T. Urbanski, *Spectrochim. Acta* **18**, 1187 (1962).
90. R. L. Foley, W. M. Lee, and B. Musulin, *Anal. Chem.* **36**, 1100 (1964).
91. M. J. Kamlet and D. J. Glover, *J. Org. Chem.* **27**, 537 (1962).
92. J. C. Neerman and O. S. Knight, *Chem. Eng.* **56**(11), 125 (1949).
93. R. M. Bethea and T. D. Wheelock, *Anal. Chem.* **31**, 1834 (1959).
94. W. Biernacki and T. Urbanski, *Bull. Acad. Polon. Sci., Ser. Sci. Chem.* **10**, 601 (1962).
95. R. M. Bethea and F. S. Adams, *Anal. Chem.* **33**, 832 (1961); *J. Chromatogr.* **8**, 532 (1962).
96. E. Camera, D. Pravisani, and W. Ohman, *Explosivstoffe* **13**(9), 237 (1965).
97. NIOSH, *Manual of Analytic Methods*, 3rd ed., 2nd Suppl. NIOSH, Cincinnati, Ohio, 1988.
98. J. Dequidt, P. Vasseur, and J. Potencier, *Bull. Soc. Pharm. Lille* **83**, 131, 137 (1972); **29** (1973).
99. *1994–1995 Threshold Limit Values and Biological Exposure Indices*, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1994.
100. J. F. Treon and F. R. Dutra, *AMA Arch. Ind. Hyg. Occup. Med.* **5**, 52 (1952).
101. T. R. Lewis, C. E. Ulrich, and W. M. Busey, *J. Environ. Pathol. Toxicol.* **2**, 233 (1979).
102. *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans*, Vol. **29**, International Agency

## 18 NITROPARAFFINS

- for Research on Cancer, Lyon, France, 1982, 331–343.
103. *Fifth Annual Report on Carcinogens, Summary*, National Toxicology Program, Research Triangle Park, N.C., 1989, 199–201.
104. T. B. Griffin and co-workers, *Ecotoxicol. Environ. Safety* **16**, 11 (1988).
105. T. B. Griffin and co-workers, *Ecotoxicol. Environ. Safety* **6**, 268 (1982).
106. E. S. Fiala and co-workers, *Carcinogenesis* **8**(12), 1947 (1987).
107. R. A. Davis, in G. D. Clayton and F. E. Clayton, eds., *Patty's Industrial Hygiene and Toxicology*, 4th ed., Vol. **II**, Pt. A, John Wiley & Sons, Inc., New York, 1993, 599–662.
108. *Environmental Health Criteria 138: 2-Nitropropane*, World Health Organization, Geneva, Switzerland, 1992.
109. M. W. Curtis and C. H. Ward, *J. Hydrol.* **51**(1–4), 359, (1981).
110. L. T. Cupitt, *Project Summary: Fate of Toxic and Hazardous Materials in the Air Environment*, U.S. Environmental Protection Agency, Research Triangle Park, N.C., 1980.
111. W. D. Taylor and co-workers, *Int. J. Chem. Kinet.* **12**, 231 (1980).
112. *Health and Environmental Effects Profile for Nitromethane*, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1985.
113. *Health and Environmental Effects Profile for 2-Nitropropane*, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1985.
114. R. E. Kass, *Specialty Chem.* (Aug. 1983).
115. L. Schmerling, *Ind. Eng. Chem.* **40**, 2072 (1948).
116. "Montreal Protocol on Substances that Deplete the Ozone Layer," Sept. 16, 1987; *Code Fed. Reg.*, Title 40, Part 82, U.S. EPA, Washington, D. C., 1988.
117. G. N. Robinson, *Amer. Paint J.* **77**(28), 42–47 (Dec. 14, 1992).

ALLEN F. BOLLMEIER JR.  
ANGUS Chemical Company

## Related Articles

Nitro alcohols; Nitration