THE NITROPARAFFINS

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I. INTRODUCTION

In May, 1940, the first production of nitroparaffins on an industrial scale occurred at the plant of the Commercial Solvents Corporation, Peoria, Illinois. The process involved the newly invented vapor-phase nitration technic, which was first employed by Hass, Hodge, and Vanderbilt (132, 133, 134) at Purdue University, and which has been in active development since the autumn of 1930. By nitrating the propane of natural gas and of petroleum, which is available in practically unlimited quantities, the first four nitroparaffins are produced: nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane. The nitration of any of the volatile higher or lower homologs of the paraffinic or naphthenic series can be accomplished by the same general procedure. From our most inexpensive organic raw materials it is thus possible to obtain nitro derivatives by the action of the acid which the researches of Haber and Ostwald have placed among our most available and cheapest inorganic reagents. It is therefore an appropriate time to review[1] the syntheses, properties, uses, and reactions of the nitroparaffins and their immediate derivatives.

II. THE VICTOR MEYER REACTION

In 1872 Meyer and Stüber (271) reported that the reaction between amyl iodide and silver nitrite had yielded nitropentane and amyl nitrite. At that time the aromatic nitro derivatives were already of substantial importance, since Mauvein had been made by Perkin sixteen years before and the aniline dye industry was in active development. It is not surprising, therefore, that this first synthesis of a nitroparaffin[2] should have aroused general interest and resulted in the publication of a considerable number of papers. The Victor Meyer reaction has been reviewed and extended by Reynolds and Adkins (329), so that no detailed discussion need be given here. It should be mentioned, however, that it has been found suitable for producing not only nitroparaffins but also polynitroparaffins (55), nitroalcohols (81), nitroölefins (56, 260), nitroethers, nitroketones, and many other aliphatic nitro compounds.

Salts of α-halocarboxylic acids react similarly even with sodium nitrite and yield salts of α-nitrocarboxylic acids which readily decompose, producing nitroparaffins and metallic bicarbonates. Kolbe (202) reported this reaction only five months after Meyer and Stüber's first announcement of the nitroparaffins.[3]

The reasons for the wide differences between the ratios of organic nitrite and nitro derivative obtained from various organic halides and metallic nitrites are still obscure. Reynolds and Adkins have postulated that an addition complex is formed between the two reagents and that every constituent of the complex is thus in a position to influence the further course of the reaction to yield either nitrite or nitro compound. It is probably of significance that nitrites readily rearrange to nitro derivatives at elevated temperatures (287). The yield may therefore fluctuate with the amount of local overheating.

III. MISCELLANEOUS METHODS OF INTRODUCING THE NITRO GROUP INTO ALIPHATIC COMPOUNDS

(*a*) A primary amine may be oxidized directly to a nitroparaffin. Thus methylamine, ethylamine, *tert*-butylamine, and benzylamine have been oxidized to the corresponding nitro compounds. Bamberger and Seligman (18) give the following equations:

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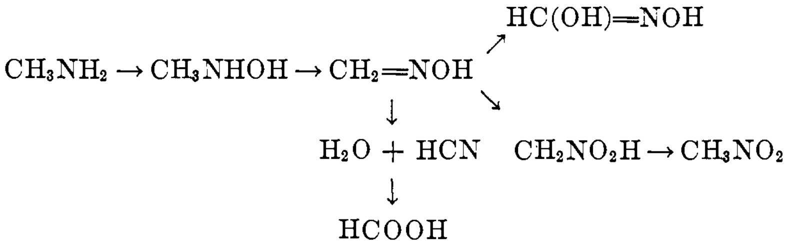
[1] Brief reviews of this general nature have recently appeared by Hurd (115), Ellis (93, 94), Hass (131), and Gabriel (107, 108). Because of the limitations of time and space and the very extensive literature, the present article is by no means exhaustive.

[2] Chloropicrin and bromopicrin had been made much earlier (365, 366).

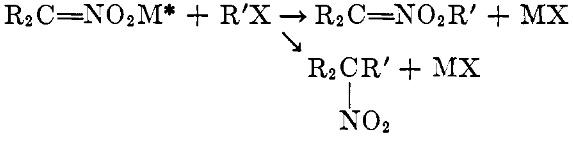
[3] For a recommended laboratory procedure, see *Organic Syntheses* (291).



$$\begin{tikzcd}
 & & & \mathrm{HC(OH){=}NOH} & \\
\mathrm{CH_3NH_2} \arrow[r] & \mathrm{CH_3NHOH} \arrow[r] & \mathrm{CH_2{=}NOH} \arrow[ur] \arrow[d] \arrow[dr] & & \\
 & & \mathrm{H_2O + HCN} \arrow[d] & \mathrm{CH_2NO_2H} \arrow[r] & \mathrm{CH_3NO_2} \\
 & & \mathrm{HCOOH} & &
\end{tikzcd}$$

(*b*) Halonitroparaffins may be treated with zinc alkyls to replace one, two, or three halogen atoms with alkyl groups. Bevad (32, 33) obtained tertiary nitrobutane by the action of dimethylzinc upon chloropicrin.

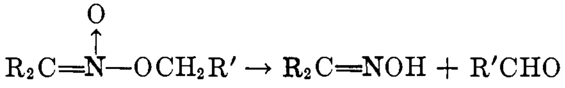
(*c*) By using a metallic derivative of an aci-nitroparaffin and an alkyl halide, one obtains either a nitronic ester or a higher nitro derivative.



$$\begin{tikzcd}
\mathrm{R_2C{=}NO_2M^* + R'X} \arrow[r] \arrow[dr] & \mathrm{R_2C{=}NO_2R' + MX} \\
 & \mathrm{R_2\underset{NO_2}{\underset{|}{C}}R' + MX}
\end{tikzcd}$$

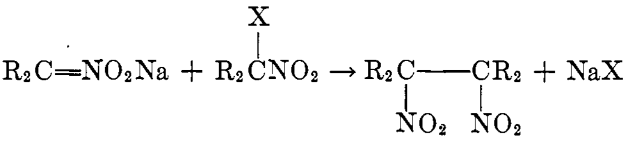
* (M = K, Na, or Ag)

This reaction has recently been reviewed and extended by Brown and Shriner (57), Thurston and Shriner (378), and Weisler (398). The nitronic esters are frequently instable, decomposing as follows:



$$\mathrm{R_2C{=}\overset{O}{\overset{\uparrow}{N}}{-}OCH_2R' \rightarrow R_2C{=}NOH + R'CHO}$$

As in the Victor Meyer reaction, very different ratios of nitro derivative to by-product are observed, depending upon the particular reactants. There is some evidence (398) that high yields of nitro derivative correlate positively with the lability of the halogen atom. In the related synthesis of the dinitroparaffins (*cf.* section VI) by the reaction

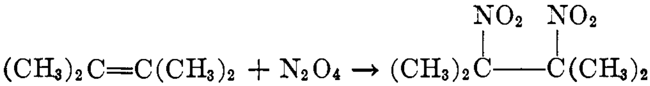


$$\mathrm{R_2C{=}NO_2Na + R_2\overset{X}{\overset{|}{C}}NO_2 \rightarrow R_2\underset{NO_2}{\underset{|}{C}}{-\!-}\underset{NO_2}{\underset{|}{C}}R_2 + NaX}$$

best yields were obtained with iodides and poorest with chlorides; these results are, of course, in harmony with the above generalization. Alkyl sulfates are also suitable as alkylating reagents for nitroparaffins (11).

(*d*) An alkyl nitrite may be caused to rearrange to form a nitroparaffin (111, 287). When ethyl nitrite and hydrogen are passed over finely divided nickel or nickelized asbestos, amines are formed. This reaction is ascribed to preliminary rearrangement of the nitrite to nitroparaffin.

(*e*) Certain olefins will add nitrogen tetroxide to yield dinitroparaffins. The reactions between olefins and the oxides of nitrogen are complex and quite worthy of a separate review; apparently either or both of the doubly bound carbon atoms may form carbon–oxygen or carbon–nitrogen linkages. 2,3-Dimethyl-2-butene reacts as follows:



$$(CH_3)_2C{=}C(CH_3)_2 + N_2O_4 \rightarrow (CH_3)_2\overset{\overset{NO_2}{|}}{C}{-}{-}\overset{\overset{NO_2}{|}}{C}(CH_3)_2$$

Tetrachloroethylene and tetrabromoethylene react analogously to yield 1,2-dinitrotetrachloroethane and 1,2-dinitrotetrabromoethane (7, 41). Haitinger (122) treated isobutylene with concentrated nitric acid and obtained the compound $C_4H_2N_2O_4$, perhaps by the same reaction. Although its structure is uncertain, the production of the same compound by the liquid-phase nitration of a petroleum distillate indicates that it may be a dinitroparaffin.

IV. Liquid-phase Nitration of Saturated Hydrocarbons

In spite of the fact that Mills (273) had nitrated chloroform in a sealed tube before the first nitroparaffin had been reported, eight years elapsed between the announcement of the Victor Meyer reaction and the first report of the production of a nitroparaffin by the direct nitration of a hydrocarbon. Beilstein and Kurbatov (24, 25) had observed that fractions of Caucasian petroleum are readily nitrated to yield nitro derivatives of cycloparaffins. A fraction of American petroleum boiling at 95–100°C. had a density between that of a paraffin and a cycloparaffin, and selective nitration was used in a successful effort to purify it from naphthenic components. The nitro derivative boiled for the most part from 193° to 197°C. and had a composition corresponding to the formula $C_7H_{15}NO_2$. On the basis of present knowledge it must have been a mixture of nitroheptanes in which 2-nitroheptane and the 3- and 4-nitro derivatives predominated.

This work was followed by a large number of articles (93) describing the nitration of paraffins and naphthenes and more complex mixtures; these materials range from pentanes to the residues from the distillation of petroleum. The following generalizations have emerged from these researches:

(*a*) Tertiary hydrogen atoms in either paraffins or cycloparaffins are most rapidly replaced, secondary hydrogen atoms react more sluggishly, and primary hydrogen atoms most slowly. The only apparent exception to this generalization is found in the work of Worstall (413, 418), who reported exclusively primary nitro derivatives from hexane, heptane, octane, nonane, and decane. Worstall refluxed his reagents at atmospheric pressure and therefore used rather low temperatures, which necessitated prolonged reaction. It seems likely that the secondary nitroparaffins were selectively attacked by the nitric acid, and that this phenomenon accounts for both the high proportion of polynitro derivatives and the preponderance of primary nitroparaffins in the mononitrated products. Henry (158) showed later that at least part of Worstall's identifications were in error.

(*b*) Reaction is slow but yields and conversions are increased at higher temperatures. For example, the report of a yield of 60 per cent in the nitration of *n*-hexane (413) was a misprint; the yield was actually 6.0 per cent. This resulted from several days' refluxing in an open vessel. Yields as high as 70 per cent were obtained with nonane which, of course, has a much higher refluxing temperature even in the presence of nitric acid. The product was a mixture of mono- and poly-nitro derivatives. By employing the sealed-tube technic, Konovalov found that, although a low yield was obtained at 115–120°C. with *n*-hexane, and nitric acid of density 1.155 (206), increase of the temperature to 140°C. and the use of more dilute nitric acid (density 1.075) resulted in a 60 per cent yield of nitrohexanes.

(*c*) A great deal of oxidation accompanies the nitration. Since the nitric acid is largely reduced to elementary nitrogen, this constitutes an economic loss. The contrast between the vapor-phase reaction (see section V), which yields almost no elementary nitrogen, and the liquid-phase nitration is presumably attributable to the effect of mineral acids upon nitroparaffins. This topic is discussed in more detail in section X, but it may be mentioned here that primary nitroparaffins yield carboxylic acids and salts of hydroxylamine. Hydroxylammonium nitrate decomposes at 100°C., yielding water, nitrogen, and oxygen (255).

(*d*) Large quantities of polynitroparaffins are formed. This may be caused by the fact that nitric acid and saturated hydrocarbons are immiscible, while the mononitro derivatives are much more soluble in the acid and are there presumably oxidized, nitrated, and hydrolyzed.

(*e*) The sulfuric acid–nitric acid mixture used for nitrating aromatic hydrocarbons is not suitable for paraffins. Primary nitroparaffins are quickly hydrolyzed by hot sulfuric acid, and the secondary and tertiary isomers are converted to brown tars. Markovnikov (244) has found that, to attack alkanes, mixtures of nitric and sulfuric acids require a higher temperature than nitric acid. Thus, while many paraffins with tertiary hydrogen atoms are attacked appreciably by nitric acid at 20°C., these same ones require a temperature of 43° to 85°C. with mixed acid. The sulfuric acid probably decreases the small mutual solubility of nitric acid and alkanes. Cycloparaffins react with mixed acid to yield dicarboxylic acid without loss of carbon atoms. In this connection it is interesting to note that highly methylated aromatic hydrocarbons are nitrated on the ring with mixed acid and on a methyl group with dilute nitric acid alone.

(*f*) In order to promote miscibility between nitrating agent and hydrocarbon, such reagents as nitric–acetic acid mixtures, benzoyl nitrate, and acetyl nitrate have been used. Ethyl nitrate and sodium ethoxide (409) are effective with compounds containing active hydrogen. Aside from the explosion hazards involved in employing such compounds as ethyl or acetyl nitrate, these reagents suffer from the disadvantage that they are gradually attacked. An attempt to nitrate isobutane in this laboratory (133) in the presence of acetic acid resulted in substantial oxidation of the acetic acid. Haines and Adkins (120) reported the rapid nitration of *n*-heptane at 0°C. by the action of nitrogen pentoxide. The products were rather involatile (b.p. 130–180°C. or higher at 25 mm.) and were not identified. They may have been polynitro derivatives.

(*g*) Aluminum nitrate has been recommended as a catalyst for liquid-phase nitrations. Work in this laboratory (83) has shown that the principal effect of the aluminum nitrate is to raise the boiling point of the nitric acid. The increased temperature of reflux results in more rapid nitration but sodium nitrate has approximately the same effect.

After Emil Fischer (99) had shown that nitromethane is an excellent solvent for cellulose nitrate, cellulose acetate, and mixtures thereof, Hopkins (169) disclosed the nitration (catalyzed by aluminum nitrate) of volatile petroleum fractions from about C_6 to C_8, and Hopkins and Buc (170) described the use of the nitrated derivatives in admixture with alcohol as cellulose ester solvents. So far as is known, the process and product never reached commercial production. This may have been a result of the decreased dilution ratios of nitroparaffins with six or more carbon atoms and the disparity in the evaporation rates of ethanol and these nitro derivatives which would have caused separation during drying of the lacquer film.

The liquid-phase nitration of alkanes has recently been investigated by Stevens and Schiessler (367), who found that the 3-nitro-3-methyloctane obtained from *l*-3-methyloctane is optically active. The mechanism therefore does not involve free radicals. The fact, reported by Markovnikov (245), that no rearrangement occurs in the nitration of neohexane is in line with Whitmore's generalization (402) that removal of a positive atom from a neo structure does not cause rearrangement.

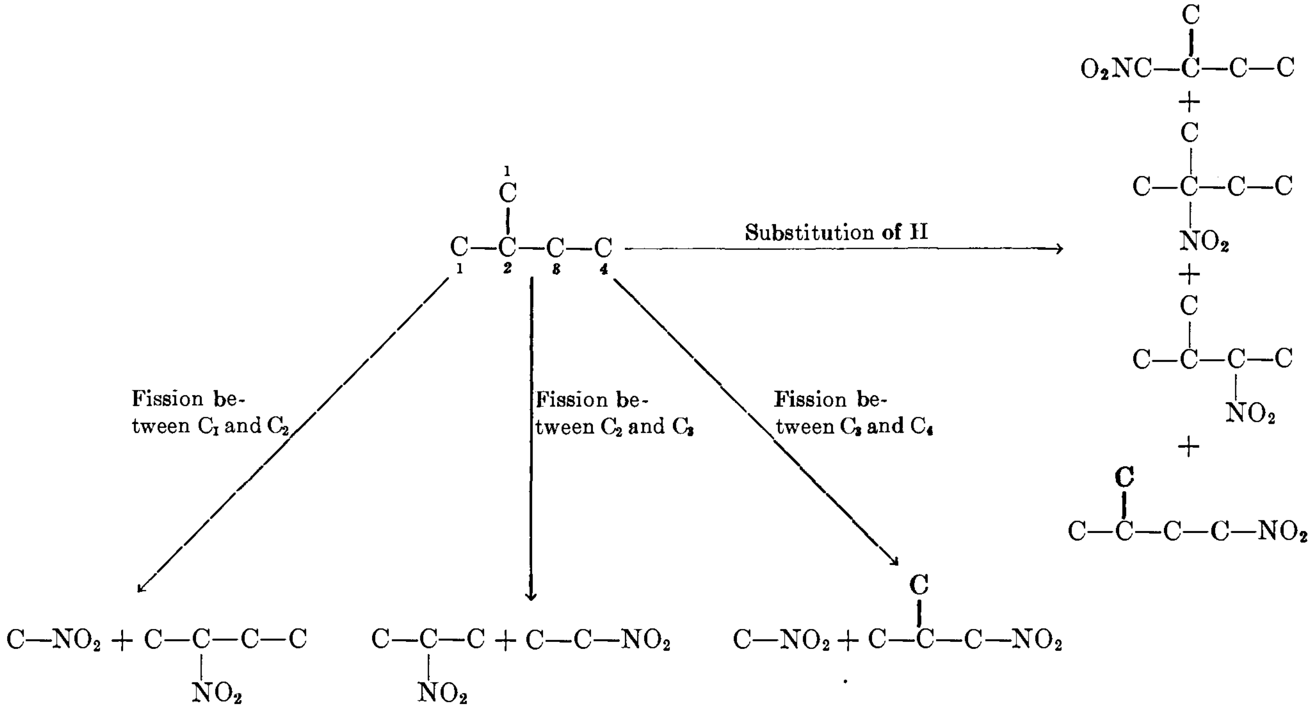
The nitration of haloparaffins in the liquid phase has been reported. Thus, chloropicrin may be obtained by the direct nitration of chloroform (273). Dănăilă and Soare (76) reported a 58 per cent yield of chloropicrin when equal volumes of chloroform and nitric acid (density 1.52) were heated at 140–150°C., under pressure for 3 hr., and Konovalov reported that 1-chloro-2-methyl-2-nitropropane constituted 95 per cent of the nitrated product in the nitration of isobutyl chloride (210, 211, 212).

V. VAPOR-PHASE NITRATION

The vapor-phase nitration process is an outgrowth of an attempt to nitrate isobutane. Almost all of the previous liquid-phase nitrations had indicated that a tertiary hydrogen atom is substituted with ease but that primary hydrogens are attacked only to a small extent (see section IV). Since isobutane contains only one tertiary hydrogen atom, the others being primary, it seemed to be uniquely suitable for yielding large amounts of the mononitro derivative. Its nitration had not been reported, and was therefore undertaken. Because of the low boiling point (−12°C.) of isobutane, the sealed-tube technic was employed and the first experiment was conducted at 115°C. When substantially no reaction was observed, the temperature was increased to 150°C. and a smooth nitration was obtained within approximately 15 min. The product was the expected tertiary nitrobutane in a high state of purity. It proved to be free from the lachrymal effects previously noted (30) in a sample made from chloropicrin and dimethylzinc and to have a melting point (25.5°C.) slightly higher than previously reported (24°C.). The conversion, however, was only 22 per cent. A similar experiment with normal butane gave an equally good nitration, indicating that the unique structure of isobutane is not a crucial factor in the reaction.

In attempting to carry out the nitration upon a larger scale, a stainless-steel bomb was used successfully, but it is evident that at 150°C. isobutane (critical

Nitration products of isopentane

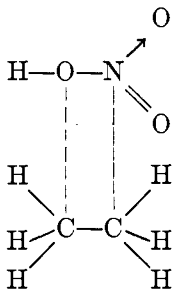


temperature 134°C.) is in vapor phase and the flow method has very great advantages in controlling such reactions. A vapor-phase nitrator was therefore constructed to operate at substantially atmospheric pressure. The great decrease in concentration resulting from the change from sealed-tube pressures to those of the flow apparatus slowed the reaction and necessitated an increase in temperature. Nitration has been obtained under these conditions at temperatures from 248° to over 600°C. but the range 400° to 450°C. is most generally suitable.

When the product was examined it was found to differ greatly from that obtained in the sealed tube. Instead of the crystalline tertiary nitrobutane, a liquid was obtained which contained relatively little of the tertiary derivative and consisted predominantly of 1-nitro-2-methylpropane with considerable amounts of 2-nitropropane and nitromethane. This work, together with subsequent nitrations of ethane, propane, butane, pentane, and isopentane, has led to the following generalization: When a paraffin is nitrated in the vapor phase at high temperatures, all of the mononitro substitution products are obtained which could result if we conceive of the nitro group as capable of substituting either any hydrogen atom or any alkyl radical present in the hydrocarbon. Thus 2-methylbutane (isopentane) yields 1-nitro-2-methylbutane, 2-nitro-2-methylbutane, 3-nitro-2-methylbutane, and 4-nitro-2-methylbutane by substituting any one of the various hydrogen atoms, and nitromethane, nitroethane, 2-nitropropane, 2-nitrobutane, and 1-nitro-2-methylpropane by substituting alkyl groups.

This reaction was formerly believed to have a free-radical mechanism (236), but this hypothesis seems to be incapable of explaining the large quantity of nitromethane (up to 27 per cent of the nitrated product) obtained when ethane is nitrated. The ethyl radical does not decompose to form any product having a single carbon atom.

R. H. Ewell (96) has suggested that hydrocarbons and nitric acid may form addition complexes which decompose, yielding alcohols and lower nitroparaffins. With ethane, for example, two complexes would be possible, as represented by the following diagrams:



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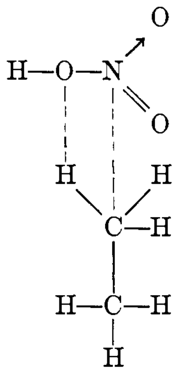

II

Compound I would undergo fission, yielding nitromethane and methanol; compound II would yield nitroethane and water.

One deduction from this mechanism is that for every molecule of nitroparaffin formed by C—C fission (i.e., having fewer carbon atoms than the hydrocarbon flowing into the reaction tube), a molecule of alcohol is produced. Qualitatively, alcohols are present in the products of the nitration reaction. Since they are not stable under the nitration conditions, being rather easily oxidized by nitric acid, and since they may in part be formed by direct oxidation of the hydrocarbon, a quantitative comparison is difficult or impossible.

Another prediction of this mechanism is that the 2-nitrobutane formed by the nitration of optically active 3-methylhexane will itself be optically active. This prediction is now in the process of being checked (61).

The addition-complex mechanism is entirely in harmony with the results obtained by Stevens and Schiessler (367) in liquid-phase nitration (*cf.* section IV).

The vapor-phase nitration process does not yield dinitroparaffins when carried out at temperatures of 248°C. or above with either nitric acid or nitrogen dioxide as the nitrating agent (86). Even when nitroparaffins are used as reactants, they are pyrolyzed and oxidized but not nitrated (236). Urbânski and Slon (384), working at 200°C., reported the formation of dinitroparaffins; while their identifications are not too conclusive, it is quite possible that the lower temperature used by them caused this difference. Dorsky's work (86) has shown that over the temperature range 248° to 600°C. nitrogen dioxide and nitric acid yield the same products, although the yields per mole of nitrating agent are higher when nitric acid is used. One reason for the difference in yield can be seen if the following equations represent the two reactions:

$$RH + HONO_2 \rightarrow RNO_2 + H_2O$$

$$RH + 2NO_2 \rightarrow RNO_2 + HNO_2$$

or

$$2RH + 3NO_2 \rightarrow 2RNO_2 + NO$$

One and one-half or 2 moles of nitrogen dioxide are necessary to do the work of 1 mole of nitric acid.

The effect of increased temperature upon the vapor-phase nitration reaction is to increase (*1*) its velocity, (*2*) the production of primary nitroparaffins at the expense of secondary and tertiary isomers, and (*3*) the yield of fission products. Conversions[4] are surprisingly constant over a wide temperature range when the exposure time and temperature are carefully matched. If one plots conversion against temperature at constant exposure time, a curve is obtained which rises, passes through a maximum, and declines (159). Temperatures below the optimum are too low for completion of the reaction, while those higher than the optimum result in too much pyrolysis of the nitroparaffins. The

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[4] By "conversion" is meant the moles of nitroparaffin times 100 divided by the moles of nitric acid passing through the reactor.

importance of this phenomenon is illustrated by the fact that in the commercial nitration of propane, the temperature is controlled to within ±1°F.

The effect of higher pressure is to increase greatly the rate of the reaction without, usually, greatly affecting the conversion. The catalysts so far studied all accelerate the competing oxidation reaction at the expense of the nitration. When the reaction was transferred from glass into stainless steel, conversions were lowered and became unreproducible. The cause is believed to be a film of metallic oxides, the effect of which Hodge and Swallen (163) showed could be eliminated by the continuous introduction of a small quantity of sodium or potassium nitrate into the reactor to poison the unwanted catalyst.

Under favorable conditions, approximately 40 per cent of the nitric acid passed through the reactor forms nitroparaffins. The remainder functions as oxidizing agent, being reduced almost exclusively to nitric oxide. Alcohols, carboxylic acids, aldehydes, ketones, carbon monoxide, carbon dioxide, and water are thus formed in various quantities. In the commercial plant the nitric oxide is separated from other reaction products and excess unchanged hydrocarbon and is reoxidized to nitric acid. Thus, eventually more than 90 moles of nitroparaffin can be produced for each 100 moles of nitric acid consumed. A study was made of the effect of excess hydrocarbon upon the conversion. The curve obtained when moles of hydrocarbon per mole of nitric acid were plotted against conversion did not extrapolate to 100 per cent conversion at infinite ratio of hydrocarbon to nitric acid. This apparently means that oxidation accompanies and does not merely follow the nitration reaction, i.e., the nitric acid oxidizes the hydrocarbon as well as the nitroparaffin. This conclusion has subsequently been verified by the isolation of 1-propanol and 2-propanol as by-products of the nitration of propane (162).

As might be expected, methane requires a higher temperature and/or longer exposure time than its homologs and gives a smaller conversion. This is the reason for the failure of the first attempt to nitrate methane in this laboratory. Landon (218, 219), of the research staff of the Hercules Powder Company, has reported the successful nitration of methane; this has been confirmed at Purdue University (54). Ethane is somewhat more easily nitrated, propane still more easily, and little difference is shown by the hydrocarbons above propane.

The nature of the hydrocarbon apparently has less influence upon the course of the vapor-phase nitration reaction than it does with liquid-phase operation. This is to be expected, since reactions are generally less selective at higher temperatures; those having lower activation energies occur more rapidly at low temperatures than competing reactions with higher activation energies; the latter, however, have higher temperature coefficients and hence are favored by temperature increases. A comparison of the nitration of hendecane in the vapor phase and in the liquid phase (83) showed that higher conversions are obtained under the former conditions even with this relatively involatile hydrocarbon.

The nitration of cycloparaffins in the vapor phase has been comparatively little studied. Cyclohexane is easily nitrated (295) to the mononitro derivative, and there is no doubt that the reaction is as widely applicable in this series as with the alkanes.

When Oleszko and McBee (289) nitrated isobutyl chloride in the vapor phase at 330–340°C., the products obtained were 1-chloro-2-methyl-3-nitropropane, 1-chloro-2-methyl-2-nitropropane, 1-chloro-2-methyl-1-nitropropane, 1-chloro-2-nitropropane, and nitromethane. The absence of monochloronitromethane and of 2-nitropropane is interesting and indicates once more that the reactions of paraffins are more readily predicted than those of the monochloroparaffins.

The vapor-phase nitration of other organic compounds represents a field which has hardly been touched. Treatment of acetic, propionic, butyric, and isobutyric acids with nitric acid at 400°C. yielded practically nothing but unchanged acids, carbon dioxide, water, and nitric oxide (236). Tetraethyllead yielded lead nitrate, ethyl nitrate, and nitroethane. Benzene forms nitrobenzene with ease, but the method (237, 406) probably is not capable of competing economically with the liquid-phase reaction in this instance. Toluene likewise yields nitrobenzene, benzaldehyde, and probably phenylnitromethane, when subjected to vapor-phase nitration (352).

This last reaction recalls the formation of tetranitromethane in the liquid-phase nitration of toluene reported by Gärtner (110). Numerous other compounds have also yielded nitro derivatives of methane when subjected to liquid-phase nitration; the list includes acetylene, acetic anhydride (292), and glycerol (75). Datta and Chatterjee (77) have shown that a great variety of organic materials yield chloropicrin and other chloronitro derivatives of methane when treated with aqua regia.

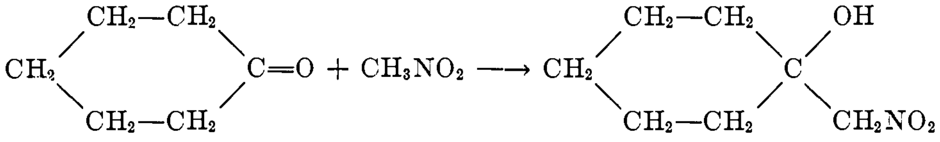
VI. Synthesis of Aliphatic Polynitro Compounds

(*a*) The addition of nitrogen tetroxide to olefinic double bonds has already been mentioned (see section III).

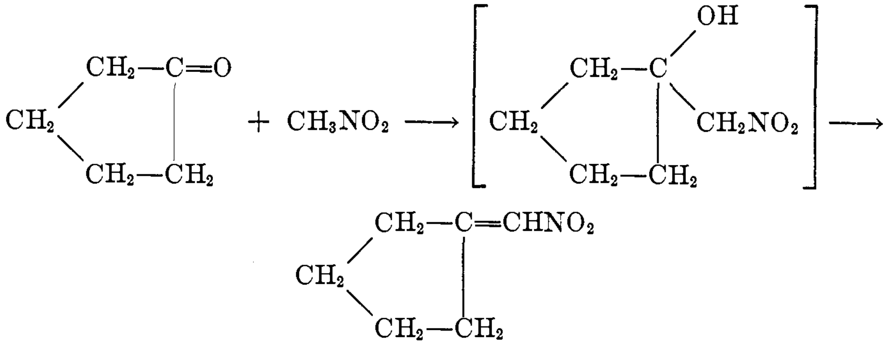
(*b*) Fraser and Kon (102) have reported the condensation of nitromethane with acetone, 2-butanone, 2-pentanone, 3-pentanone, and cyclohexanone. Except for the last, dinitroparaffins were formed by the reaction illustrated below for acetone:

$$CH_3COCH_3 + 2CH_3NO_2 \rightarrow (CH_3)_2C(CH_2NO_2)_2$$

Cyclohexanone with nitromethane, nitroethane, or 1-nitropropane yielded the corresponding nitroalcohols 1-nitromethylcyclohexanol, 1-α-nitroethylcyclohexanol, and 1-α-nitropropylcyclohexanol.



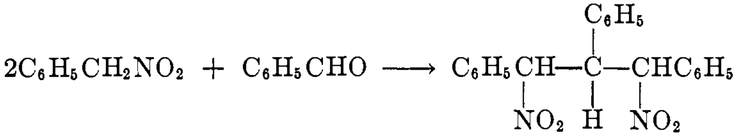
Cyclopentanone yielded the nitroölefin when treated with nitromethane.



Piperidine and other basic substances were employed as catalysts.

Three chemists at different times, either in this laboratory or at the Commercial Solvents Corporation, have attempted to repeat the work of Fraser and Kon, but with negligible success. By modifications of the conditions for the reaction, Bourland and Larrison have recently been able to achieve these syntheses with satisfactory yields and conversions (48, 221). No explanation of this divergence of results has occurred to us.

(*c*) A quite analogous reaction with aldehydes has been reported by Heim (143), who condensed 2 moles of phenylnitromethane with 1 mole of benzaldehyde to obtain 1,3-dinitro-1,2,3-triphenylpropane.

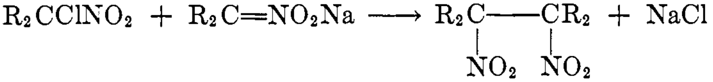


$$2C_6H_5CH_2NO_2 + C_6H_5CHO \longrightarrow C_6H_5CH(NO_2)-C(C_6H_5)(H)-CH(NO_2)C_6H_5$$

(*d*) Secondary nitroparaffins, when treated with 1 mole of alkali and 0.5 mole of halogen, yield dinitroparaffins by the following reactions (353):

$$R_2CHNO_2 + NaOH \longrightarrow R_2C{=}NO_2Na + H_2O$$

$$R_2C{=}NO_2Na + Cl_2 \longrightarrow R_2CClNO_2 + NaCl$$



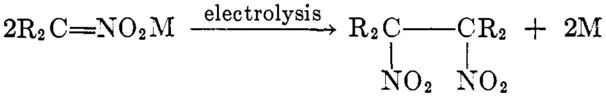
$$R_2CClNO_2 + R_2C{=}NO_2Na \longrightarrow R_2C(NO_2)-CR_2(NO_2) + NaCl$$

The yields originally reported for the conversion of 2-nitropropane to 2,3-dimethyl-2,3-dinitrobutane were 9 per cent when chlorine was the halogen used, 29 per cent with bromine, and 43 per cent with iodine. Recently this synthesis was repeated (171) in this laboratory with the more nearly pure 2-nitropropane now available from the Commercial Solvents Corporation. 2-Bromo-2-nitropropane gave an 80 per cent yield and 2-chloro-2-nitropropane a 50 per cent yield with the sodium derivative of 2-nitropropane. When either the halonitro compound or the sodium derivative was prepared from a primary nitroparaffin, a zero yield of dinitroparaffin was obtained. Adding a little nitroethane to the 2-nitropropane used greatly lowered the yield. Nitroethane and 2-nitropropane boil at 114° and 120°C., respectively, and the 2-nitropropane used by Seigle and Hass doubtless contained nitroethane.

Similar reactions have been reported for aliphatic compounds having aromatic substituents. With these compounds even derivatives of primary nitro paraffins react successfully. Thus, Nenitzescu and Isăcescu (285) treated the sodium derivative of phenylnitromethane with iodine and obtained 1,2-dinitro-1,2-diphenylethane.

(*e*) Angeli and Alessandri (6) reported that the silver salt of nitroethane decomposes spontaneously, yielding 2,3-dinitrobutane. The reaction seems to be general, since the silver salt of a nitropentane reacted similarly to give a dinitrodecane and the silver salt of phenylnitromethane (57) gave 1,2-dinitro-1,2-diphenylethane. Bevad and Pirinsky (40) reported that a similar reaction occurred on treating a *sec*-bromonitroparaffin with powdered silver.

(*f*) A closely related synthesis is the electrolysis of salts of aci-nitroparaffins, a reaction which yields substituted dinitroparaffins (352, 419).

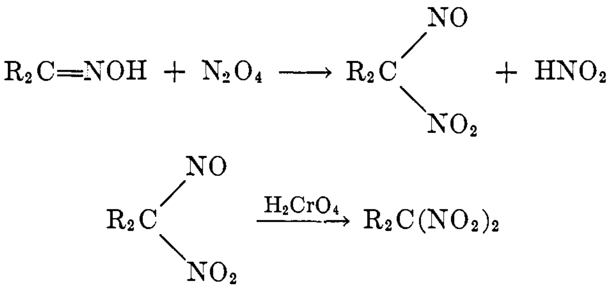


$$2R_2C{=}NO_2M \xrightarrow{\text{electrolysis}} R_2\underset{\substack{|\\ NO_2}}{C}{-}\underset{\substack{|\\ NO_2}}{C}R_2 + 2M$$

(*g*) The low-temperature nitration (20–200°C.) of paraffins, either in the liquid phase with nitric acid or in the vapor phase with nitrogen dioxide, yields di- and tri-nitroparaffins. For example, Francis and Young (101) and Poni and Costachescu (303, 304) nitrated isopentane. The latter workers identified 2,3-dinitro-2-methylbutane and 2,3,4-trinitro-2-methylbutane. This reaction is quite general.

(*h*) Polynitroparaffins can be alkylated in a manner quite analogous to that described in section III for nitroparaffins (89).

(*i*) Oximes treated with nitrogen tetroxide yield pseudo-nitroles, which can be oxidized to dinitroparaffins having the nitro groups on the same carbon atom (45).

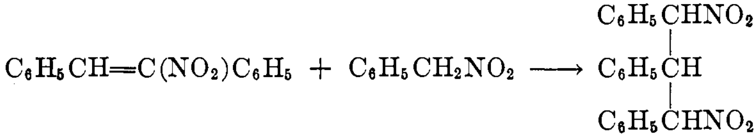


(*j*) The reaction of concentrated nitric acid upon various organic products to yield polynitro fission products has been discussed in section V. An additional example which seems quite general is the action of nitric acid upon ketones. Thus, ethyl ketones yield 1,1-dinitroethane (66, 98).

(*k*) Halogen derivatives of polynitro compounds when treated with arsenious oxide lose halogen without suffering reduction of the nitro groups. Duden (89) used this means to obtain dinitromethane from dibromodinitromethane.

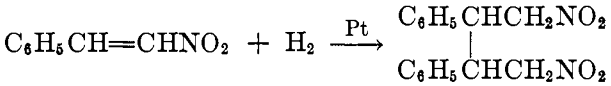
(*l*) The use of the Victor Meyer reaction to yield polynitroparaffins has been mentioned in section II. The production of 1,1-dinitropropane by reaction between the sodium salt of 1-bromo-1-nitropropane and sodium nitrite (375) recalls the Kolbe synthesis.

(*m*) The addition of a substituted nitroparaffin to a substituted nitroölefin has been reported by Heim (143).



$$C_6H_5CH{=}C(NO_2)C_6H_5 + C_6H_5CH_2NO_2 \longrightarrow \begin{array}{l} C_6H_5CHNO_2 \\ \quad\;\;| \\ C_6H_5CH \\ \quad\;\;| \\ C_6H_5CHNO_2 \end{array}$$

(*n*) Aryl-substituted nitroölefins are said to form bimolecular reduction products when hydrogenated in the presence of such catalysts as Raney nickel, platinum, and palladium (197, 361, 372).



$$C_6H_5CH{=}CHNO_2 + H_2 \xrightarrow{Pt} \begin{array}{l} C_6H_5CHCH_2NO_2 \\ \quad\;\;| \\ C_6H_5CHCH_2NO_2 \end{array}$$

This reaction, however, has been questioned by Heider (142), who believes that the product is a polymer of nitrostyrene.

(*o*) Holleman (167) treated ω-nitrostyrene in alcohol with aqueous potassium cyanide, then acidified with acetic acid, and obtained a precipitate of a cyanodinitrodiphenylbutane.

$$O_2NCH_2C(C{\equiv}N)(C_6H_5)CH(C_6H_5)CH_2NO_2$$

VII. Physical Properties of Nitroparaffins

A summary of some of the physical properties of certain nitroparaffins and dinitroparaffins is shown in table 1.

All of the mononitroparaffins are colorless when pure, have dipole moments of approximately 3.2, and boil from 101.7°C. to as high as one wishes to go as the series is ascended. Nitromethane is soluble in water to the extent of 10.5 ml. per 100 ml. of water at 20°C., but this value diminishes sharply as the complexity of the alkyl group increases. The great majority of organic solvents are miscible with nitroparaffins. This includes the aromatic hydrocarbons, alcohols, esters, ketones, ethers, and carboxylic acids. Alkanes, cycloalkanes, and bicycloalkanes are soluble in nitroparaffins with considerable difficulty, and the suggested use of nitromethane (28, 223, 333) in the solvent refining of lubricants is based upon this fact. This miscibility is the basis of Mulliken and Wakeman's classification of hydrocarbons for qualitative organic analysis (280, 281).

The solubility of cellulose esters in nitromethane has been mentioned (section IV, g). One incentive for nitrating isobutane in this laboratory was the ex-

TABLE 1

Physical properties of nitroparaffins

COMPOUND	MELTING POINT	BOILING POINT	REFRACTIVE INDEX	SPECIFIC GRAVITY	REFERENCES
	°*C.*	°*C.*			
Nitromethane	−29	101.7	1.3818	1.139 (20°/20°)	(107)
Nitroethane	−90	114	1.3916	1.052 (20°/20)	(107)
1-Nitropropane	−108	132	1.4015	1.003 (20°/20°)	(107)
2-Nitropropane	−93	120	1.3941	0.992 (20°/20°)	(107)
1-Nitrobutane		153	1.4112	0.975 (20°/20°)	(107)
2-Nitrobutane		140	1.4036	0.968 (20°/20°)	(33, 265)
1-Nitro-2-methylpropane		140			(80, 355)
2-Nitro-2-methylpropane	25.5	127			(30, 134)
1-Nitropentane		173	1.4218	0.9475 (20°/4°)	(158)
3-Nitropentane		152–154		0.9575 (0°/4°)	(33, 35)
1-Nitro-3-methylbutane		164	1.41806	0.9599 (20.6°/4°)	(277)
2-Nitro-2-methylbutane		150	1.4152	0.9783 (0°/4°)	(33, 35, 304)
1-Nitrohexane		193		0.9488 (20°/4°)	(158)
2-Nitroöctane		102–105 at 23 mm.	1.4324 (20°)	0.9224 (20°/20°)	(357)
Trinitromethane	15	45–47 at 22 mm.			(27, 125)
Tetranitromethane	13	126		1.650 (13°/4°)	(27, 343)
1,1-Dinitroethane		185–186		1.3503 (23.5°/23.5°)	(375, 405)
1,2-Dinitroethane		94–96 at 5 mm.	1.4488 (20°)	1.4597 (20°/4°)	(173)
1,1,1-Trinitroethane	56				(125)
Hexanitroethane	142				(408)
2,2-Dinitropropane	54	185.5			(265)
1,4-Dinitrobutane		176–178 at 13 mm.			(393)
1,3-Dinitro-2,2-dimethylpropane	93	140 at 15 mm.			(48)
2,3-Dinitro-2,3-dimethylbutane	210–212				(78, 349)

pectation that 2-methyl-2-nitropropane would be of value as a solvent for cellulose nitrate. It proved to have a dilution ratio[5] for toluene of only 0.5. Mixtures of nitroparaffins and alcohols, however, show favorable dilution ratios not only for cellulose nitrate but also for cellulose acetate, vinylite resins, cellulose ethers (225), and the newer mixed esters of cellulose, such as the acetate butyrate and acetate propionate. For example, a mixture of 75 per cent of 1-butanol (by volume) and 25 per cent of 2-methyl-2-nitropropane shows a value of 2.9 with toluene measured with 1/2 sec. cellulose nitrate (133). Results with petroleum diluents are somewhat less favorable.

Nitromethane is the only mononitroparaffin which can be detonated with a cap (133), but the homologous mononitroparaffins may explode when heated in a closed container under pressure (238). The polynitroparaffins are more nearly in oxygen balance and hence explode more easily. The salts of aci-nitroparaffins detonate much more easily than the parent compounds, and suitable precautions should be taken when these compounds are employed.

The dinitroparaffins are colorless; most of them are crystalline solids which are insoluble in water and have only limited solubility in alkanes but are soluble in most other organic solvents.

The structure of tetranitromethane has been the subject of some controversy, since one of the nitro groups is readily removed by the action of alkali:

$$C(NO_2)_4 + 2KOH \rightarrow KNO_3 + (O_2N)_2C{=}NO_2K + H_2O$$

This reaction does not prove that one of the nitro groups in tetranitromethane is different from the other nitro groups in tetranitromethane but does show that all of the nitro groups in tetranitromethane are different from all of the nitro groups in trinitromethane. The substitution of a hydrogen atom for a nitro group would be expected to decrease the lability of other groups attached to the same carbon atom. The symmetry of tetranitromethane has been demonstrated by the fact that its solution in carbon tetrachloride shows a zero dipole moment (399).

VIII. Toxicity of Nitroparaffins

The nitro group is often present in compounds of high toxicity. Gibbs and Reichert (113), however, reported that nitromethane, when injected into a dog, exhibited less toxicity than 1-butanol. Tests made by Henry F. Smyth, Jr.,[6] upon white rats and guinea pigs, using a sample of nitrated propane, led to the conclusion that "the vapors are considerably less toxic than . . . benzene, aniline, carbon disulfide, carbon tetrachloride or nitrobenzene . . .".

Tests made by Willard Machle[7] led to the conclusion that "the nitroparaffins were found to be of about the same order of toxicity as petroleum naphtha.

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[5] Dilution ratio is the volume of toluene, or other diluent, per unit volume of solvent which just precipitates cellulose nitrate under standard conditions. High dilution ratio is nearly synonymous with high solvent power.

[6] Laboratory of Hygiene, Philadelphia, Pennsylvania.

[7] College of Medicine, University of Cincinnati, Cincinnati, Ohio.

From the point of view of vapor pressure, they would appear to be somewhat more safe to handle than heptane and somewhat more likely to give rise to significant exposure than *n*-octane".

IX. USES OF NITROPARAFFINS

This topic has been discussed recently by Gabriel (107). The solvent powers of nitroparaffins for a great variety of organic compounds, including synthetic resins and lubricating-oil fractions, have been discussed in section VII. The proposed use of nitroparaffins as anti-detonating agents in Diesel fuels (232) has not been confirmed, although tests have been made in several laboratories.

At least for the present, the most important uses of the nitroparaffins depend upon their functioning as chemical intermediates. It is appropriate, therefore, that their chemical reactions should now be considered.

X. REACTIONS OF NITROPARAFFINS

A. REDUCTION

1. Reduction to amines

This topic has recently been reviewed and extended by Johnson and Degering in this laboratory (178, 179, 180). Successful reductions of aliphatic nitro compounds have been reported with such diverse reagents as tin and hydrochloric acid (156), vanadium sulfate (20), zinc and sulfuric acid (33, 37), zinc and hydrochloric acid (37), zinc and acetic acid (2), lead and acetic acid (318), iron and acetic acid (271), concentrated aqueous sodium hydrosulfite at its boiling point (5), iron and hydrochloric acid (213, 235), the Adams catalyst and hydrogen (339), sodium amalgam (261, 301), aluminum amalgam (274, 277, 350, 369, 381), in vapor phase by hydrogen catalyzed by nickel or copper (337), hydrogen and platinum in various forms (mainly for aromatic nitro compounds) (338), and hydrogen and a palladium catalyst (in the liquid phase) (100, 194, 311). Electrolytic reductions have been reported by Johnson (177), Rakshit (319), who reduced tetranitromethane electrolytically to guanidine, by Pierron (299, 300), and by Chilesotti (70, 71).

Johnson (178) concluded that "the use of reducing agents other than iron and hydrochloric acid gave less favorable results in the reduction of nitroparaffins".

Johnson and Degering also obtained excellent reductions to amines by the use of hydrogen catalyzed by Raney nickel in a Parr rocking bomb. The amines produced by this hydrogenation are, of course, basic and, as is shown in section X, F, such compounds react with primary and secondary nitroparaffins slowly at room temperature, and more vigorously upon heating, to yield complex derivatives such as isoxazoles. In order to obtain good yields of amines it is therefore important to use a vigorous reducing agent, to agitate thoroughly in case the reaction mixture is heterogeneous, and to keep the temperature fairly low.

The reduction of nitroalcohols and nitroglycols is most successful with Raney nickel and hydrogen (136, 137, 138, 139, 140, 179, 386, 390). The nitroalcohols are formed from nitroparaffins and aldehydes (see section X, E) by condensation in the presence of basic catalysts. The nitroalcohols are instable in the presence of bases because of a reversal of the reaction which produces them. Owing to this instability the yields of aminoalcohols, while often excellent, are sometimes indifferent or even poor. Thus Demuth and Meyer (82) obtained an impure product when sodium amalgam was used. Henry (156) and Tordoir (381) used tin and hydrochloric acid but reported low yields. Mousset (277), Stiénon (369), Tordoir (381), and Montmollin and Achermann (274) used aluminum amalgam and obtained yields of approximately 50 per cent. Buffering the solution with carbon dioxide is usually helpful in such instances.

2. Reduction to alkylhydroxylamines

Alkylhydroxylamines may be isolated from the reaction mixture obtained when nitro compounds are treated with almost any of the usual reducing agents. Often it is possible to control the reduction in such a way as to cause the alkylhydroxylamine to become the main product.

Metallic agents of various kinds may serve to accomplish this reduction. In 1877 Züblin (420) recorded that the reduction of 1-nitrobutane with tin and hydrochloric acid yields a product which acts on Fehling's solution to produce cuprous oxide. Later Meyer and Hoffman (262) reported the synthesis of methylhydroxylamine, CH_3NHOH, by the reduction of nitromethane with tin and hydrochloric acid. Three years later, after showing that boiling with zinc dust and water converted nitrobenzene to phenylhydroxylamine, Bamberger (13) tried the same agents on nitromethane and produced methylhydroxylamine without recognizable quantities of methylamine or ammonia. This result was later confirmed by Beckmann (23) and also by Scheiber (341), who used zinc dust, water, and ammonium chloride to cause the same change.

Similarly, Kirpal (192) prepared alkylhydroxylamines by the action of stannous chloride on nitromethane, nitroethane, "nitropropane", "nitropentane"[8], and 3-nitropropene. Chloropicrin and 1-bromo-1-nitroethane, under like treatment, yield substances which are oxidized by Fehling's solution and which contain halogen.

For the reduction of 2-methyl-1-nitropropene (nitroisobutylene) Bouveault and Wahl (52) employed either aluminum amalgam in ether or zinc powder and acetic acid in ether. Isobutyraldoxime is the main product of this reaction, but there is evidence for the presence of the intermediate unsaturated hydroxylamine, $(CH_3)_2C{=}CHNHOH$. A similar method serves to convert the esters of nitro acids to the corresponding hydroxylaminic acid esters (49). Charlton and Kenner (67) reduced 2-nitro-2-hydroxymethyl-1,4-butanediol with sodium amalgam and obtained a product which was believed to be $(HOCH_2)_2C(NHOH)CH_2CH_2OH$, but it was not isolated. Reduction by the use of sodium amalgam was also carried out with a number of other nitroalcohols and nitroglycols.

Duden, Bock, and Reid (90) prepared the 2-piperidyl derivative of 1,1-dinitroethane and reduced it with stannous chloride. Under this treatment the compound lost a nitro group and yielded an oily product, probably the hydroxylamine $C_5H_{10}{=}NCH_2CH_2NHOH$.

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[8] The article does not state which isomers were employed.

Catalytic hydrogenation is also a useful way in which to prepare hydroxylamine derivatives from nitro compounds. Traube and Schulz (382) preferred this method; they used a catalyst of palladinized barium sulfate and reduced nitromethane and also nitroalcohols catalytically, producing methylhydroxylamine and the hydroxylaminic alcohols. Schmidt, Ascherl, and Mayer (345), who desired to prepare the alkylhydroxylamines without simultaneously producing amines, carried out catalytic reduction with the same catalyst, but employed an aqueous or alcoholic oxalic acid solution as a medium. Alkylhydroxylamines are converted to their oxalates in this solution, and the formation of amines is thus largely prevented. Addition of acetic acid is desirable in some cases.

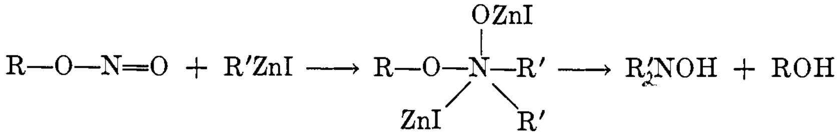
Electrolytic reduction of nitroparaffins has been reported by Pierron (300), who was able to reduce nitromethane, nitroethane, and 1-nitropropane by the electrolysis of a 10–15 per cent alcoholic solution of the nitroparaffin containing a little sulfuric acid. Satisfactory results were obtained using a nickel cathode in contact with the solution, and a platinum anode separated from it by a porous pot containing sulfuric acid. A cathodic current density of 0.4–0.75 amperes per square decimeter at a temperature not exceeding 15–20°C. gave 65 to 80 per cent of the theoretically available amount of alkylhydroxylamine. At 70°C. comparable yields of amine result. If concentrated sulfuric or hydrochloric acid is used, the products are aldehyde and hydroxylamine. Chilesotti (71) carried out a similar reduction in the presence of small amounts of copper, iron, or tin salts in a process similar to that described in German patents issued to C. F. Boehringer and Sons (43, 44) and in the Johnson patent (177), but since these processes were designed primarily for making aniline and similar compounds his examples were mainly from the aromatic series.

Bruckner, Krámli, and Vinkler (58) carried out electrolytic reductions of nitroparaffins in mixtures of glacial acetic acid, ethanol, and concentrated hydrochloric acid at lead and copper cathodes and reported good yields of both amines and hydroxylamines.

The Dominion Rubber Co., Ltd., and U. S. Rubber Products Co. have studied saturated and unsaturated carbocyclic and heterocyclic hydroxylamines. Presumably, these compounds are of possible value as preservatives for rubber. H. H. Bassford, Jr., recently received a patent on a process for the production of such compounds by reducing the nitro compound in the presence of a nonacidic aqueous solution substantially saturated with the desired cyclic hydroxylamine (22).

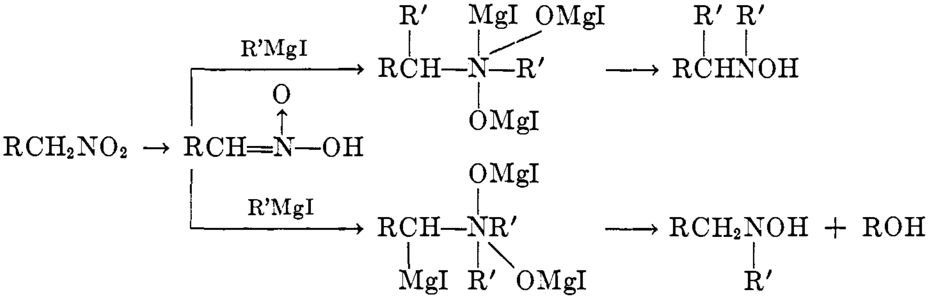
Several variations of another general method for converting nitroparaffins to alkylated hydroxylamines have been based on the use of metallic alkyls or of alkyl metallic halides. Dialkylzincs, alkylzinc iodides, and alkylmagnesium iodides have been investigated. Alkyl nitrites and nitroparaffins react with such agents to yield nitroparaffins of higher molecular weight and alkylated reduction products. Thus, nitromethane, when treated with diethylzinc, may yield, among other products, ethylpropylhydroxylamine. The net result of this treatment is, therefore, alkylation on a carbon atom, alkylation on the nitrogen atom, and reduction. The mechanism of this reaction has been variously interpreted.

Bevad (39) found the more available and less flammable alkyl metallic halides preferable to dialkylzinc, in convenience, but they gave less satisfactory yields from nitro compounds. He postulated the following mechanism (39) for the reaction of the alkylzinc iodide with nitro compounds or alkyl nitrites:



$$R{-}O{-}N{=}O + R'ZnI \longrightarrow R{-}O{-}\overset{\overset{OZnI}{|}}{N}(ZnI)(R'){-}R' \longrightarrow R'_2NOH + ROH$$

The intermediate addition product yields the dialkylhydroxylamine in which the radicals correspond to those of the alkylzinc halide used. Alkylmagnesium halides react in exactly the same way with nitrites, but with nitro compounds the reaction is different:



Not all of these products were found by every investigator. Moureu (276) had stated that diethylhydroxylamine was the only product from the action of ethylmagnesium iodide on nitroethane. Bevad demonstrated (39) the presence of more complex products, such as ethyl-*sec*-butylhydroxylamine, $CH_3CH(C_2H_5)$-$N(C_2H_5)OH$. Ethyl alcohol was found to be present. Nitroethane and propylmagnesium iodide react similarly, giving (1-methylbutyl)propylhydroxylamine and propylethylhydroxylamine. Bevad tried many variations of this reaction, most of which appear in table 2.

Wang (397) has interpreted these reactions of alkylmagnesium bromide with nitroparaffins by postulating the existence of $CH_2{=}\overset{\overset{O}{\uparrow}}{N}{-}OMgBr$ as an intermediate in the action of phenylmagnesium bromide on nitromethane.

The variety and diversity of reactions for preparations of the alkylated hydroxylamines may be seen from the summary in table 2.

3. Reduction to oximes

This reaction has been reported by Konovalov (209), by Ponzio (305), by Bamberger and Weiler (19), by von Braun and Sobecki (393), and by Johnson (178, 180). Johnson and Degering obtained a yield of 43 per cent by the use of zinc dust and glacial acetic acid, using a technic similar to that of Konovalov. The aldehyde was distilled out and estimated by reaction with excess hydroxylamine hydrochloride, followed by titration of the liberated hydrochloric acid (180).

TABLE 2

Reduction of nitroparaffins to alkylhydroxylamines

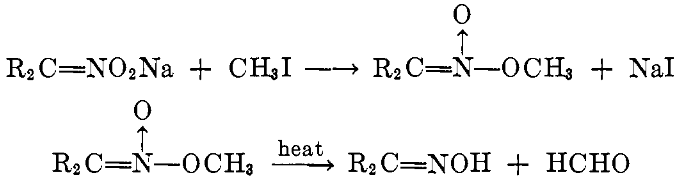
COMPOUND	REACTANTS	REFERENCES
β-Methylhydroxylamine: b.p. 62.5°C. at 15 mm. (193); m.p. 42°C. on rapid heating (193); $d^{20^\circ}_{4^\circ} = 1.003$ (59, 60); $n^{20^\circ}_{D} = 1.41638$ (60)	Nitromethane and stannous chloride	(164)
	Nitromethane and stannous chloride	(192)
	Catalytic hydrogenation in alcoholic oxalic acid in the presence of palladinized barium sulfate	(345)
	Electrolytic reduction of nitromethane in dilute alcoholic sulfuric acid at 15–20°C.	(300)
Derivatives: hydrochloride, m.p. 88–90°C.; hydrobromide, m.p. 73°C.; picrate, m.p. 128–130°C.	Nitromethane with zinc dust and water at the boiling point	(13)
	Ammonium chloride and zinc dust in water on nitromethane at 0–15°C.	(23)
β-Ethylhydroxylamine: m.p. 56–60°C. (193); $d^{20^\circ}_{4^\circ} = 0.9079$ (59, 60); $d^{63.9^\circ}_{4^\circ} = 0.9079$ (59, 60); $n^{20^\circ}_{D} = 1.41519$ (59, 60)	Electrolytic reduction of nitroethane in dilute alcoholic sulfuric acid at 15–20°C.	(300)
	Stannous chloride on nitroethane	(192)
Oxalate, m.p. 95–97°C.	1,1-Dinitroethane (as piperidyl derivative) with stannous chloride → piperidyl derivative, $C_5H_{10}{=}NCH_2CH_2NHOH$	(90)
β,β-Diethylhydroxylamine: b.p. 132–133°C. at 760 mm. (39); 40.5–41°C. at 10 mm. (39); m.p. −10°C. (276); $d^{20^\circ}_{4^\circ} = 0.8670$ (39); $d^{0^\circ}_{0^\circ} = 0.8853$ (39); $n^{20^\circ}_{D}$ not given	Diphenylnitrosamine and diethylzinc; then water	(216)
	Nitrogen dioxide on ethylmagnesium iodide in cold ether; then water	(404)
	Ethylmagnesium iodide on isoamyl nitrite in ether; then water	(276)
	Ethylmagnesium iodide on nitroethane; then decomposition of product with water	(276)
Hydrochloride, m.p. 63°C. (404)	Ethylmagnesium iodide on nitroethane; then decomposition of product with water	(39)
Hydrobromide (hygroscopic), m.p. 55–56.5°C. (39)	Ethylzinc iodide on isoamyl nitrite in ether; then decomposition of product with water	(39)
Oxalate, m.p. 138°C. (404), 136–137°C. (91)	Diethylzinc and isoamyl nitrite or other alkyl nitrite in ether; then water	(37)
	Diethylzinc in cold ether with a cold ether solution of nitrosyl chloride	(38)
β-Propylhydroxylamine: m.p. about 46°C. (193)	Electrolytic reduction of 1-nitropropane in dilute alcoholic sulfuric acid at 15–20°C.	(300)
	Stannous chloride on 1-nitropropane	(192)
β-Ethyl-β-propylhydroxylamine: b.p. 147–150°C. at atmospheric pressure (39); $d^{20^\circ}_{0^\circ} = 0.8581$, $d^{0^\circ}_{0^\circ} = 0.8735$ (39)	Propylmagnesium iodide on nitroethane	(39)
	Ethylmagnesium iodide on nitropropane	(39)
	Diethylzinc with methylzinc and nitromethane in cold ether	(35, 36)

TABLE 2—*Concluded*

COMPOUND	REACTANTS	REFERENCES
Hydrochloride (hygroscopic), m.p. 64–65°C.; hydrobromide (very hygroscopic), m.p. 49–51°C.		
β,β-Dipropylhydroxylamine: b.p. 153–156°C. (91), 156–158°C. at 753 mm. (39), 72–74°C. at 30 mm. (242), 69–70°C. at 17–20 mm. (39); m.p. 27.5–29.5°C. (39)	Propylmagnesium iodide on isopropyl nitrite in ether; then water Dipropylzinc on propyl nitrite in ether; then water	(39) (35, 36)
Hydrochloride (not hygroscopic), m.p. 88–90°C. (39); hydrobromide (slightly hygroscopic), sinters at 70°C. and melts at 74–75°C. (39); acid oxalate, m.p. 139°C. (91)		
β-Isopropylhydroxylamine: m.p. 87°C.; sublimes at 40°C. at 25 mm.		
Hydrochloride melts *ca.* 55°C. (very hygroscopic)		
β,β-Diisopropylhydroxylamine: b.p. 137–142°C. (91)	Isopropylzinc iodide with isoamyl nitrite in cold ether	(39)
Hydrochloride, m.p. 144–145°C. (39)		
β-Ethyl-β-*sec.*-butylhydroxylamine; b.p. 154–157°C., 84–87°C. at 75 mm. (M.W.); 155–158°C. at 756 mm. (39), 57–58°C. at 8 mm. (39); $d_{0^\circ}^{0^\circ}$ = 0.892, $d_{0^\circ}^{20^\circ}$ = 0.8757 (39) Hydrochloride, m.p. 56–57°C.; neutral oxalate, m.p. 114–115°C.; acid oxalate, m.p. 93–95°C.	Ethylmagnesium iodide on nitroethane in ether; then decomposition of products with water Ethylzinc iodide on nitroethane in ether; then decomposition of products with water Diethylzinc on nitroethane in cold ether; then ice water on the products Diethylzinc on nitroethane in cold ether; then ice water on the products Diethylzinc on nitroethane in ether in the absence of air; ice water after 3 weeks	(39) (39) (29, 35, 37) (215, 216) (242)

There is strong evidence that certain prior workers have confused the reduction of nitroparaffins to oximes with the Nef reaction (see section X, B, 2) by which an aldehyde or ketone is produced by the treatment of a salt of an aci-nitroparaffin with a strong acid. Thus, Markovnikov added alkali salts of aci-nitroparaffins to stannous chloride and hydrochloric acid and measured his yield by the ketones isolated. This reaction gives excellent yields of ketone even in the absence of any reducing agent. Probably if oximes *per se* are of commercial interest, so that it seems advisable to synthesize them from nitroparaffins, they will be made from aldehydes and/or ketones and the hydroxylamine produced by the action of sulfuric acid upon primary nitroparaffins. Certainly the acidification of salts of aci-nitroparaffins is the practical way of making aldehydes and ketones from nitroparaffins.

An interesting indirect method of converting primary and secondary nitroparaffins to oximes consists in alkylation to nitronic esters, followed by pyrolysis of the latter to oximes and aldehydes.



$$R_2C{=}NO_2Na + CH_3I \longrightarrow R_2C{=}\overset{\overset{O}{\uparrow}}{N}{-}OCH_3 + NaI$$

$$R_2C{=}\overset{\overset{O}{\uparrow}}{N}{-}OCH_3 \xrightarrow{\text{heat}} R_2C{=}NOH + HCHO$$

For a discussion of this reaction, the reader is referred to Thurston and Shriner (378).

B. ACTION OF MINERAL ACIDS

1. Action of mineral acids to yield hydroxamic and carboxylic acids

This is one of the first-discovered reactions of the primary nitroparaffins, having been reported by Meyer and Wurster (272) only a year after the announcement of the first nitroalkane. Table 3 summarizes much of the prior art.

This rather remarkable hydrolysis of a CH_2NO_2 group to a carboxyl group and a salt of hydroxylamine has aroused the interest of several investigators, who have proposed various mechanisms, all postulating aci-nitroparaffins and hydroxamic acids as two of the intermediates.

Conclusive evidence for the existence of aci-nitroparaffins ($RCH{=}NO_2H$ and $R_2C{=}NO_2H$) has been derived from a number of sources. They can be obtained by the action of acids upon metallic derivatives of the nitroparaffins. Holleman (166) found that *m*-nitrophenylnitromethane gives a yellow sodium salt and that acidification with an equivalent of hydrochloric acid produces a yellow solution which has a higher conductivity than that of the sodium chloride which it contains. On standing, the color disappears and the conductivity falls to that of the sodium chloride.[9] Hantzsch and Schultze (126) isolated the aci forms of phenylnitromethane and *p*-bromophenylnitromethane by passing a mineral acid into the ice-cold solution of the sodium salt.

The true aliphatic nitro compounds give no color with ferric chloride, while the aci derivatives give a red-brown hue, typical of the enol linkage. The nitro

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[9] In Sidgwick's *Organic Chemistry of Nitrogen* (revised by T. W. J. Taylor and W. Baker; Oxford University Press, London (1937)), pp. 228–47, there is an excellent treatment of this topic.

compound is but slightly soluble in water and only slowly soluble in alkali, while the aci derivative is much more soluble in water and instantly soluble in sodium hydroxide solution. The nitro derivative reacts slowly with bromine, while the aci compound adds bromine almost instantaneously. Definite melting points have been obtained for several substituted aci-nitroparaffins.

Maron and La Mer (246) have studied the kinetics of the neutralization of nitromethane, nitroethane, and 2-nitropropane, since these compounds (as well as other primary and secondary nitroparaffins) function as typical pseudo acids. The same authors studied the kinetics of the isomerization of nitroethane from the aci to the nitro form in water and in deuterium oxide. The rate constants were the same in the two media (247). Maron and Shedlovsky (249) obtained the value 4 × 10^{-5} for the ionization constant of aci-nitroethane at 23°C. This is of the same order of magnitude as the value 7 × 10^{-5} obtained by Junell from kinetic measurements at 0°C. (184). For an excellent discussion of the nitroparaffins as pseudo acids, see Maron and La Mer (248).

TABLE 3

Conversion of nitroparaffins to alkanoic acids

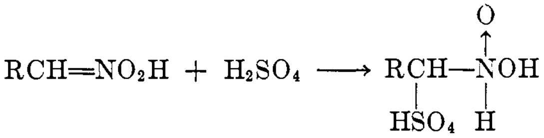
NITROPARAFFIN	ACID	PRODUCTS	PRIOR WORK (AUTHORS AND REFERENCES)
$C_2H_5NO_2$	H_2SO_4	CH_3COOH, $(NH_3OH)_2SO_4$	Meyer *et al.* (270)
CH_3NO_2	H_2SO_4	CO, $(NH_3OH)_2SO_4$	Preibisch (313)
CH_3NO_2	H_2SO_4	CO, CO_2, $(NH_3OH)_2SO_4$, $(NH_4)_2SO_4$	Mel'nikov (256)
CH_3NO_2	HCl	HCOOH, NH_3OHCl	Meyer and Locher (265)
$C_2H_5NO_2$	HCl	CH_3COOH, NH_3OHCl	
$C_3H_7NO_2$	HCl	C_2H_5COOH, NH_3OHCl	
$C_2H_5NO_2$	H_3PO_4	CH_3COOH, $NH_4H_2PO_4$	Geuther (112)
$C_2H_5NO_2$	H_3PO_4	CH_3COOH, NH_2OH salt	Werner (401)
$C_2H_5NO_2$	H_2SO_4	CH_3COOH, NH_2OH salt	
$C_2H_5NO_2$	HCl	CH_3COOH, NH_2OH salt	
$C_2H_5NO_2$	H_2SO_4	CH_3COOH, NH_2OH salt	
i-$C_3H_7C(NOH)NO_2$	H_2SO_4	$CH_3CH(CH_3)COOH$, N_2O	Demole (80)
$C_4H_9NO_2$	HCl	C_3H_7COOH	Züblin (420)
$O_2N(CH_2)_3CN$	HCl	Succinic acid	Henry (153, 154)
$C_6H_5CH_2NO_2$	HCl	C_6H_5COOH	Gabriel and Koppe (109)
n-$C_5H_{11}CH_2NO_2$	HCl	n-$C_5H_{11}COOH$	Worstall (414, 418)
n-$C_6H_{13}CH_2NO_2$	HCl	n-$C_6H_{13}COOH$ + NH_2OH salts	
n-$C_7H_{15}CH_2NO_2$	H_2SO_4 HCl	n-$C_7H_{15}COOH$ + NH_2OH salts	
n-$C_8H_{17}CH_2NO_2$	HCl	n-$C_8H_{17}COOH$ + NH_2OH salts	

When the salts of nitroparaffins are warmed with concentrated acid they decompose into fatty acids and salts of hydroxylamine, although the action of dilute acid yields aldehyde or ketone (see section X, B, 3) while acids as feeble as carbonic acid regenerate the nitroparaffin. The nitronic acids[10] may therefore be considered as intermediates in the conversion of parimary nitroparaffins to carboxylic acids.

This mechanism implies that the tautomerization of nitroparaffins to the aci derivatives is either spontaneous or is accelerated by acids. That the latter is true was demonstrated by Lowry and Magson (234), who found that nitrocamphor reaches tautomeric equilibrium between the aci and the nitro forms to the extent of 99.5 per cent in 33 min. in the presence of $N/10$ trichloracetic acid dissolved in chloroform, although a period of six years was required in the absence of a catalyst.

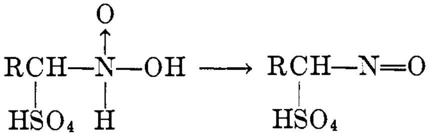
Bamberger and Rust (17) suggested that the hydroxamic acids should also be considered to function as intermediates in this reaction. They obtained a 2 per cent yield of the hydroxamic acid from phenylnitromethane. By manipulating the conditions Lippincott and Hass (229) were able to obtain a 44 per cent yield of propionohydroxamic acid from 1-nitropropane. Since yields of carboxylic acids in excess of 90 per cent were obtained (229), it is evident that under these conditions at least a large proportion of the hydrolysis proceeds through the hydroxamic acids.

The mechanism by which the aci-nitroparaffin is converted to the hydroxamic acid is still undecided, but the fact that fairly concentrated sulfuric acid gives the best rates and yields is at least suggestive. The carbon–nitrogen double bond of the aci-nitroparaffin would be expected to add sulfuric acid rapidly only if the latter were not too dilute.



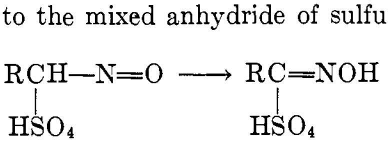
$$\mathrm{RCH{=}NO_2H} + \mathrm{H_2SO_4} \longrightarrow \underset{\mathrm{HSO_4}}{\mathrm{RCH}}-\underset{\mathrm{H}}{\overset{\substack{\mathrm{O}\\ \uparrow}}{\mathrm{N}}}\mathrm{OH}$$

This product, having a hydrogen and hydroxyl attached to the same nitrogen atom, would be expected to lose water and form a nitroso derivative:



$$\underset{\mathrm{HSO_4}}{\mathrm{RCH}}-\underset{\mathrm{H}}{\overset{\substack{\mathrm{O}\\ \uparrow}}{\mathrm{N}}}-\mathrm{OH} \longrightarrow \underset{\mathrm{HSO_4}}{\mathrm{RCH}}-\mathrm{N{=}O}$$

which would rearrange to the mixed anhydride of sulfuric acid and a hydroxamic acid,



$$\underset{\mathrm{HSO_4}}{\mathrm{RCH}}-\mathrm{N{=}O} \longrightarrow \underset{\mathrm{HSO_4}}{\mathrm{RC}}\mathrm{{=}NOH}$$

just as other nitroso compounds invariably do if a hydrogen atom is available on the carbon atom holding the nitroso group.

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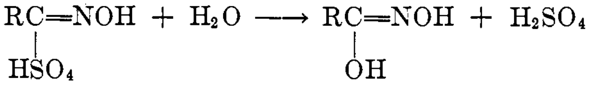
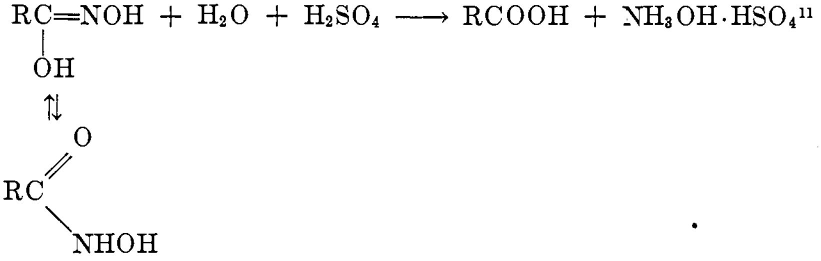
[10] The term "nitronic acid" is synonymous with "aci-nitro derivative" and should not be confused with nitrolic acid, $\mathrm{RC(NO_2){=}NOH}$.

This last compound would be hydrolyzed to the hydroxamic acid, which would undergo further hydrolysis to yield the carboxylic acid and hydroxylamine acid sulfate:



$$\underset{\mathrm{HSO_4}}{\mathrm{RC}}{=}\mathrm{NOH} + \mathrm{H_2O} \longrightarrow \underset{\mathrm{OH}}{\mathrm{RC}}{=}\mathrm{NOH} + \mathrm{H_2SO_4}$$



$$\underset{\mathrm{OH}}{\mathrm{RC}}{=}\mathrm{NOH} + \mathrm{H_2O} + \mathrm{H_2SO_4} \longrightarrow \mathrm{RCOOH} + \mathrm{NH_3OH{\cdot}HSO_4}^{11}$$

In order to increase the yield of hydroxamic acid to nearly 50 per cent it is only necessary to use anhydrous sulfuric acid at 60°C., pour the product over crushed ice, and neutralize the acid with calcium carbonate (229). This result may prove to be of more than academic interest (227), since C. C. Dewitt has discovered that the hydroxamic acids are successful as flotation agents for certain copper ores (85).

For more than a year this reaction has served as the commercial source of the hydroxylammonium salts produced in the United States. It has interesting possibilities for the manufacture of the propionic and butyric acids now used in the manufacture of cellulose esters, which can thus be produced from the hydrocarbons of natural gas by a two-step synthesis.

An application of this reaction has been suggested by Ellis (95), who disclosed the synthesis of mandelic acid (a widely used urinary antiseptic) by the following reactions:

$$\mathrm{C_6H_5CHO + CH_3NO_2 \rightarrow C_6H_5CHOHCH_2NO_2}$$

$$\mathrm{C_6H_5CHOHCH_2NO_2 + HCl + H_2O \rightarrow C_6H_5CHOHCOOH + NH_3OHCl}$$

Rosenmund (334), however, reported that 1-phenyl-2-nitroethanol yields ω-nitrostyrene when treated with mineral acids.

2. Action of mineral acids upon salts of aci-nitroparaffins

In the foregoing discussion brief mention has been made of the reaction discovered by Nef (284) by which acidification of the salts of aci-nitroparaffins by strong mineral acids yields aldehydes or ketones.

$$\mathrm{2RCH{=}NO_2Na + 2H_2SO_4 \rightarrow 2RCHO + 2NaHSO_4 + N_2O + H_2O}$$

$$\mathrm{2R_2C{=}NO_2Na + 2H_2SO_4 \rightarrow 2R_2CO + 2NaHSO_4 + N_2O + H_2O}$$

This reaction has recently been reviewed and extended by Johnson and Degering in this laboratory (178), who found that the calcium salts react as

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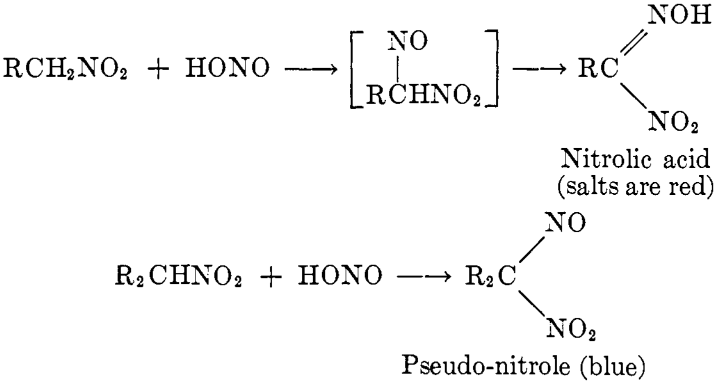
[11] This is essentially the mechanism proposed by Nenitzescu and Isăcescu (286).

readily as the sodium derivatives. Except for 2-methyl-1-nitropropane, which gave a yield of 32.4 per cent and a conversion of 27.5 per cent, all of the nitroparaffins investigated gave conversions of 80 to 85 per cent. These included nitroethane, 1-nitropropane, 2-nitropropane, 1-nitrobutane, and 2-nitrobutane. The following general directions are given: "One-sixth of a mole of nitroparaffin dissolved in 150 ml. of a solution containing 8 g. of NaOH was added dropwise to an ice-cold mixture of 25 ml. concentrated sulfuric acid in 160 ml. of water. Efficient agitation was used during the addition." The aldehyde or ketone was removed by distillation.

3. The red-white-and-blue reaction

The action of nitrous acid upon nitroparaffins is interesting because of its suitability for distinguishing between primary, secondary, and tertiary derivatives.

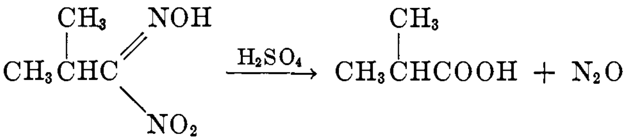


Nitrolic acid
(salts are red)

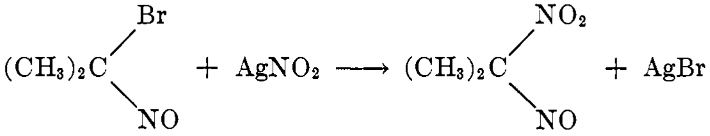
Pseudo-nitrole (blue)

$$R_3CNO_2 + HONO \longrightarrow \text{No reaction (white)}$$

The salts of the nitrolic acids are bright red even in solution and explosive when dry. With acids they yield polymers of nitrile oxides, $R—C\equiv N\rightarrow O$. They are decomposed to carboxylic acids by the action of sulfuric acid (80, 257).



The pseudo-nitroles show behavior typical of nitroso compounds; they are blue in solution but the crystalline forms are usually colorless because of dimerization. Their structure has been established by a modification of the Victor Meyer reaction (302).



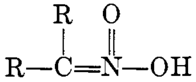
Although only historical importance can now be attached to the method of classifying alcohols as primary, secondary, or tertiary by conversion to the iodide and thence to the nitro derivative which is treated with nitrous acid, the last step is still of value in research with aliphatic nitro compounds involving proofs of structure.

C. ACTION OF BASES UPON NITROPARAFFINS

The behavior of primary and secondary nitroparaffins as pseudo acids has been referred to in section X, B, 1. There is one aspect of this phenomenon which has aroused keen controversy and is still unsettled. Kuhn and Albrecht (214) showed that when the sodium salt of optically active 2-nitrobutane was prepared by reaction between aqueous sodium hydroxide and the nitroparaffin dissolved in methanol the optical activity disappeared completely. When sodium methoxide dissolved in methanol was employed, the activity remained.

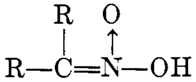
Shriner and Young (357) confirmed these results, using 2-nitroöctane and sodium ethoxide. They also regenerated the nitroparaffin by treatment with alcoholic hydrogen chloride at −70°C. and found 71 per cent of the original rotation.

The formula for an aci-nitroparaffin originally proposed by Nef was



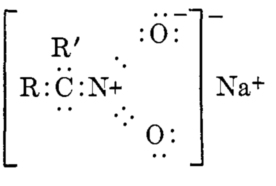
$$\mathrm{R{-}\overset{\displaystyle R}{\overset{|}{C}}{=}\overset{\displaystyle O}{\overset{\|}{N}}{-}OH}$$

which in modern notation would be written:



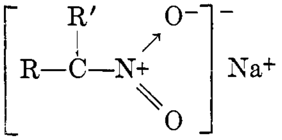
$$\mathrm{R{-}\overset{\displaystyle R}{\overset{|}{C}}{=}\overset{\displaystyle O}{\overset{\uparrow}{N}}{-}OH}$$

A compound having this structure would yield a salt possessing a plane of symmetry and hence optically inactive. The formation of this structure thus accounts for the observed racemization. Kuhn and Albrecht (214), Shriner and Young (357), and Hurd (115), after considering and rejecting a ring system, all favor for the optically active salt a formula which may be written electronically as



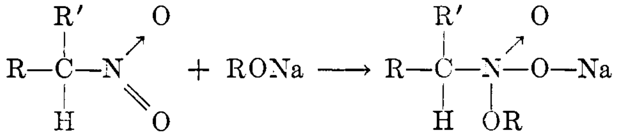
$$\left[\mathrm{R{:}\overset{\displaystyle R'}{\underset{..}{\ddot{C}}}{:}N^{+}\begin{matrix}{:}\ddot{O}{:}^{-}\\ \underset{..}{O}{:}\end{matrix}}\right]^{-}\mathrm{Na^{+}}$$

or as follows:



$$\left[\mathrm{R{-}\overset{\displaystyle R'}{\overset{|}{C}}{-}N^{+}\begin{matrix}\nearrow O^{-}\\ \searrow O\end{matrix}}\right]^{-}\mathrm{Na^{+}}$$

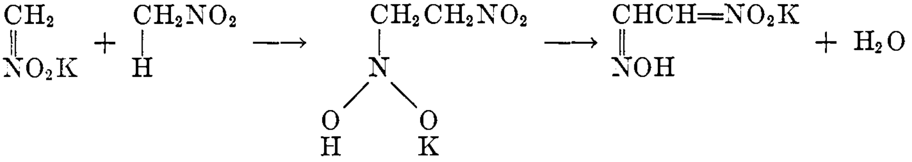
Sidgwick, Taylor, and Baker[12] have objected to this formulation and have suggested (tentatively) that the "sodium salts" formed by the action of sodium alkoxides are really produced by the addition of this reagent to the nitro group.



$$R-\overset{\overset{R'}{|}}{\underset{\underset{H}{|}}{C}}-N\begin{smallmatrix}\nearrow O\\ \searrow\!\!\searrow O\end{smallmatrix} + RONa \longrightarrow R-\overset{\overset{R'}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\nearrow O}{\underset{\underset{OR}{|}}{N}}-O-Na$$

This reaction would, of course, not destroy the asymmetry of the molecule. Meisenheimer (251) has shown that potassium methoxide adds to 2-nitronaphthalene. Shriner, Adams, and Marvel (114) report, however, that 2-methyl-2-nitropropane does not add sodium ethoxide. Since this tertiary nitroparaffin is much more closely related to the compounds in question than is 2-nitronaphthalene, it must be admitted that at present the weight of the evidence favors the formulation of Kuhn and Albrecht. The recent work of Ray and Palinchak (324) proves that the matter is still being actively investigated.

Nitromethane, compared to other nitroparaffins, is uniquely sensitive to the action of alkali. Sodium or potassium hydroxide converts it to salts of methazonic acid by a reaction in which two molecules (106, 222) condense with loss of water. This may be interpreted as an addition of nitromethane to the carbon–nitrogen double bond of the potassium salt, followed by rearrangement and loss of water. Upon further treatment with strong alkali, methazonic acid is converted to nitroacetic acid (364).



$$\begin{array}{c}CH_2\\ \|\\ NO_2K\end{array} + \begin{array}{c}CH_2NO_2\\ |\\ H\end{array} \longrightarrow \begin{array}{c}CH_2CH_2NO_2\\ |\\ N\\ \diagup\quad\diagdown\\ \begin{array}{cc}O & O\\ H & K\end{array}\end{array} \longrightarrow \begin{array}{c}CHCH{=}NO_2K\\ \|\\ NOH\end{array} + H_2O$$

$$HON{=}CHCH{=}NO_2K \xrightarrow{-H_2O} N{\equiv}CCH{=}NO_2K \xrightarrow[+H_2O]{+KOH}$$

$$KOOCCH{=}NO_2K \xrightarrow{H^+} HOOCCH_2NO_2$$

The crystalline sodium salt of nitroacetic acid can be obtained directly in a single operation by dropping nitromethane into a 50 per cent aqueous solution of sodium hydroxide maintained at 50°C., heating the solution to boiling for 10 min., and cooling. The free acid is obtained by acidification with hydrogen chloride of the finely divided salt suspended in ether.

When the sodium salt of aci-nitromethane is treated with mercuric chloride,

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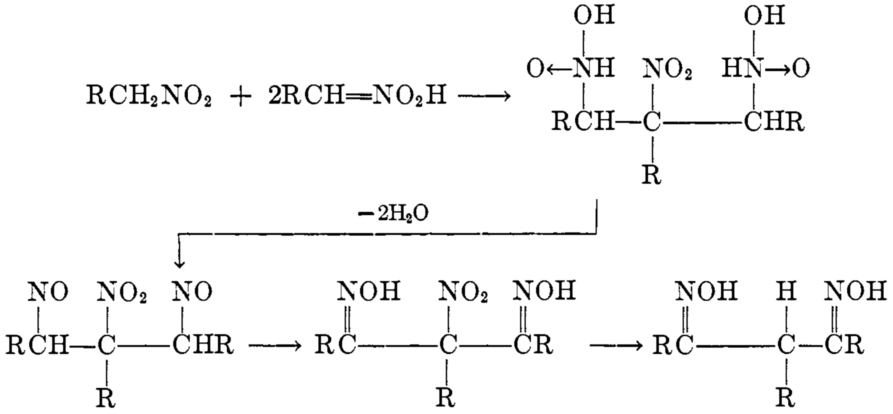
[12] See *The Organic Chemistry of Nitrogen*, by N. V. Sidgwick, revised by T. W. J. Taylor and W. Baker. Oxford University Press, London (1937).

a white precipitate is formed which is probably the mercuric salt of aci-nitromethane. This quickly loses water, forming mercuric fulminate (266, 284).

$$2CH_2{=}NO_2Na + HgCl_2 \longrightarrow (CH_2{=}NO_2)_2Hg \xrightarrow{2H_2O} Hg(ONC)_2$$

The homologous nitroparaffins yield trialkylisoxazoles upon reaction with alkali. This reaction has recently been studied by Lippincott (228) in the research laboratory of the Commercial Solvents Corporation. The following reactions are postulated:

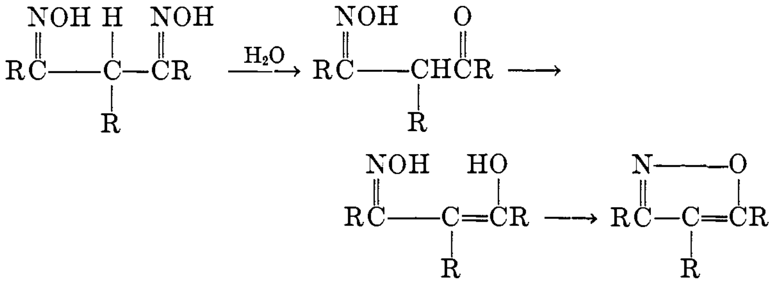
$$RCH_2NO_2 \rightleftarrows RCH{=}NO_2H$$



$$RCH_2NO_2 + 2RCH{=}NO_2H \longrightarrow R\overset{O\leftarrow \overset{OH}{N}H}{CH}-\underset{R}{\overset{NO_2}{C}}-\overset{H\overset{OH}{N}\rightarrow O}{CH}R$$

$$\xrightarrow{-2H_2O} R\overset{NO}{CH}-\underset{R}{\overset{NO_2}{C}}-\overset{NO}{CH}R \longrightarrow R\overset{NOH}{C}-\underset{R}{\overset{NO_2}{C}}-\overset{NOH}{C}R \longrightarrow R\overset{NOH}{C}-\underset{R}{\overset{H}{C}}-\overset{NOH}{C}R$$

This last step is the reversal of an ordinary nitration reaction and recalls the conversion of tetranitromethane to trinitromethane by the action of bases. In both cases a carbon atom heavily loaded with negative substituents loses a nitro group in an alkaline environment. One of the distinctive features of Lippincott's work is that, by the use of anhydrous organic amines instead of the inorganic bases employed by previous workers, the dioximes—long suspected as intermediates in this reaction—were actually isolated in fair yield.



$$R\overset{NOH}{C}-\underset{R}{\overset{H}{C}}-\overset{NOH}{C}R \xrightarrow{H_2O} R\overset{NOH}{C}-\underset{R}{CH}\overset{O}{C}R \longrightarrow R\overset{NOH}{C}-\underset{R}{C}{=}\overset{HO}{C}R \longrightarrow R\overset{N-\!-O}{C}-\underset{R}{C}{=}CR$$

D. HALOGENATION

1. *Halogenation in the presence of bases*

Aliphatic fluoronitro compounds have not so far been reported.

The first chlorination of a nitroparaffin was reported by Preibisch (314), who treated nitromethane with bleaching powder and reported that he obtained monochloronitromethane. Tscherniak (383), on repeating the work, obtained only chloropicrin and unchanged nitromethane. Since Preibisch gave a boiling point (98°C.) which is correct for the nitromethane–chloropicrin azeotrope and is incorrect for monochloronitromethane (b.p. 122–123°C.), it is evident that he was in error. Tscherniak obtained the monochloro derivative by converting nitromethane to the sodium salt, washing and drying the salt, and adding it in small portions to saturated chlorine water.

Dichloronitromethane, while not obtained by the chlorination of methane (probably because of instability in the presence of bases), was produced in poor yield by Strickland (370) by nitrating dichloromethane in the vapor phase.

A process for the conversion of nitromethane to chloropicrin was devised by Ramage (321). The chlorination is carried out in the presence of an aqueous suspension of calcium carbonate, which ensures the maintenance of faintly acidic conditions; almost quantitative yields are said to result. Vanderbilt (388) obtained similar results using an alkali or alkaline-earth hypochlorite. In both of these processes the avoidance of the prolonged action of a strong base upon nitromethane and its chlorinated derivatives is an essential feature. In view of the sensitivity of nitroparaffins to the action of alkali, this is easily understood.

Since chloropicrin has recently been comprehensively reviewed (175), little need be added here. It should be mentioned, however, that its value as a toxic vapor for military purposes seems to have been terminated by the use of efficient active carbons, which remove it completely from the air breathed by the wearer of a modern respirator. Chloropicrin is, however, finding increasing use as a fumigant and insecticide and seems to have an important future as a soil-sterilizing agent. Yields of pineapples have been increased 200 per cent by treating heavily infested soils with chloropicrin.

L. Henry (152) produced the monochloro derivatives of nitroethane, 1-nitropropane, and 2-nitropropane by bubbling gaseous chlorine into an aqueous solution of the sodium salt of the aci-nitroparaffin. Shaw (356) similarly prepared 1-chloro-1-nitro-2-methylpropane. Several other chloronitroparaffins have been obtained by means other than the chlorination of nitroparaffins. These methods include the following: (*1*) the nitration of chloroparaffins (212, 273) or of epichlorohydrin (9) or the nitration of chloroaromatic compounds such as naphthalene tetrachloride with fuming nitric acid (323); (*2*) the addition of chlorine to nitroölefins (372); (*3*) the action of nitrogen tetroxide on chloroolefins (7, 8, 41, 161, 201); (*4*) the action of nitrosyl chloride or hypochlorites on oximes (42, 307, 330, 331); (*5*) the action of aqua regia upon all sorts of organic materials (320); (*6*) the action of phosphorus pentachloride on nitroalcohols (since chlorinated aldehydes may be used to prepare the nitroalcohols, polychloronitroparaffins are easily obtained by this method) (152, 297, 355, 356); (*7*) the action of hypochlorites upon such nitro compounds as picric acid (224); (*8*) the action of silver nitrite on chloroiodoparaffins (148, 149, 150, 152, 296); (*9*) direct chlorination of trinitromethane, yielding chlorotrinitromethane in nitric acid solution (239); (*10*) the chlorination of mercuric fulminate, which yields chloropicrin (190).

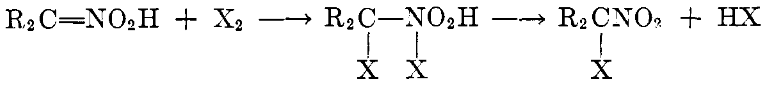
Although Henry gave directions for avoiding the formation of dichloronitroparaffins in his chlorinations, and Losanitsch (233) had dichlorinated dinitromethane, the conversion of either a mononitroparaffin or a monochloronitroparaffin to a dichloronitroparaffin was not reported until 1937. Strickland (370) found that, with the exception of monochloronitromethane, the conversion of the monochloride to the dichloride proceeds as smoothly as the production of the monochloro derivative. The dichlorination can also be performed in a single operation, using 2 moles of base and chlorine to 1 mole of nitroparaffin (54). Calcium salts may be employed. Strickland made the following compounds not previously reported: 1-chloro-1-nitrobutane, 1,1-dichloro-1-nitroethane, 1,1-dichloro-1-nitropropane, 1,1-dichloro-1-nitrobutane, and 1,1-dichloro-1-nitro-2-methylpropane.

Because of the low cost of the raw materials and the ease of their preparation, the chloronitroparaffins are of interest as readily available, relatively inexpensive compounds. 1,1-Dichloro-1-nitroethane gives promise as an insecticide. It is effective against many insects and when pure it is free from the intense lachrymal property of chloropicrin. The commercial material contains a little chloropicrin, which serves as a warning agent. Campbell (63) has reported that chloronitroparaffins are powerful inhibitors of gelling in ultra-accelerated rubber cements. Hixon and Miller (160) have disclosed the use of chloronitroparaffins as selective solvents in the refining of lubricants.

The bromination of nitroparaffins has been extensively studied. Reaction between bromine and an aci-nitroparaffin or a salt of an aci-nitroparaffin is so nearly instantaneous that it has been used as a means for measuring the change of a nitroparaffin to the tautomeric nitronic acid (182–185). Most of the possible bromo-substitution products of the simple nitroparaffins in which the bromine atom or atoms and the nitro group are on the same carbon atom have been reported. They are extremely easy to make but are, at least for most purposes, incapable of competing economically with their chlorine analogs.

The direct iodination of nitroparaffins also proceeds readily in the presence of bases. Villiers (392) treated dinitromethane with iodine and potassium hydroxide and obtained the monoiodo derivative in yellow crystals which rapidly decomposed. Seigle and Hass (353) found no difficulty in applying this reaction to mononitroparaffins, but the instability of the products renders them of little interest.

The foregoing discussion indicates that in the chlorination of nitroparaffins in the presence of bases the reaction is probably an addition to the nitronic acid or its salt, followed by loss of HX or MX.



$$R_2C{=}NO_2H + X_2 \longrightarrow R_2\underset{X}{C}{-}\underset{X}{N}O_2H \longrightarrow R_2\underset{X}{C}NO_2 + HX$$

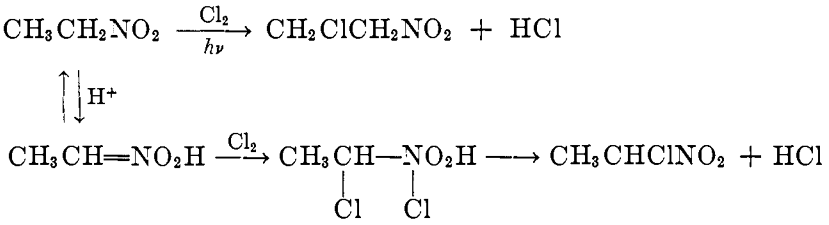
The reaction may also be viewed as an addition of a "positive" halogen atom to the anion of the nitronic acid with simultaneous formation of halide ion (403).

These mechanisms are in agreement with (*1*) the rapidity of the reaction, (*2*) its occurrence in the absence of light, and (3) the fact that the halogen atom is always bound to the carbon atom which holds the nitro group.

2. Halogenation in the absence of bases

Riley and McBee (332) in this laboratory have investigated the action of chlorine and bromine upon nitroparaffins in the absence of bases and under the influence of phosphorus pentoxide and intense illumination. Bromine gives the same products as if a base were present. Chlorine, on the other hand, gives largely derivatives formed by substitution of hydrogen atoms other than those on the carbon atom holding the nitro group. Thus nitroethane yields almost exclusively 2-chloro-1-nitroethane, 1-nitropropane yields 2-chloro-1-nitropropane and 3-chloro-1-nitropropane, 2-nitropropane yields 1-chloro-2-nitropropane, nitrobutane yields the 2-, 3-, and 4-monochloro derivatives, and 1-nitro-2-methylpropane yields both the 2- and the 3-chloro derivatives.

In addition to the inherent interest in the reaction as a source of many bifunctional compounds not otherwise readily available, this work raises several theoretical questions, such as the following: Why do bromine and chlorine behave differently? Why does the presence of phosphorus pentoxide assist the reaction, while even a little water decreases the yield? We have already noted that acids (section X, B, 1) catalyze the nitronic acid–nitroparaffin tautomerization. If we imagine two competing reactions as follows, using nitroethane as an example,



$$\begin{array}{l} \mathrm{CH_3CH_2NO_2} \xrightarrow[h\nu]{\mathrm{Cl_2}} \mathrm{CH_2ClCH_2NO_2} + \mathrm{HCl} \\ \Big\uparrow\Big\downarrow \mathrm{H^+} \\ \mathrm{CH_3CH{=}NO_2H} \xrightarrow{\mathrm{Cl_2}} \underset{\mathrm{Cl}}{\mathrm{CH_3CH}}{-}\underset{\mathrm{Cl}}{\mathrm{NO_2H}} \longrightarrow \mathrm{CH_3CHClNO_2} + \mathrm{HCl} \end{array}$$

it is evident that water would, in the presence of hydrogen chloride, form hydrogen ions which favor the reëstablishment of the nitroparaffin–nitronic acid equilibrium after the chlorine had reacted with the trace of nitronic acid normally present. This would favor substitution on the alpha carbon atom. Phosphorus pentoxide hinders the addition reactions by preventing this. Bromine substitutes much more sluggishly than chlorine does, while it often adds to double bonds even more readily, so the nitronic acid mechanism is not so easily suppressed in this case

The effect of one or more chlorine atoms in decreasing the chlorination rate of the hydrogens upon a carbon atom (135) adjacent to the one holding the chlorine atom(s) seems analogous to the effect of the oxygen atoms here. It is interesting to note the close analogy between this reaction and the chlorination of monochloroacetone in the presence and absence of bases. In the presence of bases the reaction continues on the carbon atom holding the chlorine atom, since the hydrogen atoms in this position enolize more readily than those in the methyl group. In the absence of bases and the presence of light the isomer is also formed (275).

E. CONDENSATION WITH ALDEHYDES TO YIELD NITROALCOHOLS

This reaction, discovered by L. Henry (146), is certainly the most versatile source of compounds derived from nitroparaffins. As an illustration we may use nitromethane and formaldehyde:

$$CH_3NO_2 + HCHO \xrightarrow[\text{of base}]{\text{trace}} HOCH_2CH_2NO_2 \xrightarrow{HCHO}$$

$$(HOCH_2)_2CHNO_2 \xrightarrow{HCHO} (HOCH_2)_3CNO_2$$

This is a condensation of the aldol type in which one, two, or three of the hydrogen atoms attached to the carbon atom holding the nitro group may add to the oxygen of an aldehyde with the formation of hydroxyalkyl-substituted nitroparaffins. The reaction almost certainly proceeds with the nitronic acids as intermediates. The function of the basic catalyst is to increase the concentration of aci-nitroparaffin by exerting its well-known catalytic effect in restoring the tautomeric equilibrium after the trace of nitronic acid normally present has reacted with aldehyde.

This mechanism is in harmony with the discovery of Kamlet (186) that an unusually rapid condensation between aldehydes and nitroparaffin can be obtained by using the sodium bisulfite addition compound of the aldehyde and the sodium salt of the aci-nitroparaffin. The function of the sodium bisulfite here is to liberate the nitronic acid from its salt without giving a sufficiently high concentration of hydrogen ions to destroy much of the nitronic acid *via* the Nef reaction discussed in section X, B, 2. A corollary is that other acid reagents should be capable of acting similarly, and this has been checked by Bourland (48) in this laboratory for carbonic acid, acetic acid, and sodium bisulfate. In some cases the use of carbonic acid increased the conversion appreciably over that obtainable with sodium bisulfite; in others the reverse was true.

A great variety of substances function successfully as the basic catalyst in this reaction; the list includes such diverse compounds as potassium and sodium hydroxides, carbonates, bicarbonates, and methoxides, and organic amines. Vanderbilt and Hass (390, 391) have pointed out the advantages of calcium hydroxide in view of its easy removal from the reaction mixture by conversion to insoluble salts.

In most cases the addition of aldehyde to nitroparaffin must compete with at least two other reactions: (*1*) the aldol condensation of the aldehyde with itself, and (*2*) the conversion of the nitroparaffin to an isoxazole or, in the case of nitromethane, to methazonic acid. It is therefore advisable to add as little catalyst as is necessary for a reasonably rapid reaction and to add the aldehyde gradually to the nitroparaffin so as to maintain its concentration at a low value and thus to suppress the formation of hydroxyaldehydes.

Both aldehydes and nitroparaffins vary tremendously in their ability to undergo this reaction. Formaldehyde and nitromethane are both highly reactive and the rate decreases as either homologous series is ascended. Chloral reacts very rapidly, as would be expected from other behavior of its carbonyl group. With the homologs of nitromethane great difficulty is experienced in condensing more than a single aldehyde molecule on a nitroparaffin, unless one of the reagents is formaldehyde. Even with nitromethane the reaction often tends to stop with only one or two molecules of aldehyde condensed when the latter contains more than five carbon atoms. Secondary nitroparaffins react more sluggishly than primary ones and the tertiary isomers, having no alpha hydrogen atoms, do not react at all.

TABLE 4

Reaction of aldehydes with nitroparaffins

NITROPARAFFIN	MOLES ALDEHYDE	ALDEHYDE USED								
		Formaldehyde	Acetaldehyde	Propionaldehyde	*n*-Butyraldehyde	Isobutyraldehyde	Isovaleraldehyde	Benzaldehyde	Furfuraldehyde	Chloral or its hydrate
Nitromethane	1	(118)	(156)	(181)	(181)	(345)	(362)	(334)	(187)	(69)
	2	(294)		(362)		(188)	(187)			
	3	(301)								
Nitroethane	1	(390)	(156)	(390)	(390)		(187)	(3)		(69)
	2	(390)								
1-Nitropropane	1	(390)	(390)	(390)	(390)		(187)			
	2	(390)								
2-Nitropropane	1	(390)	(390)	(390)	(390)					
1-Nitrobutane	1	(390)	(390)	(390)	(390)		(187)			
	2	(390)								
2-Nitrobutane	1	(390)	(390)	(390)	(390)					
1-Nitro-2-methylpropane	1	(390)	(390)	(390)	(390)		(187)			
	2	(390)								
1-Nitropentane	1	(158)								
	2									
Nitroisopentane	1	(278)	(277)				(187)			
	2	(278)								
1-Nitrohexane	1	(158)								
	2									
Phenylnitromethane	1	(168)						(195)		(69)

Traces of nitroölefins often are formed simultaneously with the nitroalcohols, and with aromatic aldehydes these may be the principal reaction products if amine catalysts are employed. Since many nitroölefins are prone to polymerize to form brown tars, they are objectionable impurities. Vanderbilt (389) has reported upon the removal of these compounds by polymerization, followed by distillation of the nitroalcohol.

Table 4 contains a summary of some of the nitroalcohols, nitroglycols, and "nitroglycerols" which have been produced from the simpler nitroparaffins and aldehydes. A "1" on the table means that one molecule of the aldehyde has been condensed, a "2" means two molecules, etc. The other numbers indicate the references.

The nitroalcohols available commercially, derived from nitroparaffins, are $(HOCH_2)_3CNO_2$, $(HOCH_2)_2C(CH_3)NO_2$, $HOCH_2C(CH_3)_2NO_2$, $(HOCH_2)_2C(C_2H_5)NO_2$, and $CH_2OHCHNO_2C_2H_5$.

1. Derivatives of nitroalcohols

A detailed discussion of the many derivatives of the nitroalcohols would occupy too much space, but these compounds are so important that they deserve at least brief consideration.

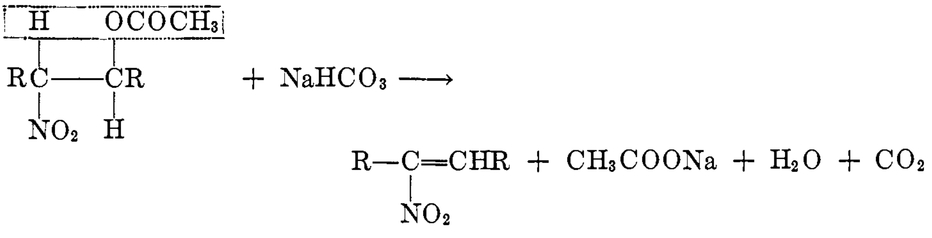
The inorganic esters are represented by certain of the chloronitroparaffins previously discussed, which may be made by the chlorination of nitroparaffins or by the action of phosphorus pentachloride upon nitroalcohols. The nitrate esters may be produced from the nitroalkanols by the action of cold (0–20°C.), colorless, 100 per cent nitric acid in the presence of sulfuric acid.

$$(HOCH_2)_3CNO_2 + 3HNO_3 \xrightarrow{H_2SO_4} (O_2NOCH_2)_3CNO_2 + 3H_2O$$

Hofwimmer (165) reported in 1912 concerning the product of this reaction that only the high cost of nitromethane stands in the way of its technological utilization. This compound is in perfect oxygen balance, has less sensitivity to shock than glycerol trinitrate, has 7 per cent more explosive power, and does not freeze under conditions ordinarily encountered. The dinitrate of 2-methyl-2-nitro-1,3-propanediol was patented in 1928 by Bergeim (26). It is also a high explosive.

The phosphate esters of the nitroalcohols and nitroglycols have been prepared by Vanderbilt, using phosphorus oxychloride (387), and have been studied as plasticizers for cellulose esters.

The esters of organic acids and nitroalcohols can be prepared by the use of acid anhydrides, acid chlorides, or, in some cases, the acids themselves in the presence of sulfuric acid and an agent, such as carbon tetrachloride, which removes water as a minimum azeotrope. Tindall (379) has recently reported ninety-six of these esters, all new compounds. They are of interest as plasticizers. While some are fairly stable at temperatures of 150°C., others are capable of being titrated at room temperature with standard alkali. This is due not to instantaneous saponification but to a reaction discovered by Schmidt and Rutz (346) which depends upon the presence of a hydrogen atom upon the carbon atom holding the nitro group.



$$R\underset{NO_2}{\overset{H}{C}}-\underset{H}{\overset{OCOCH_3}{C}}R + NaHCO_3 \longrightarrow R-\underset{NO_2}{C}=CHR + CH_3COONa + H_2O + CO_2$$

This reaction is of importance as the most general means of preparing nitroolefins.

The production of resins of the glyptal type by condensing dibasic acids with 2-amino-2-methyl-1,3-propanediol has been reported (363).

Senkus has studied the formation of cyclic acetals by the condensation of aldehydes with polyhydric nitroalcohols. The reduction products of these compounds are aminocyclic acetals (354), some of which are "instantaneous wetting agents", so-called because in the Draves test (87) the yarn sinks at once in water containing 0.5 per cent of the acetal.

The reduction of nitroalcohols to aminoalcohols has been discussed in section X, A, 1. The ones derived from nitroparaffins commercially available at present are the following: $(HOCH_2)_3CNH_2$, $(HOCH_2)_2C(CH_3)NH_2$, $HOCH_2C(CH_3)_2NH_2$, $(HOCH_2)_2C(C_2H_5)NH_2$, and $CH_2OHCHNH_2C_2H_5$. With the higher fatty acids all of these compounds form soaps which are powerful emulsifying agents. With increased size and number of alkyl groups on the cation, they undergo a gradual transition from agents promoting emulsions of oil in water to those of the opposite type which cause water to disperse in oil. The principal applications of these compounds depend upon this emulsifying property, which is useful in the preparation of such diverse materials as cosmetics, pharmaceuticals, and floor waxes.

Many substances of pharmaceutical interest, such as ephedrine, C_6H_5CHOH-$CH(CH_3)NHCH_3$ and propadrine, $C_6H_5CHOHCH(NH_2)CH_3$, can readily be made by the aldehyde–nitroparaffin condensation followed by reduction and, if necessary, by alkylation and/or other known reactions. Even before nitroparaffins were readily available, these reactions were investigated and patented by W. N. Nagai (283) and Chogi Nagai (282). Fresh impetus to this field of research has resulted from the reduction of the price of nitroethane to less than 1 per cent of its former figure.

F. CONDENSATION WITH ALDEHYDES TO YIELD NITROÖLEFINS

Although inorganic bases cause aromatic aldehydes to react with nitroparaffins, yielding nitroalcohols, these reagents in the presence of amines yield nitroölefins. This reaction may be formulated as follows:

$$ArCHO + RNH_2 \rightarrow ArCH{=}NR + H_2O$$

$$ArCH{=}NR + RCH_2NO_2 \rightarrow RNH_2 + ArCH{=}C(NO_2)R$$

By the term "aromatic aldehydes" is meant only compounds in which the aldehyde group is attached directly to a nucleus capable of resonance; phenylacetaldehyde would not be included, while furfuraldehyde would be. The difference between the behavior of the two classes of aldehydes is only one of degree, since nitroölefins are always formed to some extent when an aldehyde reacts with a nitroparaffin, and is presumably attributable to the ease of dehydration of the nitroalcohol which contains an hydroxyl group in a position alpha to an aromatic nucleus.

ω-Nitrostyrene is so easily prepared from benzaldehyde and nitromethane (410) that it has been rather widely studied. Although Simon (359) had made this compound from styrene long before, the first preparation by this condensation was made by Priebs (315), who in 1884 used zinc chloride as the catalyst. Posner in 1898 (312) confirmed and extended this work, but the next year Thiele (376) reported much better results, using alcoholic potassium hydroxide followed by acidification with hydrochloric acid. Except for the substitution of sodium hydroxide for the potassium analog, this is still the preferred procedure. Bouveault and Wahl (50) used sodium methoxide in place of potassium hydroxide, but since the alkali metal salt of nitromethane is formed in either case, it seems unlikely that the results would justify the use of the more expensive reagent.

TABLE 5

Nitrostyrene and related compounds

COMPOUND	MELTING POINT OR BOILING POINT* °C.
ω-Nitrostyrene	58 (317, 376); 57 (195)
1-Phenyl-2-nitropropene	64 (317); 64 (195); 65 (3)
1-Phenyl-2-nitro-1-butene	125–129 at 10 mm. (372)
ω,*o*-Dinitrostyrene	107 (50, 312)
ω,*m*-Dinitrostyrene	122–124 (312); 125 (376)
ω,*p*-Dinitrostyrene	196–199 (376)
p-Methoxy-ω-nitrostyrene (anisylidenenitromethane)	87 (50); 86 (195)
3,4-Methylenedioxy-ω-nitrostyrene	159 (50); 158 (195); 161.5 (220)
2,4-Dimethoxy-ω-nitrostyrene	104 (322)
3,4,5-Trimethoxy-ω-nitrostyrene	120–121 (360); 119–120 (250)
2,3,4-Trimethoxy-ω-nitrostyrene	167 (360)
p-Hydroxy-ω-nitrostyrene	154–160 (334)
3,4-Dihydroxy-ω-nitrostyrene	155–157 (334)
2-Hydroxy-4-methoxy-ω-nitrostyrene	171–172 (322)
2-Ethoxy-4-methoxy-ω-nitrostyrene	102 (322)
1-Piperonylidene-1-nitroethane	98 (195)
1-Anisylidene-1-nitroethane	48 (195); 43–44 (3)
3-Methoxy-4-hydroxy-ω-nitrostyrene	165 (195); 160–164 (334)
1-(3,4-Dimethoxybenzylidene)-1-nitroethane	70–71 (3)
1-Furyl-2-nitroethene	74 (50)
1,4-Bis(β-nitrovinyl)benzene	200–230 (376, 412)
1-Furyl-2-nitrobutylene	130–131 at 13 mm. (187)
1-Furyl-3-methyl-2-nitrobutylene	122–123 at 13 mm. (187)
1-Furyl-2-nitroamylene	136–137 at 13 mm. (187)
Vanillylidenenitromethane benzyl ether	122–123 (220)
Anisylidenenitroethane	48 (195)
5-ω-Dinitro-2,4-dimethoxystyrene	214 (322)
1,4-Bis(β-methyl-β-nitrovinyl)benzene	119–120 (412)
1,4-Bis(β-nitro-β-phenylvinyl)benzene	228–229 (decompn.) (412)

* References to the literature are given in parentheses.

Thiele found that when the alkali salt is acidified with a mineral acid, nitrostyrene results but that acetic acid yields the corresponding nitroalcohol.

$$C_6H_5CHOHCH{=}NO_2K + HCl \rightarrow C_6H_5CH{=}CHNO_2 + H_2O$$

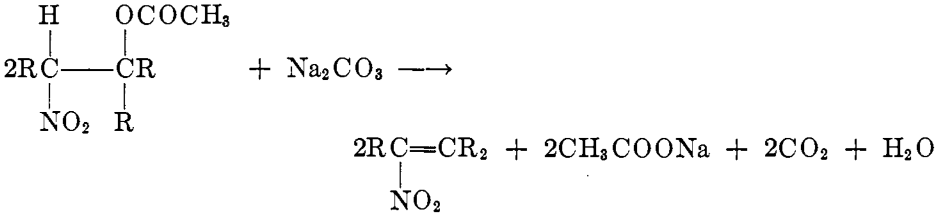
$$C_6H_5CHOHCH{=}NO_2K + CH_3COOH \rightarrow C_6H_5CHOHCH_2NO_2 + CH_3COOK$$

This result was corroborated by Holleman (168) and also by Rosenmund (334).

The aromatic nitroölefins listed in table 5 have been synthesized.

1. *Other syntheses of nitroölefins*

In 1928 Schmidt and Rutz (347) reported that acetic acid could be abstracted from certain acetates of nitroalcohols by refluxing the esters in ether solution with potassium carbonate or bicarbonate. Nitroölefins are thus produced in good yields. As modified in this laboratory by A. G. Susie (372), this synthesis is represented by the following equation:

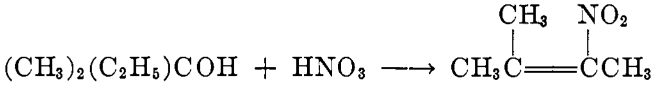


$$2\mathrm{R}\underset{\mathrm{NO_2}}{\overset{\mathrm{H}}{\mathrm{C}}}\!-\!\!-\!\underset{\mathrm{R}}{\overset{\mathrm{OCOCH_3}}{\mathrm{C}}}\mathrm{R} + \mathrm{Na_2CO_3} \longrightarrow 2\mathrm{R}\underset{\mathrm{NO_2}}{\mathrm{C}}\!=\!\mathrm{CR_2} + 2\mathrm{CH_3COONa} + 2\mathrm{CO_2} + \mathrm{H_2O}$$

Since nitroparaffins and aldehydes readily yield nitroalcohols, which in turn are easily acylated, the nitroölefins are thus readily accessible. Benzene proved to give better yields than ether when used as a solvent in this reaction. It should be pointed out that only the isomers having nitro groups on the doubly bound carbon atoms can thus be made. Naturally, in the nitroalcohol the carbon atom holding the nitro group must also be attached to a hydrogen atom.

Other means of producing nitroölefins include the nitration of tertiary alcohols (121, 122). The abstraction of HX from a halonitro compound has been used to produce nitro compounds of the acetylene series (230). The action of dehydrating agents upon nitroalcohols (405, 407), the reaction of silver nitrite upon allylic halides, and the cautious decomposition of nitronitrates (407) are also applicable.

$$(\mathrm{CH_3})_3\mathrm{COH} + \mathrm{HNO_3} \longrightarrow (\mathrm{CH_3})_2\mathrm{C}\!=\!\mathrm{CHNO_2} \quad (121)$$



$$(\mathrm{CH_3})_2(\mathrm{C_2H_5})\mathrm{COH} + \mathrm{HNO_3} \longrightarrow \mathrm{CH_3}\overset{\mathrm{CH_3}}{\mathrm{C}}\!=\!\!=\!\overset{\mathrm{NO_2}}{\mathrm{C}}\mathrm{CH_3} \quad (123)$$

$$\mathrm{HOCH_2CH_2NO_2} \xrightarrow{\mathrm{NaHSO_4}} \mathrm{CH_2}\!=\!\mathrm{CHNO_2} + \mathrm{H_2O} \quad (405)$$

$$\mathrm{CH_2}\!=\!\mathrm{CHCH_2Br} + \mathrm{AgNO_2} \longrightarrow \mathrm{CH_2}\!=\!\mathrm{CHCH_2NO_2} + \mathrm{AgBr}[13]$$

$$\mathrm{ClCH(NO_2)CH_2NO_3} \xrightarrow{\text{heat}} \mathrm{CH_2}\!=\!\mathrm{CClNO_2} + \mathrm{HNO_3} \quad (407)$$

Because of the ease of addition of halogens to nitroölefins, these reactions lead readily to polyhalonitro compounds.

Hydroxysubstituted nitroölefins may be produced by condensing unsaturated aldehydes with nitroparaffins (362):

$$\mathrm{CH_3CH}\!=\!\mathrm{CHCHO} + \mathrm{CH_3NO_2} \rightarrow \mathrm{CH_3CH}\!=\!\mathrm{CHCHOHCH_2NO_2}$$

[13] Brackebush (56) first reported this reaction, but his work was attacked and discredited by R. Schiff (342), who showed that he had not prepared a new nitroölefin but in reality the substance he reported as boiling at 96°C. was mostly water. Later Meyer and Askenasy (260) made this nitroölefin from allyl iodide, while Henry (152) prepared it from allyl bromide and silver nitrite.

2. Reduction of nitroölefins to amines

If the nitroölefins produced as described in the foregoing section can be reduced completely, these reactions indicate methods of preparing amines of definite structures free from isomers. This problem has received considerable attention.

Alles (3) attempted to produce benzedrine (α-methylphenethylamine) by the reduction of the corresponding nitroölefin. He reports that "the complete reduction of 1-phenyl-2-nitro-1-propene involves considerable difficulty, . . . and several attempts at catalytic hydrogenation or reduction with various metals or their amalgams were not at all successful." His best yield (20 per cent) was obtained electrolytically, using a mercury cathode and a catholyte comprising ethanol, acetic acid, and sulfuric acid. Employment of the more recently developed Raney nickel catalyst enables one to obtain about a 40 per cent yield in this same reduction (380).

Schales (339) converted ω-nitrostyrene to β-phenethylamine in 93 per cent yield by using the platinum oxide catalyst of Adams and Shriner and adding the nitrostyrene gradually to the hydrogenation vessel. A mixture of acetic and sulfuric acids was used as solvent. Similar results were obtained with 3,4-methylenedioxy-ω-nitrostyrene and 3-nitro-ω-nitrostyrene, both nitro groups being reduced to amino groups in the latter compound.

Reichert and Koch (326, 327) reduced the nitroölefins obtained by condensing nitromethane with the following aldehydes: *o*-methoxybenzaldehyde, anisaldehyde, veratric aldehyde, and piperonal. By the use of palladium on animal charcoal almost quantitative yields of the oximes are obtained. These can then be converted to the amines by using a platinum catalyst.

3. Reduction of nitroölefins to aldoximes, ketoximes, and ketones

O. Wallach (394) reported the reduction of 1-anisyl-2-nitropropene to 1-anisyl-2-propanone oxime and of 1-piperonyl-2-nitropropene to 1-piperonyl-2-propanone oxime by the use of zinc and acetic acid at 0°C. Bouveault and Wahl (51, 52) reported that homologous series could be ascended by the following sequence of reactions:

$$\mathrm{RCHO} + \mathrm{CH_3NO_2} \longrightarrow \mathrm{RCH{=}CHNO_2}$$

$$\mathrm{RCH{=}CHNO_2} \xrightarrow[\mathrm{Zn}\ +\ \mathrm{CH_3COOH}]{\mathrm{Al,\ Hg\ or}} \mathrm{RCH_2CHNOH}$$

$$\mathrm{RCH_2CHNOH} \xrightarrow{\text{hydrolysis}} \mathrm{RCH_2CHO}$$

Subsequent workers have been unable to repeat the work of Bouveault and Wahl.

A. G. Susie (372) in this laboratory found that iron turnings and hydrochloric acid effect the reduction of nitroölefins to mixtures of the corresponding ketones and ketoximes in yields of about 70 per cent. The reaction may be controlled to yield almost exclusively ketone when sufficient hydrochloric acid is employed and almost exclusively ketoxime when a minimal quantity of acid is present.

This work has been confirmed and extended by R. L. Heider (142). Since either the ketoxime or the ketone (in the presence of ammonia) may be reduced to the corresponding amine by the use of Raney nickel and hydrogen, this constitutes an inexpensive and efficient two-step conversion of nitroölefins to amines. So far, the reaction has been successful in every instance where tried. Table 6 gives a list of the nitroölefins reduced and the ketones obtained.

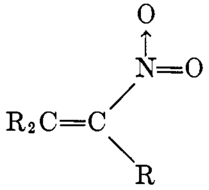
TABLE 6

Reduction of nitroölefins to ketones

NITROÖLEFIN	KETONE
3-Nitro-2-pentene	3-Pentanone
2-Nitro-2-hexene	2-Hexanone
4-Nitro-4-octene	4-Octanone
1-Phenyl-2-nitropropene	Phenylacetone
1-Phenyl-2-nitrobutene	1-Phenyl-2-butanone
1-Phenyl-2-nitropentene	1-Phenyl-2-pentanone
1-Furyl-2-nitropropene	Furylacetone
1-Anisyl-2-nitrobutene	1-Anisyl-2-butanone
1-Anisyl-2-nitropentene	1-Anisyl-2-pentanone

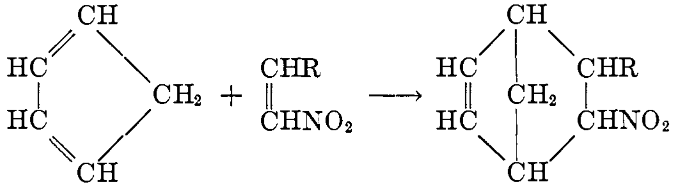
4. *Addition of nitroölefins to cyclopentadiene*

Since nitroölefins,



$$R_2C{=}C(R)(N(\rightarrow O){=}O)$$

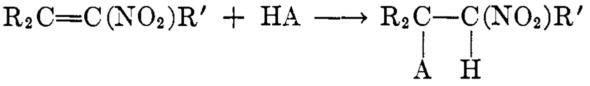
contain an activated double bond, it seems that they should be suitable reagents for the Diels–Alder reaction. This has been reported in an article by Alder, Rickert, and Windemuth (2). Nitroethylene, 1-nitropropene, and 1-nitro-1-pentene were each treated with cyclopentadiene and the expected products were obtained. 1-Nitro-1-pentene was also added to butadiene, methylbutadiene, and 2,3-dimethylbutadiene.



The nitroölefins were reduced to the saturated amines. It is evident that here is a fertile field for research.

5. Addition of nitroölefins to compounds containing active hydrogen

It is perhaps premature to state that all or most compounds with active hydrogen add to nitroölefins, but the evidence so far points in that direction.



$$R_2C{=}C(NO_2)R' + HA \longrightarrow \underset{\underset{A}{|}}{R_2C}{-}\underset{\underset{H}{|}}{C}(NO_2)R'$$

Either the concept of 1,4-addition or that of relative electronegativity would predict the direction of this reaction. The addition of phenylnitromethane to diphenylnitroethylene and the formation of dinitroneopentane from 1-nitro-2-methylpropene and nitromethane have been mentioned in section VI. This reaction is receiving further study as a means of obtaining dinitroparaffins.

Nitroölefins are readily hydrolyzed by the action of dilute sulfuric acid, as follows (372):

$$RCH{=}C(NO_2)R' + H_2O \xrightarrow{H_2SO_4} RCHOHCHNO_2R'$$

$$RCHOHCHNO_2R' \longrightarrow RCHO + R'CH_2NO_2$$

$$R'CH_2NO_2 + H_2O + H_2SO_4 \longrightarrow R'COOH + NH_3OHHSO_4$$

Askenasy and Meyer (10) had previously reported small amounts of acrylic acid from the hydrolysis of 1-nitropropene. In the first step of this reaction water functions as the compound containing active hydrogen.

P. Friedlander and J. Mähly (104) reported that treatment of *p*-nitro-ω-nitrostyrene with alcoholic potassium hydroxide dissolved it with the formation of $O_2NC_6H_4CH(OC_2H_5)CHNO_2K$.

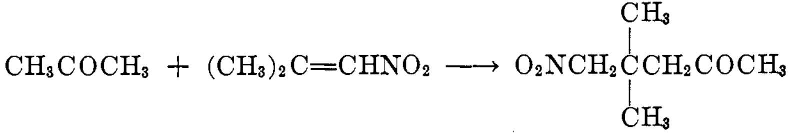
Meisenheimer and Heim (253, 254) and Rosenmund (334) reported that ω-nitrostyrene adds sodium methoxide or ethoxide instantaneously, as follows:

$$C_6H_5CH{=}CHNO_2 + NaOCH_3 \rightarrow C_6H_5CH(OCH_3)CH{=}NO_2Na$$

The resulting solution is instable and yields $C_6H_5CH(OCH_3)CHNO_2CH(C_6H_5)CH_2NO_2$.

Reichert and Koch (327) used this reaction to prepare α-(2-methoxyphenyl)-β-nitroethyl methyl ether, α-(4-methoxyphenyl)-β-nitroethyl methyl ether, and α-(3,4-dimethoxyphenyl)-β-nitroethyl methyl ether.

The addition of acetone to 1-nitro-2-methylpropene yields 5-nitro-4,4-dimethyl-2-pentanone (48).



$$CH_3COCH_3 + (CH_3)_2C{=}CHNO_2 \longrightarrow O_2NCH_2\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}CH_2COCH_3$$

An interesting addition reaction which might be mentioned in this connection is that postulated by Holleman (167) to explain the changes observed when ω-nitrostyrene was treated with potassium cyanide and then acidified. Before the formation of a bimolecular condensation product he postulated the reaction:

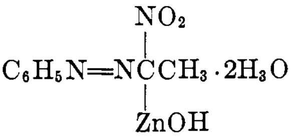
$$C_6H_5CH{=}CHNO_2 + KCN \rightarrow C_6H_5CH(CN)CH{=}NOOK$$

Upon acidification, hydrocyanic acid splits out between two molecules and a bimolecular product results.

The action of amines or ammonia on 1-bromo-1-nitro-1-butene and on 1-bromo-1-nitro-1-pentene yields the corresponding amine derivative (231) in each case.

G. REACTION OF ARYLDIAZONIUM SALTS WITH SALTS OF ACI-NITROPARAFFINS

This condensation was discovered by Victor Meyer and Ambühl (259), who mixed aqueous solutions of benzenediazonium sulfate and sodium nitroethane and obtained an orange solid, which they formulated as $C_6H_5N{=}NCH(NO_2)CH_3$ and which possessed the definitely acidic properties to be expected of such a compound. The fact that two equivalents of metal were present in the salts was entirely unanticipated, since the formula indicates only one replaceable hydrogen atom. The corresponding compound was therefore made from 2-nitropropane and when this proved to have no acidic properties the metallic derivatives of phenyldiazo-1-nitroethane were formulated as basic salts, e.g.,



$$C_6H_5N{=}N\overset{\displaystyle NO_2}{\underset{\displaystyle ZnOH}{C}}CH_3\cdot 2H_3O$$

The same year Friese, working in Meyer's laboratory, reported the condensation of benzenediazonium nitrate with sodium nitromethane to yield phenyldiazonitromethane (105), a red solid giving a blue-violet solution in sulfuric acid, from which it can be recovered unchanged by diluting with water. His results were later shown to be incorrect, however, the compound obtained from nitromethane being formulated by Bamberger (12) as *N*,*N'*-diphenyl-*C*-nitroformazyl, $C_6H_5N{=}NC(NO_2){=}NNHC_6H_5$.

In rapid succession the following compounds were reported: 1-phenyldiazo-1-nitropropane; 1-(*p*-tolyldiazo)-1-nitroethane; 1-(*o*-tolyldiazo)-1-nitroethane; 1-(*p*-bromophenyldiazo)-1-nitroethane; and 1-(*m*-nitrophenyldiazo)-1-nitroethane (269).

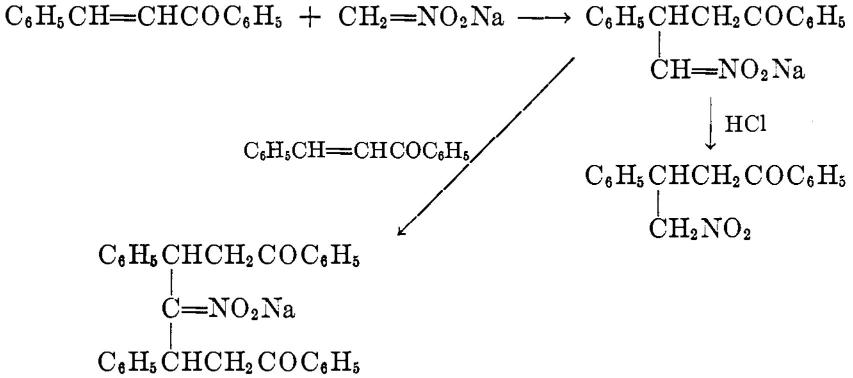
Askenasy and Meyer (10) obtained 3-nitropropene—after previous efforts over twenty years had been unsuccessful—and caused it to react with benzenediazonium sulfate, *p*-toluenediazonium sulfate, *o*-toluenediazonium sulfate, *p*-anisolediazonium sulfate, *p*-phenetolediazonium sulfate, *m*-carboxybenzenediazonium sulfate, *m*-bromobenzenediazonium sulfate, *p*-chlorobenzenediazonium sulfate, and pseudocumenediazonium sulfate; in each case they obtained the expected compound.

When Keppler and Meyer prepared 1,3-dinitropropane (191) they condensed it with 2 moles of benzenediazonium sulfate, and also made the corresponding derivatives of *p*-toluidine and *p*-methoxyaniline. Many other compounds have been similarly prepared by Bamberger *et al.* (14, 15, 16), Chattaway, Drewitt, and Parkes (68), Hantzsch and Kissel (124), Jones and Kenner (181), and Ponzio and students (308, 309, 310). Feasley, working in this laboratory, has synthesized a large number of diazo derivatives of 2-nitropropane and 2-nitrobutane.

H. ADDITION OF NITROPARAFFINS TO ACTIVATED DOUBLE BONDS

The addition of nitroparaffins to nitroölefins has already been mentioned in sections VI and X, F, 5.

The addition of nitroparaffins to unsaturated ketones was first reported by Kohler (196), who found that primary or secondary nitroparaffins in the presence of various bases add to α,β-unsaturated ketones, esters, nitriles, and nitro compounds. Organic bases such as diethylamine or piperidine are recommended as catalysts for the addition to methyl ketones, such as benzalacetone, while sodium ethoxide gives better results with benzalacetophenone. "A small quantity of sodium alcoholate is sufficient to cause rapid disappearance of both ketone and nitro compound; but under these conditions the result is always a mixture of complex products."



$$C_6H_5CH{=}CHCOC_6H_5 + CH_2{=}NO_2Na \longrightarrow \underset{\displaystyle CH{=}NO_2Na}{C_6H_5CHCH_2COC_6H_5} \xrightarrow{HCl} \underset{\displaystyle CH_2NO_2}{C_6H_5CHCH_2COC_6H_5}$$

$$\underset{\displaystyle CH{=}NO_2Na}{C_6H_5CHCH_2COC_6H_5} \xrightarrow{C_6H_5CH{=}CHCOC_6H_5} \begin{array}{c} C_6H_5CHCH_2COC_6H_5 \\ | \\ C{=}NO_2Na \\ | \\ C_6H_5CHCH_2COC_6H_5 \end{array}$$

"These are due to the fact that the sodium compound formed from one molecule each of ketone and sodium nitromethane readily combines with more of the unsaturated ketone . . . therefore it is necessary to have an excess of sodium nitromethane *in solution*."

Table 7 contains a summary of the work of Kohler and students.

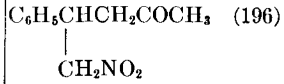
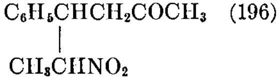
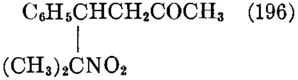
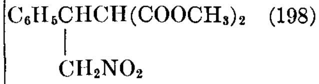
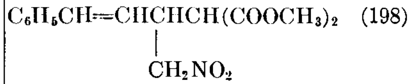
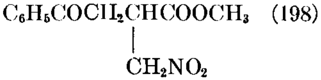
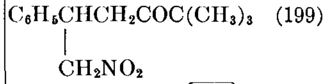
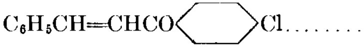
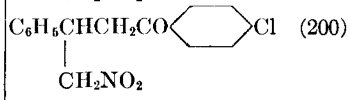
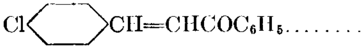
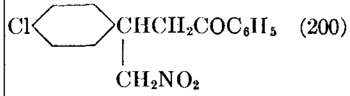
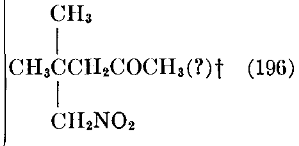
I. ANALYTICAL REACTIONS OF NITROPARAFFINS

Early students of the nitroparaffins frequently utilized combustion analyses for the determination of carbon, hydrogen, and nitrogen. Meyer, Henry, Worstall, Konovalov, and other investigators who carried out many such experiments gave analytical data of this kind and, in addition, gave the results of vapor-density determinations carried out by Hoffman's method. While the results of combustion analyses are valid when the work is carefully done, they present difficulties when the compound is especially volatile or when it tends to burn too readily. While the nitroparaffins *per se* are not particularly explosive, some compounds derived from them are explosible under such conditions.

Almström (4) was aware of this difficulty and gave a modification of Pregl's method of microanalysis adapted for use when the compound showed these undesirable characteristics. He mixed the sample with washed and ignited sand, which modified the burning so that it proceeded quietly and the analysis

TABLE 7

Compounds prepared from nitroparaffins by Kohler and students

COMPOUND REACTED	PRODUCT FORMED FROM NITROMETHANE*	PRODUCT FORMED FROM NITROETHANE	PRODUCT FORMED FROM 2-NITROPROPANE
$C_6H_5CH{=}CHCOCH_3$	 $\underset{\underset{\textstyle CH_2NO_2}{\vert}}{C_6H_5CH}CH_2COCH_3$ (196)	 $\underset{\underset{\textstyle CH_3CHNO_2}{\vert}}{C_6H_5CH}CH_2COCH_3$ (196)	 $\underset{\underset{\textstyle (CH_3)_2CNO_2}{\vert}}{C_6H_5CH}CH_2COCH_3$ (196)
$C_6H_5CH{=}C(COOCH_3)_2$	 $\underset{\underset{\textstyle CH_2NO_2}{\vert}}{C_6H_5CH}CH(COOCH_3)_2$ (198)		
$C_6H_5CH{=}CHCH{=}C(COOCH_3)_2$	 $C_6H_5CH{=}CH\underset{\underset{\textstyle CH_2NO_2}{\vert}}{CH}CH(COOCH_3)_2$ (198)		
$C_6H_5COCH{=}CHCOOCH_3$	 $C_6H_5COCH_2\underset{\underset{\textstyle CH_2NO_2}{\vert}}{CH}COOCH_3$ (198)		
$C_6H_5CH{=}CHCOC(CH_3)_3$	 $\underset{\underset{\textstyle CH_2NO_2}{\vert}}{C_6H_5CH}CH_2COC(CH_3)_3$ (199)		
			
			
$(CH_3)_2C{=}CHCOCH_3$	 $CH_3\overset{\overset{\textstyle CH_3}{\vert}}{\underset{\underset{\textstyle CH_2NO_2}{\vert}}{C}}CH_2COCH_3$(?)† (196)		

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* References to the literature are given in parentheses.

† The reason for the question mark opposite the formula of mesityl oxide is that, although Kohler states, in discussing the use of organic amines as catalysts, "In the case of . . . mesityl oxide this is the best procedure," he apparently never reported the expected compound. Inquiry by the authors since Professor Kohler's demise has been unavailing.

gave dependable results. When salts of the alkali metals were analyzed, lead chromate was used instead of sand in order to prevent the formation of a residue of alkali carbonate.

Friedemann (103) suggested an analysis based on oxidation by chromic acid. In this method a 0.1-g. sample is dissolved in concentrated sulfuric acid and 0.2 *N* potassium dichromate solution is added. The material is oxidized by boiling gently under reflux, then potassium iodide is added, and the mixture is titrated with sodium thiosulfate. More sulfuric acid is required for difficultly combustible compounds; sugar requires about 2 ml., trinitrotoluene about 10 ml. An accuracy of 0.0001 to 0.001 g. is claimed for this method.

Other procedures for analysis have been modified in a manner which permits their application to the nitroparaffins. The unmodified Kjeldahl method for nitrogen determination is not satisfactory for such compounds, because most nitroparaffins and their derivatives are difficult to digest to colorless solutions by the use of sulfuric acid alone. Their high volatility makes an unduly prolonged process untenable. Šimek (358) proposed a modified method, and Harte (130) devised a method of shortening the digestion period by using dextrose, potassium sulfate, copper sulfate, and alundum and digesting the sample in sulfuric acid.

A different means of attacking the problem of analysis of nitroparaffins is offered by Kirpal (192), Limpricht (226), and Mulliken and Barker (279), who describe a quantitative method based on reduction of the nitro group. In all the examples given in Limpricht's paper aromatic nitro compounds were employed, but Mulliken and Barker (279) and Kirpal (192) reduced nitroparaffins as well. Wallerius (395) showed that the nitrogen content of aliphatic or aromatic nitro compounds can be determined by reducing them with stannous chloride and subsequently titrating with iodine. Ponzio (306) reported that this method is not applicable to dinitroparaffins, since they sometimes have only one nitro group which is capable of reacting with stannous chloride.

Oldham (288) has given a titration method designed to determine the number of nitro groups in a compound. Hearon and Gustavson (141) proposed a semimicro qualitative test for the detection of nitroparaffins, and Priebs (315) suggested that the reaction between benzaldehyde and nitromethane to yield nitrostyrene could be made a quantitative test for nitromethane.

Colorimetric methods of analysis have been widely tested with a view to developing more rapid means of determining nitroparaffins. Meyer, whose tests to distinguish primary, secondary, and tertiary nitroparaffins have already been discussed (section X, B, 3), was one of the first to use such methods. Konovalov (207, 208) studied the bright red color produced by ferric chloride in benzene solutions of primary nitroparaffins in the presence of alcoholic potassium hydroxide and reported that 5 ml. of a solution of 1-phenyl-1-nitropropane containing 1 part in 1400 parts of benzene gave a distinct red color after 1 hr. This method was suggested by Konovalov for use with nitroparaffins of more than six carbon atoms, which do not react very satisfactorily when treated with nitrous acid by Meyer's method.

Bose (46) pointed out the disadvantage that Meyer's method possesses, i.e., it gives no reaction with tertiary nitro groups. He also noted that the Kjeldahl and other quantitative methods for nitrogen determination provide no means of distinguishing various types of nitrogen-containing groups. He proposed instead a colorimetric method based on the Greiss-Ilosvay sulfanilic acid reagent. The nitro compound is heated with potassium hydroxide solution, the mixture is cooled, water is added, and the alkaline solution is acidified with acetic acid and then treated with the Greiss-Ilosvay reagent[14]; a red color develops in the presence of a nitro group. Only a few of the many compounds investigated failed to respond to this test, and the list of inert compounds included no nitroparaffins.

Bost and Nicholson (47) give color tests for the identification of mono- and tri-nitro compounds which seem, however, more applicable to members of the aromatic series.

Scott, Treon, and other investigators at the Kettering Laboratory of Applied Physiology have developed colorimetric analyses for nitroparaffins. They have found it possible to use several reactions, such as that with ferric chloride, which produces a red color in the presence of acid. The color is believed to depend on the presence of aci-nitroparaffin. Absorption curves in the visible range show maxima at 500 mμ. At this wave length they follow Beer's law in the concentrations used. Data obtained by the analysis of air samples were presented (351). Machle, Scott, and Treon (241), in the work on the analysis of air–nitroparaffin mixtures, found that samples containing high concentrations of mononitroparaffins could be aspirated through a 50-cm. interferometer, but this method was not sufficiently sensitive for air containing lower concentrations, and chemical detection was therefore necessary. The samples were taken in evacuated bulbs in which the nitroparaffin was dissolved in alkali. The method was based on the color formed by heating nitromethane and vanillin in ammoniacal solution. This color does not follow Beer's law, so two known concentrations of nitromethane, one greater and one less than that of the unknown, must be determined at the same time.

These investigators also developed a color test for 1,1-dichloro-1-nitroethane. The dichloronitroparaffin is dissolved in methanol and treated with a 5 per cent solution of resorcinol in methanol, 5 per cent aqueous sodium hydroxide is added, and water is put in; after the solution has stood in an ice chest for 4 hr. a green color develops which becomes light yellow on acidification. The color is read against a water blank in 1-in. matched cells at 480 mμ on a spectrophotometer. From a previously prepared standardization curve, after subtraction of the blank, the result is read as milligrams of 1,1-dichloro-1-nitroethane. The standardization curve must be rechecked each time a new batch of alcohol is used. The blank is determined each time and is consistently low.

Manzoff (243) had previously developed a test based on the color resulting from the reaction of nitromethane with vanillin in the presence of ammonia.

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[14] Sulfanilic acid (0.5 g.) plus 150 ml. of 2 N acetic acid is mixed with a colorless solution prepared by adding 0.1 g. of pure α-naphthylamine to 20 ml. of boiling water.

He proposed it as a test for methanol in ethanol, since a mixture of the alcohols, converted to nitromethane and nitroethane *via* the Victor Meyer reaction, gives a red color, while nitroethane when similarly treated gives only a pale yellow color.

Desvergnes (84) described a colorimetric method for determination of nitroparaffins, which utilizes the reaction with bases to produce a yellow color. Since the color thus produced seems to vary somewhat with the temperature of reaction, high accuracy would not be predicted for this method unless the temperature were carefully controlled.

Ivett (174), using the dropping-mercury electrode, determined the half-wave potentials of six aliphatic nitro compounds in solutions containing an excess of sulfuric acid or sodium sulfate, and the possibility of determining these compounds quantitatively was investigated. The compounds were found to be reduced at a lower potential in acid than in neutral solutions. The ease of reduction increases with increasing molecular weight and is greater for secondary than for primary nitro compounds. The current flow was found to be proportional to the concentrations of nitroparaffins in acid solutions, but in the neutral solutions there were slight but reproducible deviations from this linear relationship.

Numerous analyses designed to determine chloropicrin and other halonitroparaffins appear in the literature (88, 97), and numerous stability tests usually applied to explosives (for example, the well-known Abel test (1)) have been extended to some of the nitroparaffins.

Macbeth and Pratt (240) have shown that in the case of most halogen-substituted nitromethanes the halogen is labile. Chlorotrinitromethane is reduced quantitatively according to the equation:

$$2CCl(NO_2)_3 + 4KOH + N_2H_4 \rightarrow 2CK(NO_2)_3 + N_2 + 4H_2O + 2KCl$$

This reaction may be used to estimate the amounts of different nitro compounds in a mixture.

Polynitroparaffins as analytical reagents

Because of their tendency to react with unsaturated compounds with the production of characteristic colors, many polynitro- or halonitro-paraffins have been employed as analytical reagents. Papers noting this means of characterizing the colored materials are too numerous to summarize but are listed with the compounds which may be so tested.

Harper and Macbeth (128) believe the colors are due to intermediate addition products and that the final products are colorless.

Clarke, Macbeth, and Steward (74) investigated a number of reactants, both organic and inorganic, and found that reagents prepared from polynitroparaffins give characteristic colors with compounds containing elements capable of showing valence changes.

Mononitroparaffins find other uses in analysis. Mulliken and Wakeman (280, 281) proposed the use of nitromethane as a group reagent in qualitative organic analysis. Alkanes, cycloalkanes, dicycloalkanes, alkenes (usually), cycloalkenes, and alkadienes containing eight or more carbon atoms are immiscible with nitromethane at 20°C. Aromatic compounds are much more soluble. The presence of an aromatic ring is indicated if an unknown hydrocarbon boiling in the ranges 100–220°C. and 220–300°C. shows miscibility at 20°C. and 55°C., respectively, with nitromethane.

TABLE 8

*Color tests using polynitroparaffins**

REAGENT	REACTANTS	INVESTIGATORS
Tetranitromethane	S^{--}	Harper and Macbeth (127)
Tetranitromethane	$-NH_2$ compounds	Harper and Macbeth (127)
Tetranitromethane	$C=C$	Harper and Macbeth (127)
Tetranitromethane	Unsaturated compounds	Hurd and Bollman (172)
Dibromodinitromethane	Unsaturated compounds	Hurd and Bollman (172)
Nitroform	Unsaturated compounds	Hurd and Bollman (172)
Tetranitromethane	Unsaturated compounds	Werner (400)
Tetranitromethane	Amines of androsterone series, etc.	Ruzicka (336)
Tetranitromethane	Unsaturated compounds	Ostromisslensky (293)
Dibromodinitromethane	Unsaturated compounds	Ostromisslensky (293)
Nitroform	Unsaturated compounds	Ostromisslensky (293)
Alkyl nitrites	S^{--}, $C=C$, $-NH_2$	Harper and Macbeth (128)
Tetranitromethane	Unsaturated compounds	Harper and Macbeth (129)
Substituted nitroforms	Unsaturated compounds	Graham and Macbeth (119)
Tetranitromethane	Sterols and aminosterols	Butenandt and Tscherning (62)
Tetranitromethane	Unsaturated compounds	Will (408)

* Other papers along similar lines are those of references 72, 116, 117, 176, 290, 328, 337, 371, 396. The list is not exhaustive.

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