THE REACTIONS OF NITROGEN TETROXIDE WITH ORGANIC COMPOUNDS

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I. INTRODUCTION

While certain reactions of nitrogen tetroxide with organic compounds were studied more than seventy-five years ago, no one has ever published a comprehensive review of this field. The variety of reactions which nitrogen tetroxide exhibits and the fact that in recent years it has become readily available at low cost make such a review seem very desirable.

The difficulties besetting this literature search and the interpretation of the experimental work should be stated at the outset. In much of the earlier work the authors allowed "nitrous fumes" (which generally referred to nitrogen trioxide) to react with organic compounds. These "nitrous fumes" were usually generated from arsenious oxide and nitric acid of various concentrations. Obviously, this reagent consisted not only of nitrogen trioxide but also of the equilibrium mixture of nitric oxide and nitrogen tetroxide. Since it has been demonstrated by Lunge (108) that the composition of "nitrous fumes" varies, depending upon the concentration of the nitric acid, it is obvious that the research done with this reagent is subject to criticism because one of the reactants was probably of unknown composition. While it may be assumed in some instances that the nitrogen tetroxide reacts independently of the nitric oxide, such is not necessarily the case. In some cases "nitrous fumes" give substantially the same products as pure nitrogen tetroxide. Accordingly, it was considered necessary to include for this study reactions in which "nitrous fumes" or nitrogen trioxide were used.

Studies involving the reaction of organic compounds with nitric oxide or nitrogen pentoxide, where these were the only oxides used, have been purposely omitted.

Many interesting investigations have been carried out by allowing organic compounds to react with either organic or inorganic nitrites in aqueous solutions of acids such as hydrochloric acid. The first step in most of these reactions is the formation of nitrous acid, which may in turn form oxides of nitrogen as well as nitric acid. Since these studies would lead to the consideration of diazotizations as well as other transformations, they have been considered outside the scope of this review. Most reactions of oxides of nitrogen in aqueous solutions have not been given consideration, because in such cases one is dealing with mixtures of nitric and nitrous acids.

Unfortunately, in many of the investigations the authors were not always clear as to whether the oxides of nitrogen and the solvents were dried before use. In much of the work yields of the products formed and the conditions of the experiments were not stated. It is reasonable to assume that some of the yields were not published because they were embarrassingly low. In many cases the proof of the nature of the products formed rested only on an analysis, which often leaves much to be desired.

Finally, the experimental work and its interpretation are often very difficult because of the multiplicity of products and the formation of explosive, unstable, and inseparable oils. Regardless of whether one starts with pure dry reagents, there is always the probability (especially at higher temperatures) of the partial oxidation of the organic compound to form water, which in turn gives rise to more or less nitric and nitrous acids.

At best one is often dealing with a mixture of reactants. Accordingly, it is well to be charitable with any criticism concerning yields of products or interpretations offered in this area of research.

Because of the difficulties and uncertainties pointed out above, it is clear that much of the work already done needs repetition under conditions controlled as accurately as possible. In view of the availability of low-cost nitrogen tetroxide, some of these reactions should be of commercial value.

The reactions of nitrogen tetroxide may be classified under six main headings: (*1*) nitration, (*2*) oxidation, (*3*) reactions with compounds containing carbon–carbon multiple bonds, (*4*) reactions with alkali metal salts of organic acids, (*5*) reactions with organometallic compounds, (*6*) miscellaneous. In some instances these reactions are difficult to classify because several types may take place simultaneously.

II. STRUCTURE AND PROPERTIES OF NITROGEN TETROXIDE

Nitrogen tetroxide has long been regarded as an equilibrium mixture, as indicated by the following equation:

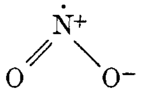
$$N_2O_4 \rightleftharpoons 2NO_2$$

The dimolecular form is predominant at lower temperatures, but vapor-density measurements indicate complete conversion to the monomolecular form above 140°C. At 26.7°C. about 20 per cent of the tetroxide exists in the simpler form. In appearance nitrogen tetroxide varies from colorless crystals at -50°C. to black vapor at 183°C.; near room temperature the mixture is brown. The color changes are assumed to be related to the state of the equilibrium. It is believed that above 140°C. nitrogen tetroxide decomposes to form nitric oxide and oxygen, a change which is complete at 619.5°C. (117).

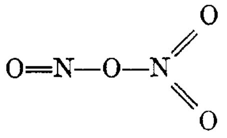
The boiling point of nitrogen tetroxide is reported variously from 20°C. to 69°C. (10). *International Critical Tables* gives 21.3°C. at 760 mm. The boiling point of 69°C. was reported for the substance after it had stood for one year in a sealed tube with phosphorus pentoxide. The high boiling point observed after intensive drying may indicate a change in molecular state. The melting point of nitrogen tetroxide is -11.5°C.

As would be expected nitrogen tetroxide is toxic, since it reacts with water to give nitric acid (98). Animals exposed to a concentration of one part per thousand die in a few minutes. Concentrations greater than five parts per million are harmful (103).

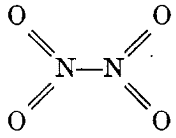
Nitrogen dioxide is an odd molecule and is paramagnetic (130a). Infrared studies indicate that the molecule is triangular in shape.



The structure of nitrogen tetroxide has not been clearly established (117). The three arrangements given in the older literature are shown by formulas I, II, and III. The modern counterparts of I and II are shown by formulas Ia and IIa (88a).



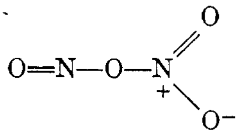
I



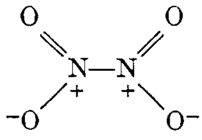
II

$$O{=}N{-}O{-}O{-}N{=}O$$

III



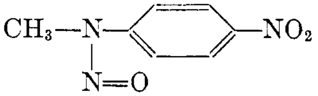
Ia



IIa

X-ray analysis of solid nitrogen tetroxide gives evidence for structure IIa. However, the N—N bond is weak, as indicated by the very small free-energy change of 1.2 Calories per mole for the dimerization of nitrogen dioxide (130a). The N—N bond is also abnormally long, 1.6 to 1.7 Å., whereas the usual single-bond N—N distance is about 1.4 Å.

Chemical evidence bearing on the above structures rather favors formula I (or Ia). Houston and Johnson (91) have assembled a series of arguments in favor of formula I. They point out that this formula shows nitrogen with valences of three and five, in accord with its reaction with water to produce both nitric and nitrous acids. Formulas II and III show nitrogen with a valence of five or three, respectively. The presence of a nitroso group is inferred from the reaction of methylphenylamine to form *N*-methyl-*N*-nitroso-*p*-nitroaniline (211):



The reaction with malonic ester to produce as the first step both nitro- and isonitroso-malonic esters (25) would follow from formula I. Alkyl halides were reported by Henry (90) to form alkyl nitrates, a fact which also would be in accord with formula I. Finally, the observation by Bamberger (11) that diphenylmercury gave nitrosobenzene and mercury phenyl nitrate would clearly suggest that both nitroso and nitrate groups were present in the original molecule.

The arguments in favor of formulas II and III are generally less weighty. Meyer (119) concluded that formula III was correct on the basis of the reduction of the addition product of nitrogen tetroxide with amylene. This reduction gave no diamine; Meyer took this as evidence that the compound was $C_5H_{11}(ONO)_2$ and that it contained no carbon–nitrogen linkage. His dinitrite formula was later shown to be incorrect (121).

Nitrations with nitrogen tetroxide and possibly its thermal decomposition into nitric oxide and oxygen may be explained by formula II.

Schaarschmidt (171) suggested that nitrogen tetroxide might be considered an equilibrium mixture of I, II, and III.

III. NITRATION WITH NITROGEN TETROXIDE AND NITROGEN TRIOXIDE

(SEE TABLE 1)

A. *Aromatic hydrocarbons*

In general it seems safe to say that for the majority of nitrations nitrogen tetroxide offers no advantage over the classical methods using nitric and sulfuric acid mixtures. It has the disadvantage of being gaseous and accordingly more difficult to handle. In the preparation of certain specific isomers it may have an advantage.

As might be expected, the reaction of benzene with nitrogen tetroxide has probably been studied more than that of any other single aromatic compound and under a greater variety of conditions. The results have been variable.

As early as 1880, Leeds (100, 101) treated benzene with nitrogen trioxide at a low temperature for several days and reported the formation of nitrobenzene, oxalic acid, and picric acid. Yields were not stated. Apparently most of the benzene was recovered unchanged. The products formed with the reagents at the boiling point of benzene were not clearly established. Friedburg (63, 64) modified Leeds's experiment by first dissolving the nitrogen trioxide in carbon disulfide and then mixing this solution with benzene; he obtained a mixture of nitrobenzene and *p*-dinitrobenzene.

Wieland (244) allowed dry benzene and nitrogen tetroxide to react in a sealed tube at 80°C. for 6 hr. and obtained a low yield of nitrobenzene, 1,3,5-trinitrobenzene, picric acid, oxalic acid, and unidentified products. When these same reagents were allowed to stand 35 days at room temperature, more than 30 per cent of the benzene was converted to nitrobenzene (175) and unidentified products were formed. When Bass and Johnson (15) sealed dry benzene and nitrogen tetroxide in a tube and stored the mixture in the dark for three months, a trace of nitrobenzene was formed and most of the benzene was recovered. The same experiment carried out in sunlight resulted in an increased yield of nitrobenzene, accompanied by the formation of some *m*-dinitrobenzene and a 60 per cent recovery of the benzene.

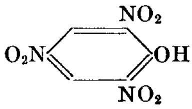
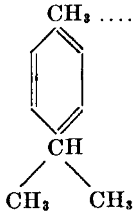
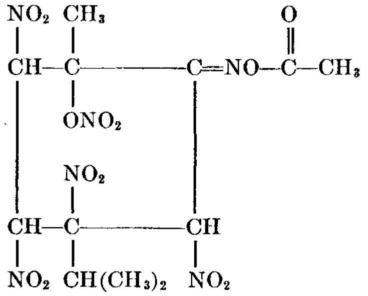
More promising results were obtained by Shorygin and Topchiev (200, 203), who produced yields of nitrobenzene as high as 65 per cent by allowing benzene and nitrogen tetroxide to react in the vapor phase diluted with an inert gas such as carbon dioxide or nitrogen. McKee and Wilhelm (109) produced nitrobenzene in yields as high as 36 per cent by passing benzene and nitrogen tetroxide over silica gel at 300–330°C. Activated alumina, pumice, titanium dioxide, or dehydrated bauxite substituted for the silica gel was ineffective as catalyst. German patent 207,170 (69) claimed that zinc oxide and cupric oxide (and other weakly basic metallic oxides) are effective in catalyzing the vapor-phase nitration of aromatic compounds with oxides of nitrogen (69). Anhydrous aluminum chloride and ferric chloride are also believed to catalyze the reaction of benzene with nitrogen tetroxide (21, 171, 215). When benzene and nitrogen tetroxide were allowed to stand at low temperature in the presence of mercury, dinitrophenol (isomer unstated) was formed (70).

Another interesting variation has been to mix benzene with 90–95 per cent sulfuric acid and then introduce nitrogen tetroxide at relatively low temperatures (17, 131, 149). By means of this procedure yields of nitrobenzene as high as 98 per cent have been obtained (218). Obviously, this method approaches the usual nitric–sulfuric acid nitration method, but the idea might be useful.

When benzene and nitrogen tetroxide were subjected to a glow discharge in a Siemens type of tube, nitrobenzene, *m*-dinitrobenzene, and trinitrophenol were formed (8).

The reactions of nitrogen tetroxide with toluene do not present as clear a picture as those with benzene because of the mixtures of isomers which may form. These reactions are further complicated because under some conditions oxidation

TABLE 1
Nitration

COMPOUND NITRATED	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
C_6H_6	N_2O_4	$C_6H_5NO_2$, m-$C_6H_4(NO_2)_2$,  p-$C_6H_4(NO_2)_2$, 1,3,5-$C_6H_3(NO_2)_3$	(15, 17, 21, 63, 64, 109, 131, 149, 175, 200, 203, 215, 218, 244)
C_6H_6	N_2O_3	$C_6H_5NO_2$, oxalic acid, picric acid	(100, 101)
$C_6H_5CH_3$	N_2O_4	o-$NO_2C_6H_4CH_3$, $C_6H_5CH_2NO_2$, $C_6H_5CH(NO_2)_2$, p-$NO_2C_6H_4CH_3$, $C_6H_5CH_2NO$, $(COOH)_2$, C_6H_5COOH, C_6H_5OH, C_6H_5CHO, $C_6H_5CH_2NO_2$	(17, 131, 175, 200, 201, 215, 216, 217, 218)
	N_2O_3		(147)
Naphthalene	N_2O_4	1-Nitronaphthalene, 1,5-dinitronaphthalene, 1,8-dinitronaphthalene	(131, 203)
Anthracene	N_2O_4	9,10-Dinitro-9,10-dihydroanthracene (heated with pyridine gave 9-nitroanthracene)	(14, 116)
		9,10-Dinitroanthracene, 9-nitroanthracene	(203)

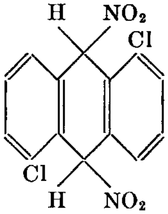
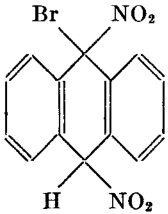
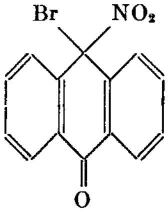
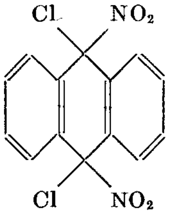
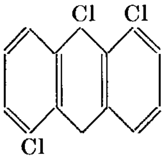
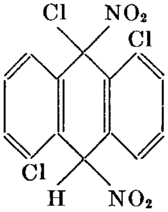
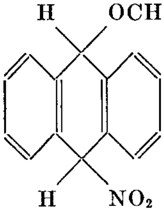
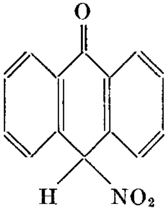
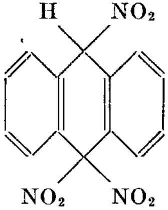
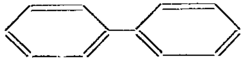
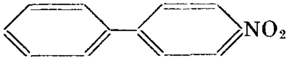
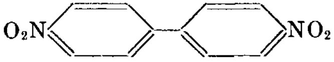
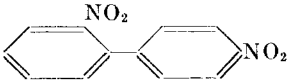
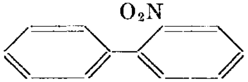
9-Phenylanthracene	N_2O_4	10-Nitro-9-phenylanthracene	(14)
9-Nitroanthracene	N_2O_4	Intermediate (heated with pyridine gave 9,10-dinitroanthracene)	(14)
1-Chloroanthracene	N_2O_4	Intermediate (heated with pyridine gave 1-chloro-9(or 10)-dinitroanthracene)	(14)
1,5-Dichloroanthracene	N_2O_4		(14)
1,8-Dichloroanthracene	N_2O_4	Intermediate (heated with pyridine gave 1,8-dichloro-9(or 10)-nitroanthracene)	(14)
9-Bromoanthracene	N_2O_4		(14)
9,10-Dibromoanthracene	N_2O_4		(14)

TABLE 1—*Continued*

COMPOUND NITRATED	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
9,10-Dichloroanthracene	N_2O_4		(14)
	N_2O_4		(14)
	N_2O_3	 	(116)
	N_2O_3 or N_2O_4	   	(63, 64, 127, 203)

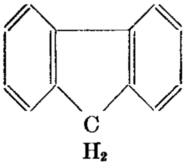
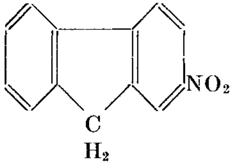
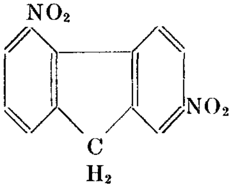
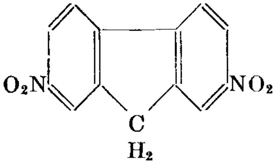
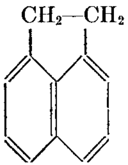
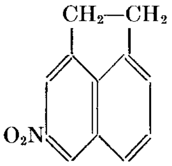
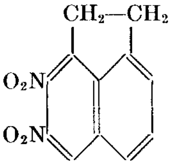
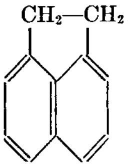
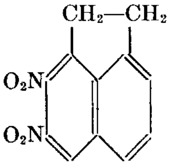
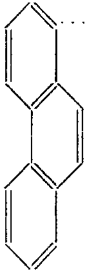
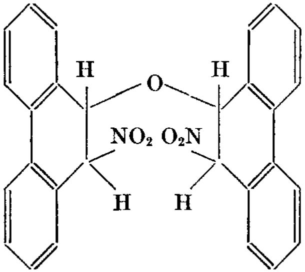
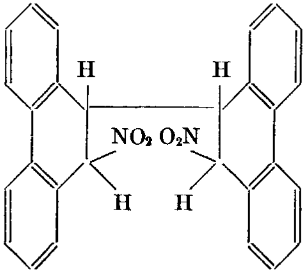
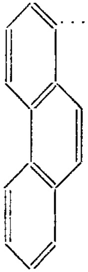
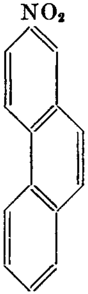
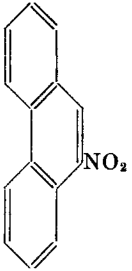
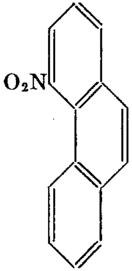
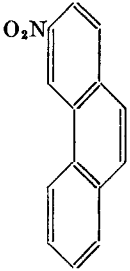
	N_2O_3 or N_2O_4	  	(127)
	N_2O_3	 	(127)
	N_2O_4		(127)

TABLE 1—*Continued*

COMPOUND NITRATED	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
	N_2O_3	 	(181)
	N_2O_4	   	(203)
C_6H_5F	N_2O_4	*p*-$FC_6H_4NO_2$, *o*-$FC_6H_4NO_2$	(172, 173)
C_6H_5Cl	N_2O_4	*p*-$NO_2C_6H_4Cl$ and isomers	(17, 170, 172, 173, 215, 218)
C_6H_5Br	N_2O_4	*p*-$BrC_6H_4NO_2$, *o*-$BrC_6H_4NO_2$	(172, 173)

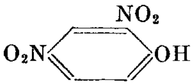
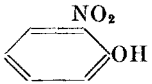
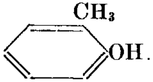
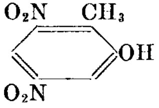
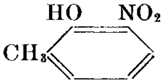
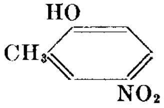
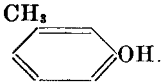
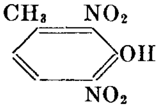
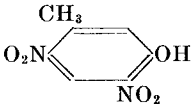
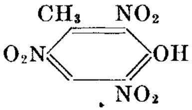
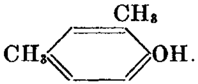
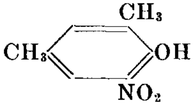
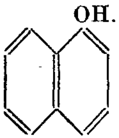
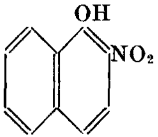
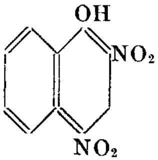
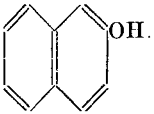
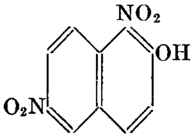
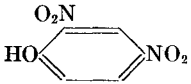
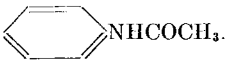
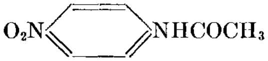
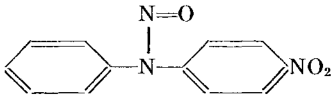
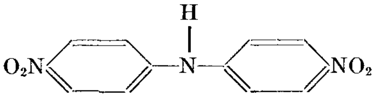
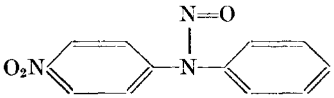
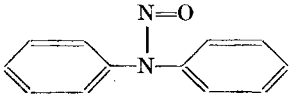
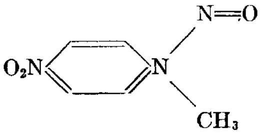
C_6H_5I	N_2O_4	p-$IC_6H_4NO_2$, o-$IC_6H_4NO_2$	(172, 173)
p-$ClC_6H_4NO_2$	N_2O_4	1,2,3,5-$C_6H_2Cl(NO_2)_3$	(215)
C_6H_5OH	N_2O_3	p-$NO_2C_6H_4OH$, o-$NO_2C_6H_4OH$, 2,4-$C_6H_3OH(NO_2)_2$, 2,4,6-$C_6H_2OH(NO_2)_3$	(63, 64, 102, 203)
C_6H_5OH	N_2O_4	  	(148, 244)
C_6H_5ONa	N_2O_4	o-$HOC_6H_4NO_2$, p-$HOC_6H_4NO_2$	(177)
	N_2O_4	  	(148, 244)
	N_2O_4	  	(148, 203)
	N_2O_4		(244)
	N_2O_4	 	(244)

TABLE 1—*Continued*

COMPOUND NITRATED	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
	N_2O_4		(203)
$C_6H_5NH_2$	N_2O_4	 	(203)
	N_2O_4		(203)
$(C_6H_5)_2NH$	N_2O_3	(p-$NO_2C_6H_4)_2NH$, (2,4-$(NO_2)_2C_6H_3)_2NH$	(63, 64)
		 	(211)
$(C_6H_5)_2NH$	N_2O_4	 	(244)
$C_6H_5NHCH_3$	N_2O_4		(211)
$C_6H_5N(CH_3)_2$	N_2O_4	p-$O_2NC_6H_4N(CH_3)_2$	(173, 203)

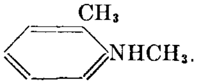
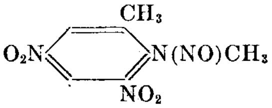
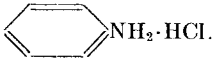
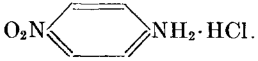
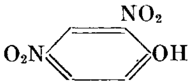
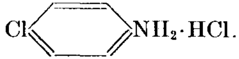
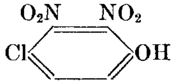
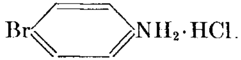
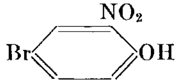
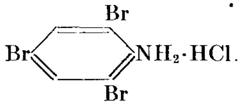
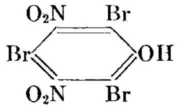
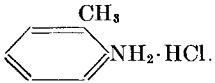
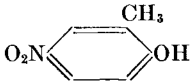
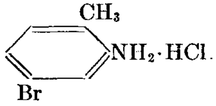
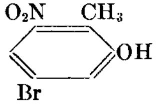
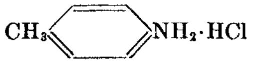
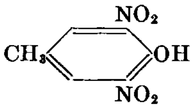
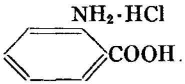
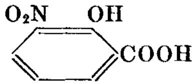
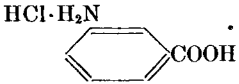
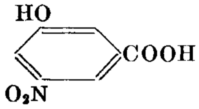
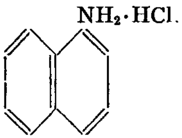
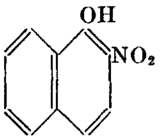
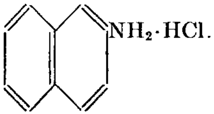
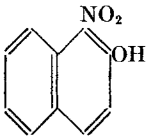
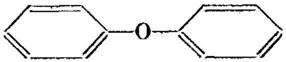
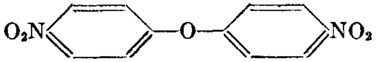
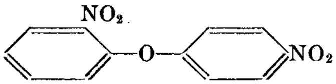
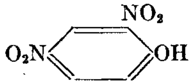
	N_2O_3		(211)
	N_2O_3		(227)
	N_2O_3		(227)
	N_2O_3		(227)
	N_2O_3		(227)
	N_2O_3		(227)
	N_2O_3		(227)
	N_2O_3		(227)

TABLE 1—*Continued*

COMPOUND NITRATED	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
	N_2O_3		(227)
	N_2O_3		(227)
	N_2O_3		(227)
	N_2O_3		(227)
	N_2O_3		(227)
	N_2O_4	  	(158, 160)

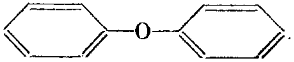
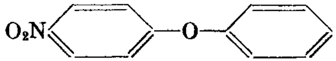
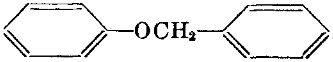
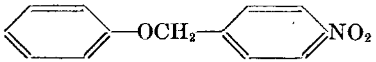
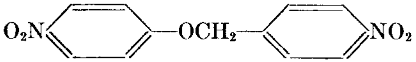
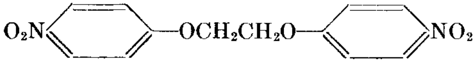
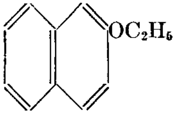
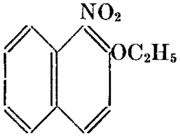
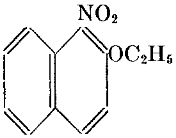
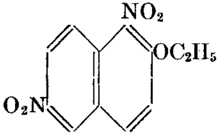
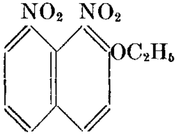
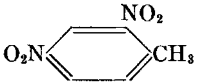
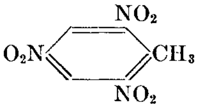
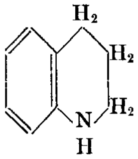
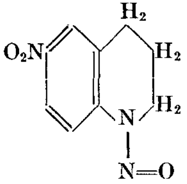
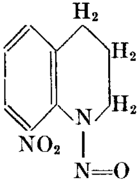
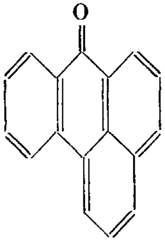
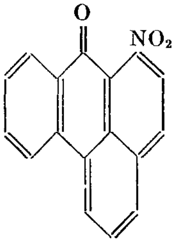
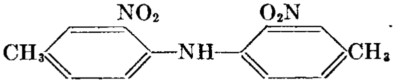
	N_2O_3		(160)
	N_2O_4	 	(163)
	N_2O_4		(165)
	N_2O_3 or N_2O_4		(164)
	N_2O_4	 	(164)
$(CH_3)_2CHCH_2CH_2OC_6H_5$	N_2O_4	Product which on reduction gave $(CH_3)_2CHCH_2CH_2OC_6H_4NH_2$-*p*	(53, 54)
$C_6H_5NO_2$	N_2O_4	$C_6H_4(NO_2)_2$	(215)
p-$CH_3C_6H_4NO_2$	N_2O_4	 	(215)
Pyridine	N_2O_4	3-Nitropyridine	(202)

TABLE 1—*Continued*

COMPOUND NITRATED	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
Quinoline	N_2O_4	7-Nitroquinoline, 5,7-dinitroquinoline	(202)
Cyclohexane	N_2O_4	Nitrocyclohexane	(200)
	N_2O_3	 	(211)
p-$CH_3C_6H_4NHSO_2C_6H_4CH_3$	N_2O_4	4,2-$CH_3(NO_2)C_6H_3NHSO_2C_6H_4CH_3$ 4,2,6-$CH_3(NO_2)_2C_6H_2NHSO_2C_6H_4CH_3$ 4,2,6-$CH_3(NO_2)_2C_6H_2N(N{=}O)SO_2C_6H_4CH_3$	(14)
	N_2O_4		(99)
$(C_6H_5)_2N{=}O$	N_2O_4	$(p$-$O_2NC_6H_4)_2N{=}O$	(252)
$(C_6H_5)_2NOH$	N_2O_4	$(p$-$O_2NC_6H_4)_2N{=}O$	(252)
$(p$-$CH_3C_6H_4)_2NOH$	N_2O_4		(252)

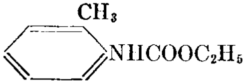
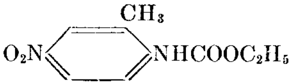
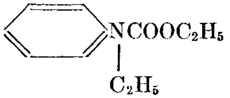
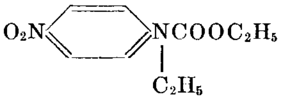
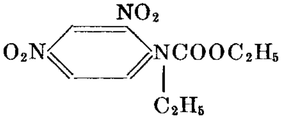
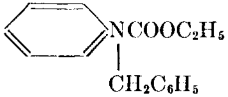
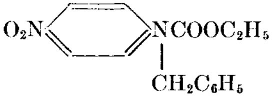
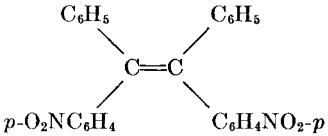
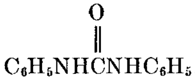
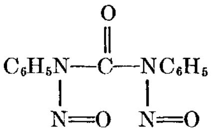
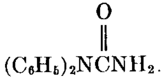
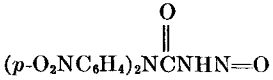
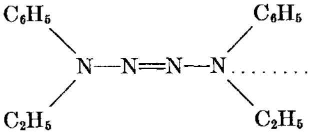
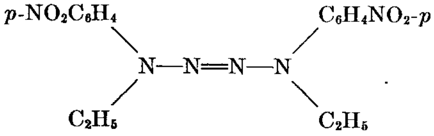
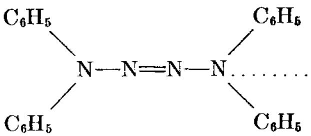
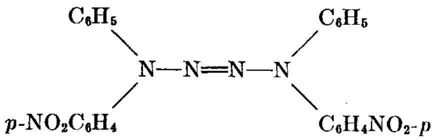
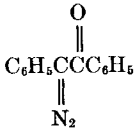
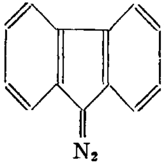
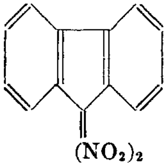
	N_2O_4		(157, 161)
	N_2O_4	 	(156)
$(C_6H_5)_2NCOOC_2H_5$	N_2O_4	$(p\text{-}O_2NC_6H_4)_2NCOOC_2H_5$	(159, 161)
	N_2O_4		(167)
$(C_6H_5)_2C{=}C(C_6H_5)_2$	N_2O_4		(178)
$C_6H_5NHCONH_2$	N_2O_3 or N_2O_4		(168)
 $C_6H_5NH\overset{O}{\overset{\Vert}{C}}NHC_6H_5$	N_2O_3 or N_2O_4	 	(168)

TABLE 1—*Continued*

COMPOUND NITRATED	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
 $(C_6H_5)_2N\overset{\overset{O}{\|}}{C}NH_2$	N_2O_3	 $(p\text{-}O_2NC_6H_4)_2N\overset{\overset{O}{\|}}{C}NHN{=}O$	(168)
	N_2O_4		(251)
	N_2O_4		(251)
$N_2{=}CHCOOC_2H_5$	N_2O_4	$(NO_2)_2CHCOOC_2H_5$	(251)
 $C_6H_5\underset{\underset{N_2}{\|}}{C}\overset{\overset{O}{\|}}{C}C_6H_5$	N_2O_4	$C_6H_5CH(NO_2)_2$	(251)

	N_2O_4		(251)
CH_4	N_2O_4	CH_3NO_2	(221, 226)
$CH_3CH_2CH_3$	N_2O_4	CH_3NO_2, $CH_3CH_2NO_2$, $CH_3CH_2CH_2NO_2$, $CH_3CH(NO_2)CH_3$	(86, 87, 221, 226)
$CH_3(CH_2)_nCH_3$ ($n = 3$ to 7)	N_2O_4	$CH_3(CH_2)_nCH_2NO_2$, $O_2NCH_2(CH_2)_nCH_2NO_2$	(222, 223, 224, 225, 226)

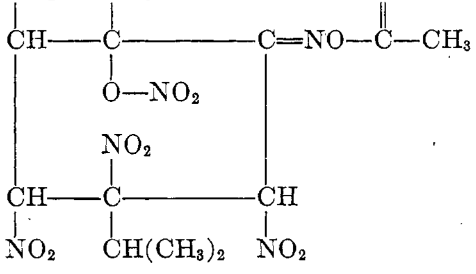
of the side chain occurs. Leeds (102) allowed toluene to react with nitrogen trioxide and reported the formation of oxalic acid, benzoic acid, dihydroxybenzoic acid (orientation unstated), *o*-nitrotoluene, and a methyldinitrodihydroxybenzene. The conditions of the reaction were poorly defined, and the yields were not stated. Schaarschmidt and Smolla (175) mixed toluene with technical nitrogen tetroxide at room temperature and allowed these mixtures to stand for varying periods of time (32–108 days). They obtained yields of 19–35 per cent oxalic acid, 31–59 per cent benzoic acid, 0–0.5 per cent phenol, 0.5–21 per cent benzaldehyde, and 41–44 per cent nitrotoluenes. Bass and Johnson (15) observed no evidence of nitration when dry nitrogen tetroxide and toluene were sealed in a tube and allowed to stand. About 63 per cent of the toluene was recovered, and about a 25 per cent yield of benzoic acid was produced. No nitration was observed when the same mixture was sealed in a quartz tube and exposed to a quartz mercury arc at 55°C. for 4 hr.

When nitrogen tetroxide diluted with carbon dioxide was allowed to react with toluene for 2 hr. at 140–145°C., a 45 per cent conversion to nitrotoluenes was observed with the simultaneous formation of 4–8.3 per cent of nitrophenylmethane (α-nitrotoluene). The presence of ultraviolet light generally increased the yields (200). At 14°C. and without carbon dioxide as a diluent some nitrosophenylmethane was formed (201). Titov (216, 217) found a slight tendency for nitrogen tetroxide to cause nitration in the benzene ring but obtained mainly nitrophenylmethane, dinitrophenylmethane, and oxidation products, the latter being formed especially at higher temperatures (218).

When toluene was treated with nitrogen tetroxide in the presence of 90–94 per cent sulfuric acid, yields of mixed nitrotoluenes as high as 98 per cent were observed (17, 131, 218). Aluminum chloride also favored the formation of nitrotoluenes (215).

Xylene and mesitylene seemed to react with nitrogen tetroxide; evidently the products were a complex mixture (175). According to Leeds (102) xylene (isomer not stated) reacted with nitrogen trioxide to give oxalic acid, a nitroxylene, *p*-toluic acid, and phthalic acid.

p-Cymene reacted with nitrogen trioxide to produce *p*-toluic acid, oxalic acid, and a nitrocymene (100, 101, 102). However, Puranen (147) found that *p*-cymene reacted with nitrogen tetroxide in acetic acid solution to give a compound to which formula I was assigned.



I

Naphthalene reacted with nitrogen trioxide to produce a mixture of nitronaphthalenes (100, 101). Shorygin and Topchiev (203) obtained a quantitative conversion of naphthalene to 1-nitronaphthalene by heating equimolar portions of naphthalene and nitrogen tetroxide at 150°C. Under other conditions various polynitro derivatives were formed. A high yield of 1-nitronaphthalene was also obtained by Pinck (131) by allowing the above substances to react in the presence of concentrated sulfuric acid.

Leeds (102) obtained a good yield of anthraquinone by adding nitrogen trioxide to anthracene in acetic acid. When no solvent was used, anthraquinone and an unidentified red oil were formed. Liebermann (106), using the same reagents, obtained 9-nitrosoanthrone and other products.

Anthracene and nitrogen tetroxide suspended in benzene reacted to give only a trace of anthraquinone (15). Anthracene in nitrobenzene was converted to anthraquinone in high yields (92). Meisenheimer and Connerade (116), as well as Barnett (14), carried out the same reaction in chloroform and obtained 9,10-dinitro-9,10-dihyrdoanthracene. Using the same reagents and solvent Shorygin and Topchiev (203) reported a 40 per cent yield of 9,10-dinitroanthracene along with 4–8 per cent of 9-nitroanthracene. It is not probable that both of these latter reports can be correct, since the conditions of the experiments seem to be substantially the same. The above examples, from which markedly different results were obtained depending on the solvent used, serve to illustrate the importance of the solvent in reactions involving nitrogen tetroxide.

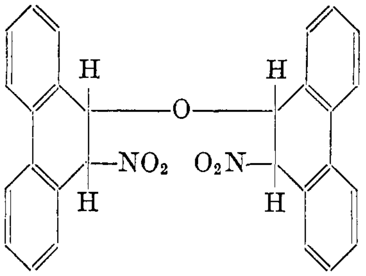
Biphenyl was treated with nitrogen tetroxide under various conditions. When the reagents were mixed at room temperature 4-nitrobiphenyl and 2-nitrobiphenyl were produced (63, 64, 203). Monti *et al.* (127) reported an almost 100 per cent yield of 4-nitrobiphenyl when the reaction was carried out using "nitrous vapors" without a solvent. When acetic acid, ether, ligroin, or benzene was used as solvent at 0–25°C., no nitration took place. With acetic acid as solvent at 90–95°C., both 4,4′- and 2,4′-dinitrobiphenyl were formed.

When fluorene reacted in various solvents with "nitrous vapors" (127) near room temperature, 2-nitrofluorene was obtained in yields as high as 70 per cent. When the reaction was carried out in acetic acid at 90–95°C., a mixture of 2,5- and 2,7-dinitrofluorenes was formed; with pure nitrogen tetroxide only 2-nitrofluorene was reported.

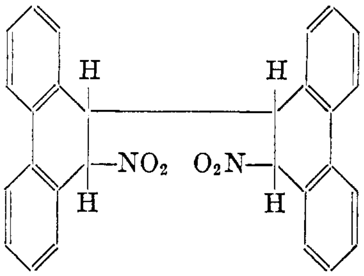
Acenaphthene was nitrated with "nitrous fumes," using ether or petroleum ether as solvent; a 90–95 per cent yield of 5-nitroacenaphthene was formed. In benzene or acetic acid at 8–10°C., 5,6-dinitroacenaphthene was produced. When nitrogen tetroxide was used without a solvent, acenaphthene reacted very vigorously even at low temperatures, giving 5,6-dinitroacenaphthene (127).

When triphenylmethane was treated with "nitrous vapors" at room temperature in various solvents, triphenylcarbinol was formed (127). Neither diphenylmethane nor 1,2-diphenylethane reacted with "nitrous" fumes at 15–20°C.

Schmidt (181) allowed phenanthrene to react with nitrogen trioxide and obtained a small yield of products which he named bismononitrodihydrophenanthrene oxide (II) and bismononitrodihydrophenanthrene (III).



II



III

Nitrogen tetroxide and phenanthrene at 0°C. formed a mixture of isomers including the 2-nitro- (32 per cent), 9-nitro- (11 per cent), 4-nitro- (3 per cent), and a small amount of 3-nitro-phenanthrene (203)

B. Halogenated aromatic compounds

In general the simple halogenated aromatic compounds do not nitrate very efficiently with nitrogen tetroxide in the absence of concentrated sulfuric acid, aluminum chloride, or other catalytic agents (173). Fluorobenzene did not react with nitrogen tetroxide in carbon tetrachloride solution even after 72 hr. of contact. Iodobenzene under the same conditions was converted to the extent of 45 per cent to a mixture of *o*- and *p*-iodonitrobenzenes. Chloro- and bromobenzenes behaved similarly to iodobenzene with lower conversions. *p*-Chlorotoluene gave *p*-chlorobenzoic acid and unidentified nitration products (175). Purgotti (148) reported no nitration of bromobenzene, symmetrical tribromobenzene, 1,2,3,4-tetrabromobenzene, or hexabromobenzene by nitrogen tetroxide in various solvents. When chlorobenzene was nitrated in the presence of concentrated sulfuric acid, *p*-nitrochlorobenzene was the main product (17).

With aluminum chloride, ferric chloride, or phosphorus pentachloride as catalysts, nitrations of halogenated benzenes by means of nitrogen tetroxide have been more successful (170, 172, 173, 215). Titov (215) obtained a 96 per cent yield of the isomeric nitrochlorobenzenes from chlorobenzene. Comparable results have been obtained with fluoro-, bromo-, and iodo-benzenes. The *p*-nitro derivative was formed in the greatest proportion in all cases observed, usually to the extent of 90 per cent or more of the isomeric mixture. With homologues such as the chlorotoluenes, oxidation as well as nitration occurred. Schaarschmidt (170, 172) suggested that these reactions proceed with the intermediate formation of complexes of the type shown in formula IV:

$$2AlCl_3 \cdot 3(C_6H_5Cl:N_2O_4)$$

IV

These complexes decompose upon addition of water to give an unstable product (V), which then forms the nitro derivatives.

$$C_6H_5Cl:N_2O_4$$

V

Barnett (14) treated various chloroanthracene derivatives with dry nitrogen tetroxide in carbon tetrachloride. 1-Chloroanthracene gave an addition compound which when heated with pyridine gave 1-chloro-9(or 10)-nitroanthracene. 1,5-Dichloroanthracene gave 1,5-dichloro-9,10-dinitro-9,10-dihydroanthracene, which upon heating with pyridine gave 1,5-dichloro-9-nitroanthracene. 9-Bromoanthracene gave 9-bromo-9,10-dinitro-9,10-dihydroanthracene, which upon heating with pyridine gave 9,10-dinitroanthracene. 9,10-Dichloro- and 9,10-dibromo-anthracenes gave unstable intermediate products which readily changed to produce anthraquinone.

C. Phenolic compounds

In the reaction of nitrogen trioxide with phenol Leeds (102) reported much carbonization with the formation of picric acid. The conditions of the experiment were not clearly defined. Nitrogen trioxide dissolved in carbon bisulfide reacted with phenol to give *o*- and *p*-nitrophenols and nitrosophenol (63, 64).

With nitrogen tetroxide phenol was readily nitrated, giving a mixture of the *o*- and *p*-nitro derivatives in good yields (60, 244). When chloroform or carbon tetrachloride was used as solvent, 2,4-dinitrophenol was the main product (148, 203). Anisole and phenetole under comparable conditions did not react.

Sodium phenoxide in carbon bisulfide reacted with nitrogen tetroxide to form a mixture of *o*- and *p*-nitrophenols (177) with the simultaneous formation of sodium nitrite.

Cresols when nitrated with nitrogen tetroxide generally formed polynitro derivatives (148, 203, 244). There is wide speculation as to which isomers are formed. The treatment of halogenated phenols with nitrogen tetroxide leads to ill-defined mixtures.

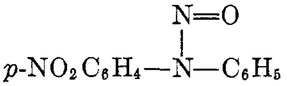
More promising results were reported by Shorygin and Topchiev (203) when 2-naphthol was allowed to react with nitrogen tetroxide in chloroform. About an 80 per cent yield of 1,6-dinitro-2-naphthol was formed.

D. Aromatic and aromatic-aliphatic amines

Vigorous reactions were observed by Leeds (102) when aniline, *p*-toluidine, and xylidine were brought in contact with nitrogen trioxide, but no definite products were obtained. Friedburg (63, 64) obtained 4-nitrodiphenylamine and 2,4-dinitrodiphenylamine by allowing diphenylamine to react with nitrogen trioxide in carbon disulfide solution.

According to Filippuichev and Petrov (57) and San Fourche and Bureau (169), primary aromatic amines are readily diazotized when treated with oxides of nitrogen (57). Varma and Krishnamurthy (227) allowed a series of aromatic amines (in the form of their hydrochlorides) to react with nitrogen trioxide; they generally obtained nitrophenols as products. In all instances reported the amino group was removed from the aromatic ring. For example, aniline hydrochloride was converted to 2,5-dinitrophenol; *p*-nitroaniline to 2,4-dinitrophenol; *p*-toluidine to 2,6-dinitro-*p*-cresol; *o*-aminobenzoic acid to 3-nitrosalicylic acid; and 1-aminonaphthalene to 2-nitro-1-naphthol.

Ryan and Egan (161) allowed diphenylamine to react with nitrous acid (presumably nitrogen trioxide) and obtained compound VI.



$$p\text{-}NO_2C_6H_4-\overset{\overset{\displaystyle N=O}{|}}{N}-C_6H_5$$

VI

Similar results were obtained by Stoermer (211).

Stoermer (211) allowed a series of mixed aromatic-aliphatic amines to react with nitrogen trioxide or with nitrogen tetroxide in various solvents. In all instances reported the *N*-nitroso derivative was formed. In some instances nitration in the ring took place at the same time. As illustrations, methyl-*m*-tolylamine and nitrogen trioxide produced methyl-3,5-dinitrotolyl-*N*-nitrosoamine; ethyl-*p*-nitrophenylamine gave ethyl-*p*-nitrophenyl-*N*-nitrosoamine; and methyl-*p*-nitrophenylamine gave methyl-*p*-nitrophenyl-*N*-nitrosoamine.

Aniline reacted with nitrogen tetroxide in chloroform solution to give a 23 per cent yield of 2,4-dinitrophenol and a small quantity of *p*-nitroaniline (203). In benzene solution Witt (256) obtained a quantitative yield of benzenediazonium nitrate. Acetanilide under the same conditions produced 60 per cent of *p*-nitroacetanilide and 30 per cent of the ortho isomer, while *N*,*N*-dimethylaniline gave as high as 86 per cent of *p*-nitrodimethylaniline (173) and traces of the meta isomer.

Wieland (244) found that acetanilide and nitrogen tetroxide reacted in cold ether to form benzenediazonium nitrate and acetic acid and that *p*-dimethylaminoacetanilide gave no diazonium salt. Diphenylamine and nitrogen tetroxide reacted in cold ether to produce *N*-nitrosodiphenylamine, while in cold benzene or petroleum ether some *N*-nitrosodiphenylamine along with *p*-nitro-*N*-nitrosodiphenylamine was formed.

Ryan and Egan (161) reported an indefinite mixture of polynitro derivatives from the reaction between triphenylamine and nitrogen tetroxide.

p-Nitroaniline reacted with nitrogen tetroxide in benzene to give a mixture of 4,4′-dinitrodiazoaminobenzene and *p*-nitrobenzenediazonium nitrate. Either product could be formed in high yield depending on the conditions (91).

Battlegay and Kern (16) allowed *p*-toluenesulfonyl-*p*-toluidide to react with nitrogen tetroxide and obtained a mixture of *p*-toluenesulfonyl-2,4-dinitro-*p*-toluidide, *p*-toluenesulfonyl-*p*-2,6-dinitrotoluidide, and the *N*-nitroso derivative of the latter compound. Other *p*-toluenesulfonyl derivatives of highly substituted aromatic amines gave mainly the *N*-nitroso derivatives in high yields.

E. Aromatic ethers

In general the aromatic ethers which have been allowed to react with nitrogen tetroxide have produced a mixture of mono and (or) dinitro derivatives (14, 53, 54, 116, 158, 160, 161, 163, 164, 165). This type of reaction has been studied mainly by Ryan *et al.* Diphenyl ether gave 2,4′- and 4,4′-dinitrodiphenyl ether and 2,4-dinitrophenol. 4-Nitrodiphenyl ether was formed when acetic acid was used as a solvent. Here, as in many other instances, the solvent has an important bearing on the course of the reaction. In some reactions considerable oxidation accompanied the nitration.

F. Miscellaneous aromatic and heterocyclic compounds

Salicylic acid reacted with nitrogen tetroxide to form 5-nitrosalicylic acid and picric acid (60). Nitrobenzene failed to undergo further nitration with nitrogen tetroxide even in the presence of aluminum chloride. Negative results were also obtained with benzoyl chloride and *p*-xylene, a result which is surprising, particularly for the latter compound (215).

With fuming sulfuric acid and nitrogen tetroxide at 5–7°C., nitrobenzene reacted to give dinitrobenzene (isomer not stated) in a 97.6 per cent yield. The same method with *p*-nitrotoluene gave a high yield of a mixture of 2,4-dinitro- and 2,4,6-trinitro-toluenes, while *p*-chloronitrobenzene gave a 98 per cent yield of trinitrochlorobenzene. *p*-Nitrotoluene reacted with fuming sulfuric acid, potassium persulfate, and nitrogen tetroxide to produce a 97.1 per cent yield of 2,4-dinitrotoluene.

Thiophene reacted with nitrogen tetroxide to give unidentified products (173). Schaarschmidt, Balzerkiewicz, and Gante (173) stated that pyridine did not undergo nitration, while Schorygin and Topchiev (202) found that when the reagents were diluted with carbon dioxide and heated in a sealed tube at 115–120°C. a 7–10 per cent yield of 3-nitropyridine was formed. The same authors observed no nitration of quinoline at room temperature and obtained less than 15 per cent of 7-nitroquinoline at 95–105°C. At 105–160°C. both 7-nitroquinoline and 5,7-dinitroquinoline were formed.

1,9-Benzanthrone reacted with dry nitrogen tetroxide without a solvent to produce a 96–98 per cent yield of 1-nitrobenzanthrone (99).

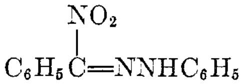
Di-*p*-tolylhydroxylamine produced *o*,*o*′-dinitrodi-*p*-tolylamine when it reacted with nitrogen tetroxide in cold ether or benzene solution (252). In the same publication Wieland reported that diphenylhydroxylamine reacted with nitrogen tetroxide to produce *p*,*p*′-dinitrodiphenylamine oxide and that diphenylamine oxide with nitrogen tetroxide also produced *p*,*p*′-dinitrodiphenylamine oxide.

Aryl urethans reacted with "nitrous fumes" to produce nitrourethans (156, 157, 159, 161, 167), along with smaller amounts of polynitro derivatives.

Tetraphenylethylene produced 1,2-diphenyl-1,2-di(*p*-nitrophenyl)ethylene when it reacted in chloroform solution with nitrogen tetroxide.

Various phenylureas were allowed to react with nitrogen trioxide or nitrogen tetroxide (168). For the most part nitro or polynitro derivatives were formed along with nitroso compounds. For example, symmetrical diphenylurea gave with nitrogen tetroxide *sym*-4,4′-dinitrodiphenylurea and *sym*-diphenyl-*N*,*N*′-dinitrosourea.

Ciusa and Pestalozza (28, 29, 30) added nitrogen tetroxide to ether solutions of the phenylhydrazones of aromatic aldehydes. With benzaldehyde an almost quantitative yield of VII was formed, along with a little benzaldehyde and



$$C_6H_5\overset{\overset{\displaystyle NO_2}{|}}{C}{=}NNHC_6H_5$$

VII

benzenediazonium nitrate, and oxidation products. The phenylhydrazones of other aromatic aldehydes behaved similarly.

Wieland and Reisenegger (251) allowed various diazo compounds and tetrazenes to react with nitrogen tetroxide in benzene solution. Ethyl diazoacetate produced a low yield of ethyl dinitroacetate; diazodesoxybenzoin gave dinitrophenylmethane; diazofluorene gave 9,9-dinitrofluorene; tetraphenyltetrazene gave *sym-p,p′*-dinitrotetraphenyltetrazene.

G. *Aliphatic hydrocarbons*

The nitroparaffins are most commonly prepared by the vapor-phase nitration with nitric acid of the lower molecular weight aliphatic hydrocarbons (86, 87, 88, 94). Up to the present better yields of the nitroparaffins are obtained with nitric acid than with nitrogen tetroxide.

A careful study was made by Hass, Dorsky, and Hodge (86) of the nitration of propane with nitrogen tetroxide. At 790–795°C. approximately equal quantities of nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane were formed. Lower temperatures favored the formation of 2-nitropropane. In addition to the nitroparaffins mentioned, miscellaneous oxidation products including acids and aldehydes were formed. A large percentage of the starting materials did not react.

The only other work of significance in which nitrogen tetroxide was allowed to react with aliphatic hydrocarbons seems to be that of Urbânski and Sloń (221, 222, 223, 224, 225, 226). Nitration of propane at 100°C. gave 1-nitropropane, some dinitroparaffins, and oxidation products soluble in water. Nitration of methane at 200°C. gave nitromethane, polynitro derivatives, and oxidation products.

The hydrocarbons from *n*-pentane through *n*-nonane were nitrated with nitrogen tetroxide mostly at 200°C. They gave mixtures of mononitro derivatives, $CH_3(CH_2)_nNO_2$, and dinitro derivatives, $O_2NCH_2(CH_2)_nCH_2NO_2$, with conversions of 30 to 80 per cent depending upon the conditions. It would appear that the above-mentioned types of nitroparaffins would represent an oversimplification. On the basis of the work of Hass *et al.* one would expect a much greater variety of products. Perhaps it should be pointed out that this discussion of the work of Urbânski and Sloń has been based for the most part on abstracts. Accordingly, it may or may not represent a complete listing of the products found by these authors.

Shorygin and Topchiev (200) found that *n*-hexane produced a low yield of 2-nitrohexane when it reacted with nitrogen tetroxide diluted with carbon dioxide. The reaction was carried out for 1 hr. at 10–80°C. Application of the same procedure to cyclohexane produced about a 15 per cent yield of mononitrocyclohexane.

IV. OXIDATION WITH NITROGEN TETROXIDE AND NITROGEN TRIOXIDE (SEE TABLE 2)

From what has gone before it is obvious that many reactions involving nitrogen tetroxide are accompanied by more or less oxidation. There are other reactions in which oxidation products are the most important. There are also borderline examples which might be placed in more than one category.

A. Oxidation of paraffin hydrocarbons

Frolich, Harrington, and Waitt (65) made a careful study of the reaction of methane and nitrogen tetroxide when passed through Pyrex tubes at 440–680°C. and in the presence of various catalysts, including platinum, vanadium pentoxide, pumice, and nickel. Yields of formaldehyde somewhat under 25 per cent (based on the methane used) were formed. Methanol was not found among the products. Bibb (18) did similar work. The formation of formaldehyde from methane is the subject of a French patent (62) and a U.S. patent (9).

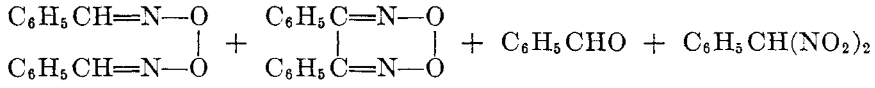
Chemists have been attracted by the hope of devising schemes of oxidizing paraffins to aliphatic acids. At best, one could expect a relatively complex mixture. Gränacher and Schaufelberger reported the oxidation of paraffin when treated with nitrogen tetroxide at 140°C. for 8 to 10 hr. to products completely soluble in alkali (77) but apparently did not identify any of them. This mixture may have contained nitroparaffins as well as carboxylic acids. According to another report (78) the paraffin was oxidized at 120–130°C. for 30 hr. The acids were esterified, and the resulting esters boiled from 37° to 300°C. at 23 mm. Apparently no distinct product was isolated. Undecane yielded a mixture of fatty acids, from which pelargonic acid was reported to have been isolated (77).

Schaarschmidt (171) also studied the action of nitrogen tetroxide with paraffin, but his success was apparently even less than that of Gränacher.

B. Reactions with oximes

Ponzio (133, 134, 142) studied the reactions of a number of oximes with nitrogen tetroxide. Scholl (196, 197) made similar studies. With the oxime of benzaldehyde and nitrogen tetroxide in dry ether (140) the reaction was reported as proceeding to give 16 per cent of benzaldoxime peroxide (I), 16 per cent of diphenylglyoxime peroxide (II), 12 per cent of benzaldehyde (III), and 50 per cent of dinitrophenylmethane (IV).

$$C_6H_5CH{=}NOH + N_2O_4 \rightarrow$$

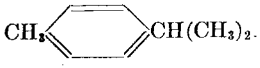
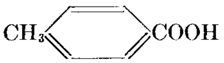


$$\begin{array}{l} C_6H_5CH{=}N{-}O \\ \qquad\qquad\quad | \\ C_6H_5CH{=}N{-}O \end{array} + \begin{array}{l} C_6H_5C{=}N{-}O \\ \quad\;\; | \qquad\quad | \\ C_6H_5C{=}N{-}O \end{array} + C_6H_5CHO + C_6H_5CH(NO_2)_2$$

I	II	III	IV
Benzaldoxime peroxide	Diphenylglyoxime peroxide	Benzaldehyde	Dinitrophenylmethane

TABLE 2

Oxidation

COMPOUND OXIDIZED	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
CH_4	N_2O_4	HCHO	(18, 65)
$C_6H_5CH_3$	N_2O_3	$(COOH)_2$, a dihydroxybenzoic acid, C_6H_5COOH, C_6H_5CHO, *o*-$NO_2C_6H_4CH_3$	(72, 102)
$C_6H_5CH_3$	N_2O_4	C_6H_5COOH, $(COOH)_2$, C_6H_5OH, C_6H_5CHO	(15, 72, 175)
	N_2O_3		(100, 101)
p-$ClC_6H_4CH_3$	N_2O_4	*p*-ClC_6H_4COOH	(175)
Anthracene	N_2O_3	Anthraquinone, red oil	(102)
Anthracene	N_2O_4	Anthraquinone	(15, 71, 92)
o-$CH_3C_6H_4NO_2$	N_2O_4	*o*-$NO_2C_6H_4COOH$	(15)
m-$CH_3C_6H_4NO_2$	N_2O_4	*m*-$NO_2C_6H_4COOH$	(15)
p-$CH_3C_6H_4NO_2$	N_2O_4	*p*-$NO_2C_6H_4COOH$	(15)
CH_3OH	N_2O_4	HCHO	(31)
C_2H_5OH	N_2O_4	CH_3CHO	(31)
$CH_3(CH_2)_3CH_2OH$	N_2O_4	$CH_3(CH_2)_3CHO$	(31)
$C_6H_5CH_2OH$	N_2O_4 or N_2O_3	C_6H_5COOH, C_6H_5CHO	(15, 31)

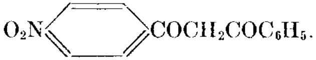
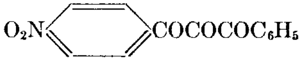
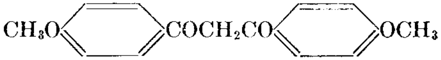
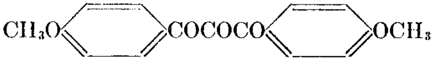
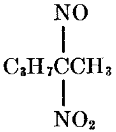
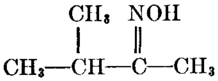
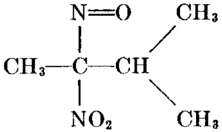
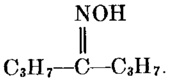
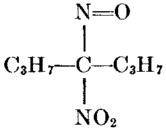
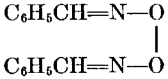
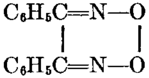
o-$NO_2C_6H_4CH_2OH$	N_2O_4	o-$NO_2C_6H_4CHO$	(31, 32)
p-$NO_2C_6H_4CH_2OH$	N_2O_4	p-$NO_2C_6H_4CHO$	(31)
C_6H_5CHO	N_2O_4	C_6H_5COOH	(15, 63, 64)
m-$NO_2C_6H_4CHO$	N_2O_4	m-$NO_2C_6H_4COOH$	(15)
p-$NO_2C_6H_4CHO$	N_2O_4	p-$NO_2C_6H_4COOH$	(15)
o-$NO_2C_6H_4CHO$	N_2O_4	o-$NO_2C_6H_4COOH$	(15)
$HOCH_2CH(OC_2H_5)_2$	N_2O_4	$HOOCCH_2CH(OC_2H_5)_2$	(114)
$HOCH_2(CHOH)_4CHO$ (galactose)	N_2O_4	$HOOC(CHOH)_4COOH$ (mucic acid)	(114)
α-Methylglucoside	N_2O_4	Glucuronic acid (as barium salt)	(114)
α-Methylgalactoside	N_2O_4	α-Methylgalacturonic acid	(114)
$C_6H_5COCH_2COC_6H_5$	N_2O_3	$C_6H_5COCOCOC_6H_5$, $(C_6H_5CO)_2CH(N_2O_2)CH(COC_6H_5)_2$	(245, 246)
	N_2O_3		(245)
	N_2O_3	 $(p$-$CH_3OC_6H_4CO)_2CH(N_2O_2)CH(COC_6H_4OCH_3$-$p)_2$	(245)
$C_6H_5COCH_2COCH_3$	N_2O_3	$(C_6H_5CO)_2CH(N_2O_2)CH(COC_6H_5)_2$	(245)
$CH_3COCH_2COOC_2H_5$	N_2O_3	$CH_3COCOCOOC_2H_5$	(24)

TABLE 2—*Continued*

COMPOUND OXIDIZED	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
$CH_2(COOC_2H_5)_2$	N_2O_3 or N_2O_4	$CH(NO)(COOC_2H_5)_2$, $CH(NO_2)(COOC_2H_5)_2$	(33, 34, 35, 36, 73, 195)
		$CO(COOC_2H_5)_2$, $C(NO_2)_2(COOC_2H_5)_2$	(31, 32)
$C_3H_7C(=NOH)CH_3$	N_2O_4	 $C_3H_7C(NO)(NO_2)CH_3$	(22)
 $CH_3—CH(CH_3)—C(=NOH)—CH_3$	N_2O_4		(22)
 $C_3H_7—C(=NOH)—C_3H_7$	N_2O_4	 $C_3H_7—C(N{=}O)(NO_2)—C_3H_7$	(22)
$C_6H_5CH{=}NOH$	N_2O_4	 C_6H_5CHO $C_6H_5CH(NO_2)_2$ 	(138, 139, 140, 141)

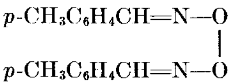
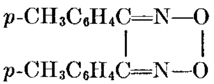
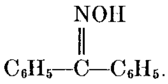
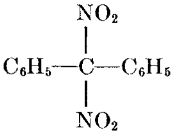
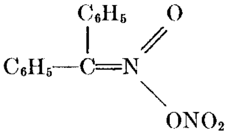
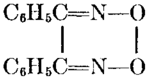
$p\text{-}CH_3C_6H_4CH{=}NOH$	N_2O_4	 $p\text{-}CH_3C_6H_4CHO$	(140)
		 $p\text{-}CH_3C_6H_4CH(NO_2)_2$	
 $C_6H_5\text{—}\overset{\overset{NOH}{\Vert}}{C}\text{—}C_6H_5$	N_2O_4	 $C_6H_5\text{—}\overset{NO_2}{\underset{NO_2}{C}}\text{—}C_6H_5$ or 	(197)
$p\text{-}CH_3OC_6H_4CH{=}NOH$	N_2O_4	$p\text{-}CH_3OC_6H_4CH(N_2O_4)$ and small amounts of other products	(140)
$C_6H_5C({=}NOH)COOH$	N_2O_4		(142)
$C_6H_5C({=}NOH)CH_2OH$	N_2O_4	$C_6H_5CH(NO_2)_2$	(142)
$p\text{-}ClC_6H_4CH{=}NOH$	N_2O_4	$p\text{-}ClC_6H_4C({=}NOH)NO_2$, $p\text{-}ClC_6H_4CH(N_2O_4)$	(154)
$m\text{-}NO_2C_6H_4CH{=}NOH$	N_2O_4	$m\text{-}NO_2C_6H_4C({=}NOH)NO_2$	(154)
$CH_3C({=}NOH)COOH$	N_2O_4	$CH_3C({=}NOH)NO_2$	(137)
$C_2H_5(C{=}NOH)COOH$	N_2O_4	$C_2H_5(C{=}NOH)NO_2$	(137)
$CH({=}NOH)COOH$	N_2O_4	$CH({=}NOH)NO_2$	(137)
$CH_2(NO)COOC_2H_5$	N_2O_4	$C({=}NOH)(NO_2)COOC_2H_5$	(25)

TABLE 2—*Continued*

COMPOUND OXIDIZED	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
$CH_2(NO)COOC_4H_9$(iso)	N_2O_3	$CHOCOOC_4H_9$(iso)	(25)
$C_2H_5CO(C{=}NOH)CH_3$	N_2O_4	$C_2H_5COCOCH_3$, $CH_3CH(NO_2)_2$, $CH_3C(N_2O_4)COC_2H_5$	(133)
$CH_3C({=}NOH)COC_3H_7$	N_2O_4	$CH_3C(N_2O_4)COC_3H_7$	(143)
$C_2H_5COC({=}NOH)C_3H_7$	N_2O_4	$C_2H_5COC(N_2O_4)C_3H_7$	(143)
$CH_3C({=}NOH)COC_4H_9$	N_2O_4	$CH_3C(N_2O_4)COC_4H_9$	(143)
$CH_3C({=}NOH)COC_5H_{11}$	N_2O_4	$CH_3C(N_2O_4)COC_5H_{11}$	(143)
$C_2H_5COC({=}NOH)C_4H_9$	N_2O_4	$C_2H_5COC(N_2O_4)C_4H_9$	(143)
$CH_3C({=}NOH)COC_4H_9$(iso)	N_2O_4	$CH_3C(N_2O_4)COC_4H_9$(iso)	(143)
$C_2H_5COC({=}NOH)C_3H_7$(iso)	N_2O_4	$C_2H_5COC(N_2O_4)C_3H_7$(iso)	(143)
$CH_3C({=}NOH)COC_5H_{11}$(iso)	N_2O_4	$CH_3C(N_2O_4)COC_5H_{11}$(iso)	(143)
$C_2H_5COC({=}NOH)C_4H_9$(iso)	N_2O_4	$C_2H_5COC(N_2O_4)C_4H_9$(iso)	(143)
$CH_3C({=}NOH)COC_6H_{13}$(iso)	N_2O_4	$CH_3C(N_2O_4)COC_6H_{13}$(iso)	(143)
$C_2H_5COC({=}NOH)C_5H_{11}$(iso)	N_2O_4	$C_2H_5COC(N_2O_4)C_5H_{11}$(iso)	(143)
$C_6H_5COC({=}NOH)C_6H_5$	N_2O_4	$C_6H_5COCOC_6H_5$, $C_6H_5COCOC_6H_4NO_2$-*p*, C_6H_5COOH, *p*-$O_2NC_6H_4COOH$	(134, 135)
$CH_3COC({=}NOH)C_6H_5$	N_2O_4	$CH_3COCOC_6H_5$, $C_6H_5CH(N_2O_4)$	(136)

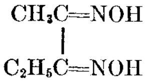
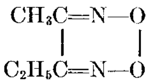
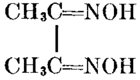
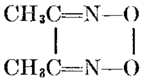
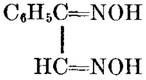
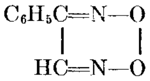
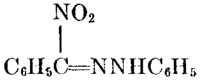
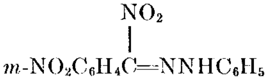
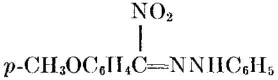
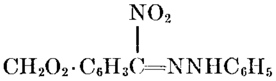
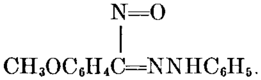
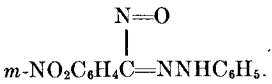
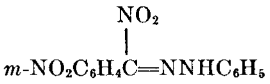
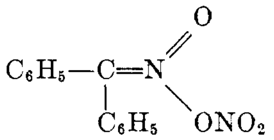
 $\begin{array}{l}CH_3C{=}NOH\\ \quad\;\,|\\ C_2H_5C{=}NOH\end{array}$	N_2O_4	 $\begin{array}{l}CH_3C{=}N{-}O\\ \quad\;\,|\quad\;\;\;|\\ C_2H_5C{=}N{-}O\end{array}$	(197)
 $\begin{array}{l}CH_3C{=}NOH\\ \quad\;\,|\\ CH_3C{=}NOH\end{array}$	N_2O_4	 $\begin{array}{l}CH_3C{=}N{-}O\\ \quad\;\,|\quad\;\;\;|\\ CH_3C{=}N{-}O\end{array}$	(197)
 $\begin{array}{l}C_6H_5C{=}NOH\\ \quad\;\,|\\ \quad HC{=}NOH\end{array}$	N_2O_4	 $\begin{array}{l}C_6H_5C{=}N{-}O\\ \quad\;\,|\quad\;\;\;|\\ \quad HC{=}N{-}O\end{array}$	(197)
$C_6H_5CH{=}NNHC_6H_5$	N_2O_4	 $C_6H_5\overset{NO_2}{\overset{\vert}{C}}{=}NNHC_6H_5$	(28, 29, 30)
$m\text{-}NO_2C_6H_4CH{=}NNHC_6H_5$	N_2O_4	 $m\text{-}NO_2C_6H_4\overset{NO_2}{\overset{\vert}{C}}{=}NNHC_6H_5$	(28, 29, 30)
$p\text{-}CH_3OC_6H_4CH{=}NNHC_6H_5$	N_2O_4	 $p\text{-}CH_3OC_6H_4\overset{NO_2}{\overset{\vert}{C}}{=}NNHC_6H_5$	(28, 29, 30)
$CH_2O_2\cdot C_6H_3CH{=}NNHC_6H_5$ (piperonal phenylhydrazone)	N_2O_4	 $CH_2O_2\cdot C_6H_3\overset{NO_2}{\overset{\vert}{C}}{=}NNHC_6H_5$	(28, 29, 30)
 $CH_3OC_6H_4\overset{N=O}{\overset{\vert}{C}}{=}NNHC_6H_5$	N_2O_3	 $CH_3OC_6H_4\overset{NO_2}{\overset{\vert}{C}}{=}NNHC_6H_5$, $C_6H_5N{=}NNO_3$	(13)

TABLE 2—*Continued*

COMPOUND OXIDIZED	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
 $m\text{-}NO_2C_6H_4C(N{=}O){=}NNHC_6H_5$	N_2O_3	 $m\text{-}NO_2C_6H_4C(NO_2){=}NNHC_6H_5$	(13)
$C_6H_5CH{=}CCl_2$	N_2O_4	C_6H_5COH, $p\text{-}NO_2C_6H_4COOH$	(20)
$C_6H_5CCl{=}CCl_2$	N_2O_4	C_6H_5COOH, $p\text{-}NO_2C_6H_4COOH$	(20)
$(C_6H_5C_6H_4)_2C{=}C(C_6H_4C_6H_5)_2$	N_2O_4	$C_6H_5C_6H_4COC_6H_4C_6H_5$	(178)

Analogous reactions were reported for *p*-tolylaldoxime, anisaldoxime, benzophenone oxime, and acetophenone oxime. The ratios of the products (typified by I, II, III, IV) varied, depending upon the conditions and the specific oxime. There seems to be some doubt as to whether the dinitro compounds (IV) are true nitro compounds. Scholl (197) preferred to regard dinitrodiphenylmethane (V) as having the following structure:

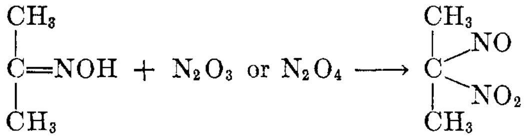


V

Dinitrodiphenylmethane

Neither Scholl nor Ponzio gave a rigid proof of the structure of this compound.

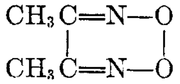
Scholl (196) concluded that the oximes of acetone, ethyl methyl ketone, and diethyl ketone reacted as indicated in the following equation:



VI

Compound VI was referred to as "propyl pseudonitrol" and was obtained in 25 per cent yield. A similar conclusion was reached by Born (22) for the reaction products of nitrogen tetroxide with methyl propyl ketoxime, isopropyl methyl ketoxime, and di-*n*-propyl ketoxime.

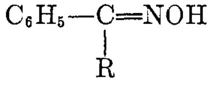
With the glyoximes such as dimethyl, methyl, ethylmethyl, and phenyl, the main reaction product with nitrogen tetroxide was the glyoxime peroxide. Formula VII represents the product formed from dimethylglyoxime.



$$\begin{array}{l} CH_3C{=}N{-}O \\ \qquad\ |\qquad\ | \\ CH_3C{=}N{-}O \end{array}$$

VII

Ponzio concluded from his series of experiments that when compounds of type VIII were allowed to react with nitrogen tetroxide the major product was the

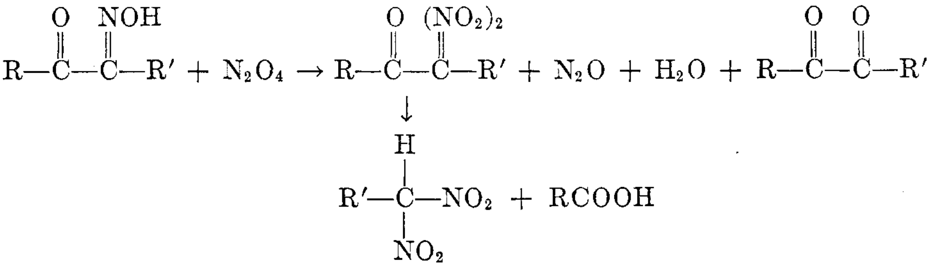


$$C_6H_5{-}\underset{\displaystyle R}{\underset{|}{C}}{=}NOH$$

VIII

corresponding dinitromethane when R was H, —CH_2OH, or $CH_3\overset{\overset{\displaystyle O}{\|}}{C}$—, but not when R was —COOH, —CH_3, or —C_6H_5.

Ponzio (133, 134, 135, 136, 143) also studied the reactions of the monoximes of a few 1,2-diketones with nitrogen tetroxide. These reactions were carried out in cold dry ether, and the reaction mixtures were allowed to stand 1 hr. The product was washed with water and dried, and the ether was removed. The reactions were generally believed to proceed as follows:

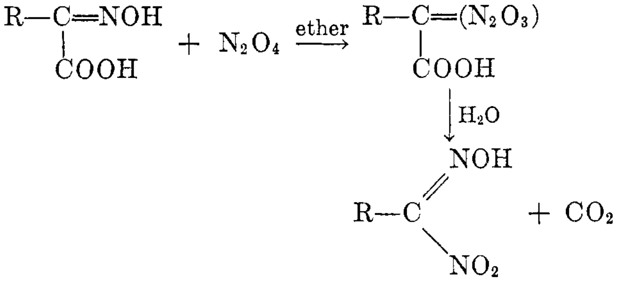


$$R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{NOH}{\|}}{C}{-}R' + N_2O_4 \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{(NO_2)_2}{\|}}{C}{-}R' + N_2O + H_2O + R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}R'$$

$$\downarrow$$

$$R'{-}\underset{\underset{NO_2}{|}}{\overset{\overset{H}{|}}{C}}{-}NO_2 + RCOOH$$

Nitrolic acids (IX) have been prepared by Ponzio (137) with nitrogen tetroxide reacting with α-isonitroso acids as indicated by the type equation:

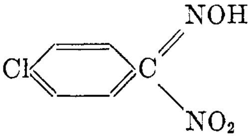


$$\underset{\underset{COOH}{|}}{R{-}C{=}NOH} + N_2O_4 \xrightarrow{\text{ether}} \underset{\underset{COOH}{|}}{R{-}C{=}(N_2O_3)} \xrightarrow{H_2O} R{-}C\begin{matrix}{\diagup\!\!\diagup} NOH \\ \diagdown NO_2\end{matrix} + CO_2$$

IX

Starting with isonitrosoacetic acid or isonitrosopropionic acid, yields of more than 80 per cent of the corresponding nitrolic acids were produced.

Aromatic nitrolic acids were prepared by Ruggeri by allowing the oximes of aromatic aldehydes to react with nitrogen tetroxide in ether (154). For example, p-chlorobenzaldoxime gave (p-chlorophenyl)methylnitrolic acid (X):



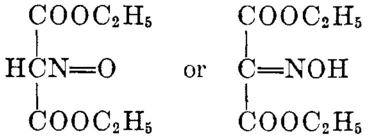
X

Boubeault and Wahl (25) allowed the ethyl ester of isonitrosoacetic acid to react with nitrogen tetroxide and obtained the corresponding isonitrosonitroacetic ester ($HON{=}C(NO_2)COOC_2H_5$) along with the ethyl ester of bisanhydronitroacetic acid.

C. Reactions with compounds containing active methylene groups

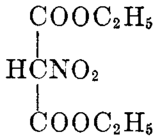
A useful laboratory reaction is the oxidation of malonic ester with nitrogen trioxide (33, 34, 35, 36, 74, 194) or nitrogen tetroxide (73) to produce ethyl oxomalonate. The reagents are mixed while cold and allowed to warm gradually to room temperature, and the product is distilled. Explosive by-products are formed during the reaction, the amount depending on the conditions. Gilman and Johnson (73) obtained almost quantitative yields by adding a little sodium to the reaction mixture. They also showed that esters other than the ethyl ester could be used successfully to give analogous products. The reaction proceeds more satisfactorily with nitrogen tetroxide than with the trioxide.

The nitroso or isonitroso compound (XI) is generally believed to be the main by-product which tends to decompose upon distillation.



$$\begin{array}{c} COOC_2H_5 \\ | \\ HCN{=}O \\ | \\ COOC_2H_5 \end{array} \quad \text{or} \quad \begin{array}{c} COOC_2H_5 \\ | \\ C{=}NOH \\ | \\ COOC_2H_5 \end{array}$$

XI



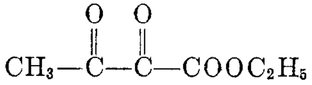
$$\begin{array}{c} COOC_2H_5 \\ | \\ HCNO_2 \\ | \\ COOC_2H_5 \end{array}$$

XII

Curtis and Kostalek (36) believed that XII was formed during the reaction, and possibly ethyl dinitroacetate also.

If ethyl oxomalonate were needed on a large scale it should be possible to prepare it successfully by this method.

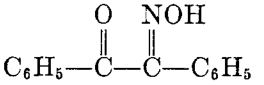
Another reaction related to this has been studied by Bouveault and Wahl, who converted acetoacetic ester with "nitrous fumes" into the diketone (XIII).



$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}COOC_2H_5$$

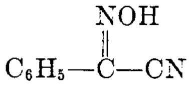
XIII

It was anticipated that ethyl methyl ketone would be converted to diacetyl and that ethyl cyanoacetate would be converted to ethyl ketocyanoacetate. These expectations were not realized under the conditions tried (150). Benzyl phenyl ketone and benzyl cyanide with nitrous acid (probably nitrogen trioxide) gave XIV and XV, respectively.



$$C_6H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle NOH}{\|}}{C}{-}C_6H_5$$

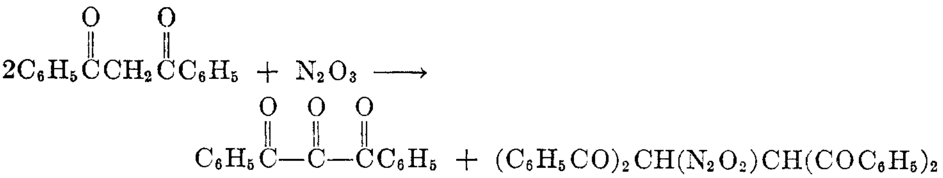
XIV
Benzil monoxime



$$C_6H_5{-}\overset{\overset{\displaystyle NOH}{\|}}{C}{-}CN$$

XV
α-Cyanobenzaldoxime

Wieland and Block (245, 246) studied the action of nitrogen trioxide with certain 1,3-diketones. With dibenzoylmethane the reaction proceeded as indicated:

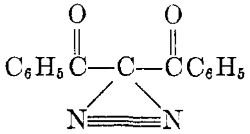


$$2C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}CH_2\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5 + N_2O_3 \longrightarrow$$

$$C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle O}{\|}}{C}C_6H_5 + (C_6H_5CO)_2CH(N_2O_2)CH(COC_6H_5)_2$$

XVI XVII

In addition to the above, about 15 per cent of an explosive product was formed to which the formula XVIII was assigned:



XVIII

With benzoyl-*p*-nitrobenzoylmethane a quantitative yield of the corresponding triketone was formed. With di-*p*-methoxybenzoylmethane products corresponding to both XVI and XVII were formed. With acetylbenzoylmethane only the product analogous to XVI was obtained.

It would be interesting to try other compounds containing active methylene groups.

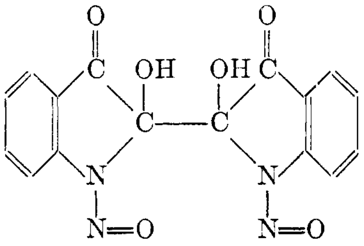
D. Miscellaneous oxidations

A number of simple oxidation reactions with nitrogen tetroxide have been carried out. Toluene gave a mixture of benzaldehyde and benzoic acid (72); *o*-, *m*-, and *p*-nitrotoluenes gave a low yield of the corresponding nitrobenzoic acids (15); benzyl alcohol gave benzaldehyde and benzoic acid (15, 31); *o*- and *p*-nitrobenzyl alcohols gave the corresponding nitro derivatives (31, 32); benzaldehyde was converted in 75 per cent yield to benzoic acid (15, 63, 64); *o*-, *m*-, and *p*-nitrobenzaldehydes gave the corresponding nitrobenzoic acids (15); 1-phenyl-2-dichloroethylene gave benzoic and *p*-nitrobenzoic acids; phenyltrichloroethylene gave benzoic and *p*-nitrobenzoic acids (20). Methods have been patented for the production of anthraquinone from anthracene and nitrogen tetroxide (71).

Yackel, Kenyon, and Unruh (220, 258) oxidized cellulose with dry nitrogen tetroxide to form a product readily soluble in 2 per cent sodium hydroxide, ammonium hydroxide, sodium carbonate, or warm pyridine. This oxidized cellulose is believed to have as high as 25 per cent carboxyl content, and it is believed that the primary hydroxyl groups are attacked preferentially. The material is especially interesting because it has a great affinity for basic dyes. Shorygin and Khait (199) and Maurer and Reiff (115) reported similar work with similar results. No nitration products were observed. Pinck (132) found it possible to nitrate cellulose quite satisfactorily by means of 85 to 99 per cent sulfuric acid and nitrogen tetroxide.

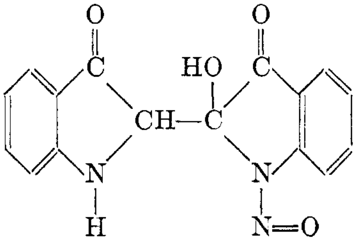
Maurer and Drefahl (114) found that nitrogen tetroxide oxidized galactose in chloroform to mucic acid in 75 per cent yields. α-Methylglucoside was oxidized to glucuronic acid (isolated as the barium salt) and α-methylgalactoside was oxidized to α-methylgalacturonic acid under similar conditions.

Indigo was allowed to react with nitrogen trioxide in 95 per cent alcohol. Ethyl benzoylformate was isolated (144, 145). When the reaction was carried out in ether, the unstable compound XIX was believed by Posner and Aschermann (144) to be formed.



XIX

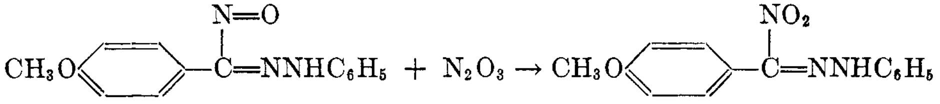
Compound XIX was converted into XX in low yield by warming with ethanol.



XX

Compound XX was treated with nitrogen trioxide in methanol and formed ethyl benzoylformate. *p*-Tolylindigo gave an analogous series of reactions.

Bamberger and Pemsel (13) allowed the phenylhydrazone of nitrosoanisaldehyde (XXI) to react with "nitrous fumes" and oxidized the nitroso group to the nitro group, forming XXII in about a 60 per cent yield. A trace of benzenediazonium nitrate was also formed.

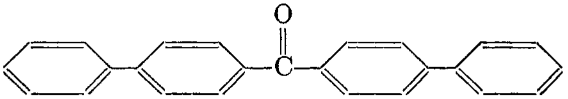


$$CH_3OC_6H_4-\overset{N=O}{C}=NNHC_6H_5 + N_2O_3 \rightarrow CH_3OC_6H_4-\overset{NO_2}{C}=NNHC_6H_5$$

XXI XXII

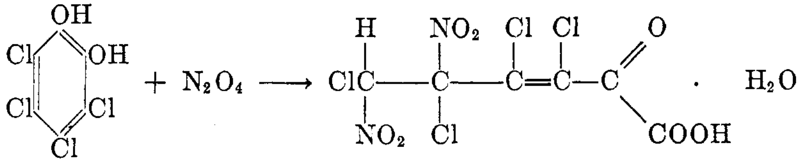
The phenylhydrazone of nitroso-*m*-nitrobenzaldehyde behaved in a similar manner.

Schlenk (178) added nitrogen tetroxide to tetrabiphenylethylene in carbon tetrachloride solution and reported an almost quantitative yield of the ketone XXIII.



XXIII

An interesting type of oxidation with nitrogen tetroxide was carried out by Zincke (260). Tetrachlorocatechol, tetrabromocatechol, 2,3,6-trichlorohomocatechol, and 2,3,4-trichlorohomocatechol were added to cold liquid nitrogen tetroxide. In the case of tetrachlorocatechol these reactions followed the course indicated:



These changes were believed to proceed through the primary oxidation to the quinones, followed by the opening of the rings. The products were relatively unstable.

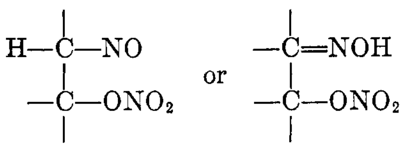
V. REACTIONS OF NITROGEN TETROXIDE AND NITROGEN DIOXIDE WITH COMPOUNDS CONTAINING CARBON–CARBON MULTIPLE BONDS (SEE TABLE 3)

The reactions of nitrogen tetroxide with compounds containing ethylenic or acetylenic linkages have received considerable attention. Investigators have no doubt been fascinated by the hope that these reactions would result in the formation of nitro compounds which might be valuable as explosives or might be reduced to useful amines. Up to the present time this hope has not been realized except in a few instances.

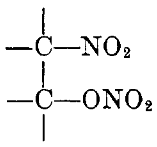
In general, the products from these reactions are unstable solids or intractable unstable oils from which it is often difficult or impossible to isolate pure compounds. Actually, the reports in the literature are conflicting and are confused by a lack of consistent nomenclature. Because of the unstable nature of many of the products, analyses are often open to doubt. Any interpretations based on such analyses must necessarily be scrutinized. In much of the earlier work the conditions of the experiments were not made clear. Even with the best attempts on record the products are complex, partly owing to polymerization, especially with the olefins of lower molecular weight.

In spite of the discouraging results up to the present time, it is still possible that with the appropriate choice of solvents and conditions some useful reactions may be found.

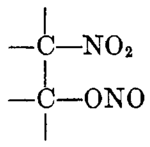
Looking at this problem first from a general point of view it would be expected that compounds with —C═C— linkages could react with nitrogen tetroxide in a variety of ways. On the basis of the structures suggested for nitrogen tetroxide the following possibilities have been suggested (174, 184, 233, 237, 242):



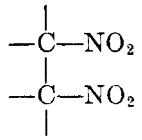
Nitrosonitrate
or
Nitrosate



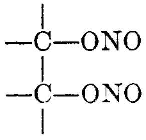
Nitronitrate



Nitronitrite



Dinitro

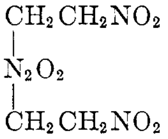


Dinitrite

There seems to be no instance in which it has been shown clearly that the dinitrite was formed. The other four types may have been found. The nitronitrate could be formed by addition followed by oxidation.

A. Ethylene and simple ethylene derivatives

Sidorenko (208) passed oxides of nitrogen and ethylene through ether and collected the solid which formed. It was postulated that the solid formed was I.



$$\begin{array}{l} CH_2CH_2NO_2 \\ | \\ N_2O_2 \\ | \\ CH_2CH_2NO_2 \end{array}$$

I

Heating I with concentrated hydrochloric acid gave carbon dioxide, oxides of nitrogen, and a carbonaceous residue. When warmed with amines I lost nitrous acid to give $(C_2H_4NO_2)_2{=}NCH_2R$. Dem'yanov (39) claimed that ethylene and nitrogen tetroxide reacted in ether to give $C_2H_4 \cdot N_2O_3$, which could be reduced with tin and hydrochloric acid to ethylenediamine. The production of nitrosites from ethylene and propylene, etc. was patented by Marshall (111).

Semenoff (198) probably succeeded in isolating a small yield of 1,2-dinitroethane from the reaction of ethylene and nitrogen tetroxide. In these experiments dry ethylene gas was passed through liquid nitrogen tetroxide or the reagents were warmed to 60–70°C.

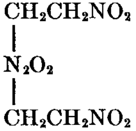
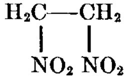
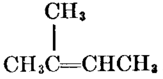
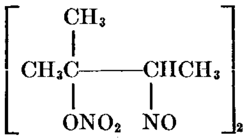
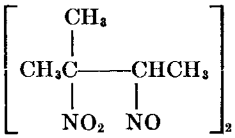
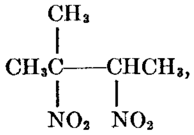
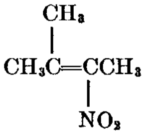
As early as 1869 Kolbe (96) heated tetrachloroethylene and nitrogen trioxide in a sealed tube at 120°C. and obtained a product to which was ascribed the formula $C_2Cl_4(NO_2)_2$. This compound was not reduced. Argo and Donnelly (7) claimed 50 per cent yields of the same dinitro compound under about the same conditions. Biltz (20) claimed a good yield of *sym*-dinitrotetrachloroethane from tetrachloroethylene and nitrogen tetroxide when heated at 100°C. in a sealed tube for 3 hr. A similar reaction was claimed for tetrabromoethylene. The proof of the nature of these nitro compounds rested upon analyses. In view of much of the experience of later investigations it is questionable whether or not they were nitro compounds. Biltz (19) also believed that *sym*-diiododinitroethylene was produced from tetraiodoethylene and nitrogen tetroxide when they were heated in a sealed tube at 90°C. The proof was not rigid.

Burrows and Hunter (26) allowed *sym*-tetrachloroethylene to react with nitrogen tetroxide and reported the formation of *sym*-tetrachlorodinitroethane. With tribromoethylene 1,2-dinitrotribromoethane was formed. These claims also lack rigid proof. From 1,2-dichloroethylene and trichloroethylene no definite products were isolated except oxalic acid.

A number of investigations have been made of the reactions of nitrogen tetroxide with tetramethylethylene. Schmidt (190) believed that the main product of these reactions was II when ether was used as the solvent. His conclusion

TABLE 3

Ethylenic compounds

ETHYLENIC COMPOUND	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
$CH_2{=}CH_2$	N_2O_3	 $CH_2CH_2NO_2-N_2O_2-CH_2CH_2NO_2$	(208)
$CH_2{=}CH_2$	N_2O_4	$C_2H_4 \cdot N_2O_3$,  $\underset{NO_2}{H_2C}-\underset{NO_2}{CH_2}$	(39, 198)
$C_2H_5CH{=}CH_2$	N_2O_3	$(C_4H_8 \cdot N_2O_3)_2$	(40)
 $CH_3\overset{CH_3}{C}{=}CHCH_3$	N_2O_3	 $\left[CH_3\overset{CH_3}{\underset{ONO_2}{C}}-\underset{NO}{CHCH_3}\right]_2$  $\left[CH_3\overset{CH_3}{\underset{NO_2}{C}}-\underset{NO}{CHCH_3}\right]_2$  $CH_3\overset{CH_3}{\underset{NO_2}{C}}-\underset{NO_2}{CHCH_3}$,  $CH_3\overset{CH_3}{C}{=}\underset{NO_2}{CCH_3}$	(122, 185, 186, 207, 214, 229, 231)

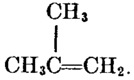
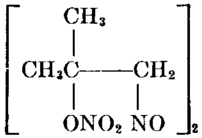
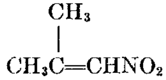
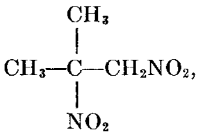
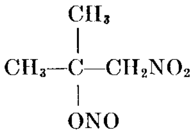
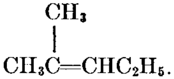
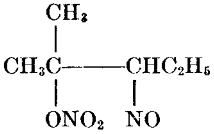
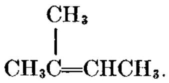
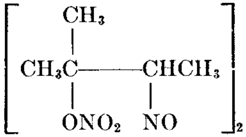
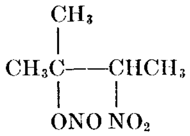
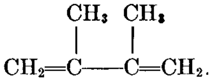
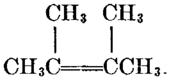
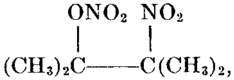
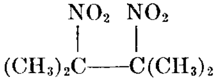
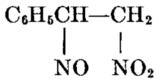
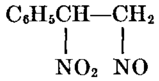
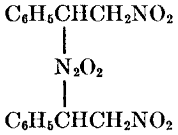
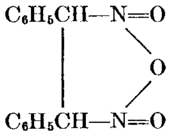
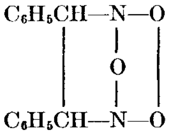
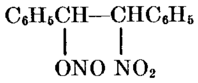
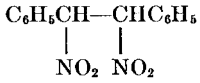
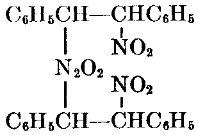
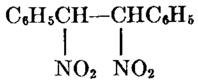
 $CH_3\overset{\overset{CH_3}{\vert}}{C}{=}CH_2$	N_2O_4	 $\left[CH_3\underset{\underset{ONO_2}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}—\underset{\underset{NO}{\vert}}{CH_2}\right]_2$  $CH_3\overset{\overset{CH_3}{\vert}}{C}{=}CHNO_2$  $CH_3—\underset{\underset{NO_2}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}—CH_2NO_2$,  $CH_3—\underset{\underset{ONO}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}—CH_2NO_2$	(123)
 $CH_3\overset{\overset{CH_3}{\vert}}{C}{=}CHC_2H_5$	N_2O_4	 $CH_3\underset{\underset{ONO_2}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}—\underset{\underset{NO}{\vert}}{C}HC_2H_5$	(95)
 $CH_3\overset{\overset{CH_3}{\vert}}{C}{=}CHCH_3$	N_2O_4	 $\left[CH_3\underset{\underset{ONO_2}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}—\underset{\underset{NO}{\vert}}{C}HCH_3\right]_2$  $CH_3\underset{\underset{ONO}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}—\underset{\underset{NO_2}{\vert}}{C}HCH_3$	(79, 80, 95, 119, 121, 125)
 $CH_2{=}\overset{\overset{CH_3}{\vert}}{C}—\overset{\overset{CH_3}{\vert}}{C}{=}CH_2$	N_2O_3	$C_6H_{10}\cdot N_2O_3$	(43)
 $CH_3\overset{\overset{CH_3}{\vert}}{C}{=}\overset{\overset{CH_3}{\vert}}{C}CH_3$	N_2O_4	 $(CH_3)_2\overset{\overset{ONO_2}{\vert}}{C}—\overset{\overset{NO_2}{\vert}}{C}(CH_3)_2$,  $(CH_3)_2\overset{\overset{NO_2}{\vert}}{C}—\overset{\overset{NO_2}{\vert}}{C}(CH_3)_2$	(41, 124, 190)

TABLE 3—*Continued*

ETHYLENIC COMPOUND	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
$C_6H_5CH{=}CH_2$	N_2O_3	 $\underset{NO}{C_6H_5CH}-\underset{NO_2}{CH_2}$ or  $\underset{NO_2}{C_6H_5CH}-\underset{NO}{CH_2}$  $\begin{array}{l} C_6H_5CHCH_2NO_2 \\ \vert \\ N_2O_2 \\ \vert \\ C_6H_5CHCH_2NO_2 \end{array}$ $C_6H_5CH{=}CHNO_2$	(146, 210, 239)
$C_6H_5CH{=}CHC_6H_5$	N_2O_3	 or   $\underset{ONO}{C_6H_5CH}-\underset{NO_2}{CHC_6H_5}$  $\underset{NO_2}{C_6H_5CH}-\underset{NO_2}{CHC_6H_5}$  $\begin{array}{l} C_6H_5CH-CHC_6H_5 \\ \vert \qquad\ \ \vert \\ \vert \qquad NO_2 \\ N_2O_2 \\ \vert \qquad NO_2 \\ \vert \qquad\ \ \vert \\ C_6H_5CH-CHC_6H_5 \end{array}$ $(C_6H_5CH{=}CHC_6H_5 \cdot N_2O_4)$	(67, 183, 243)
$C_6H_5CH{=}CHC_6H_5$	N_2O_4	 $\underset{NO_2}{C_6H_5CH}-\underset{NO_2}{CHC_6H_5}$	(184, 188)

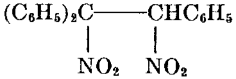
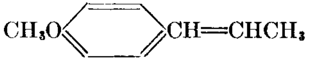
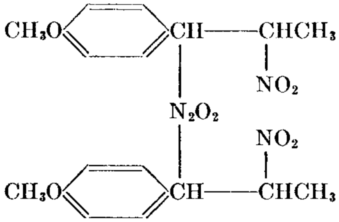
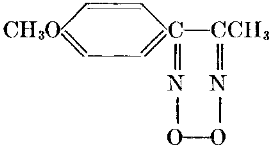
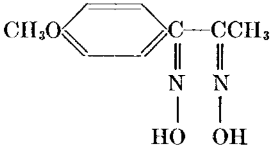
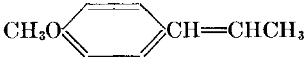
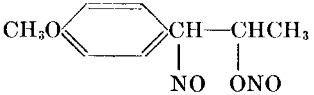
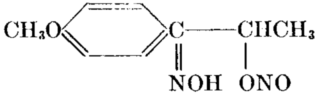
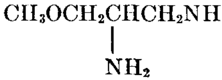
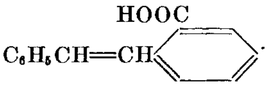
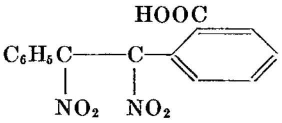
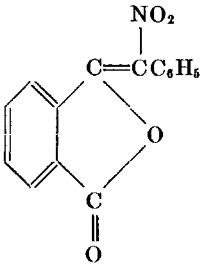
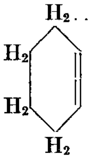
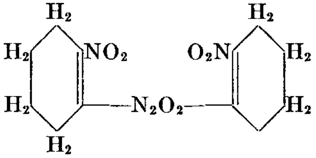
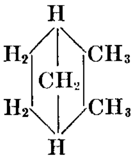
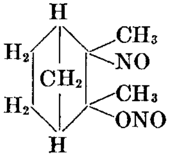
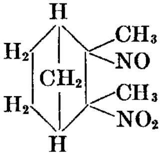
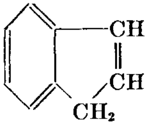
$(C_6H_5)_2C{=}CH_2$	N_2O_4	$(C_6H_5)_2COHCH_2NO_2$	(250)
$(C_6H_5)_2C{=}CHC_6H_5$	N_2O_3	 $(C_6H_5)_2C(NO_2)-CH(NO_2)C_6H_5$	(204)
	N_2O_3	  	(237, 240)
	N_2O_3	 or 	(219)
$CH_3OCH_2CH{=}CH_2$	N_2O_3	Product on reduction with $SnCl_2$ and HCl gave  $CH_3OCH_2CH(NH_2)CH_2NH_2$	(112)

TABLE 3—*Continued*

ETHYLENIC COMPOUND	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
	N_2O_3	 	(104)
	N_2O_3 or N_2O_4		(243)
	N_2O_3	 	(129)
	N_2O_3	$C_9H_8 \cdot N_2O_3$	(45)

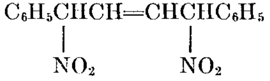
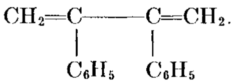
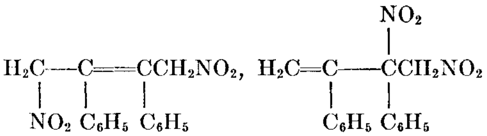
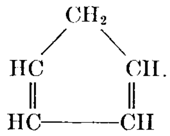
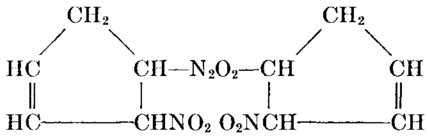
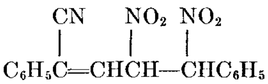
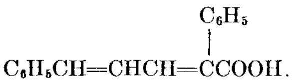
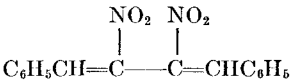
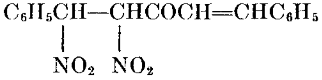
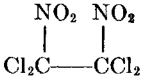
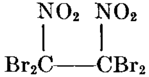
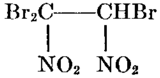
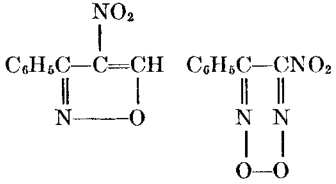
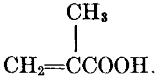
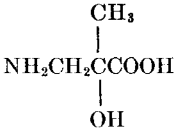
$CH_2{=}C{=}CH_2$	N_2O_3	$C_3H_4 \cdot N_2O_3$	(43)
$C_6H_5CH{=}CHCH{=}CHC_6H_5$	N_2O_4	 $C_6H_5\underset{NO_2}{CH}CH{=}CH\underset{NO_2}{CH}C_6H_5$	(213, 254, 255)
 $CH_2{=}\underset{C_6H_5}{C}{-}\underset{C_6H_5}{C}{=}CH_2$	N_2O_4	 $H_2\underset{NO_2}{C}{-}\underset{C_6H_5}{C}{=}\underset{C_6H_5}{C}CH_2NO_2$, $H_2C{=}\underset{C_6H_5}{C}{-}\overset{NO_2}{\underset{C_6H_5}{C}}CH_2NO_2$	(4)
	N_2O_3		(255)
 $C_6H_5\overset{CN}{C}{=}CHCH{=}CHC_6H_5$	N_2O_4	 $C_6H_5\overset{CN}{C}{=}CH\overset{NO_2}{CH}{-}\overset{NO_2}{CH}C_6H_5$	(128)
 $C_6H_5CH{=}CHCH{=}\overset{C_6H_5}{C}COOH$	N_2O_4	 $C_6H_5CH{=}\overset{NO_2}{C}{-}\overset{NO_2}{C}{=}CHC_6H_5$	(128)
$CH_2{=}CHCH_2CH_2CH{=}CH_2$	N_2O_4	$C_6H_{10}(NO_2)_2$	(89, 94, 206)
$C_6H_5CH{=}CHCOCH{=}CHC_6H_5$	N_2O_4	 $C_6H_5\underset{NO_2}{CH}{-}\underset{NO_2}{CH}COCH{=}CHC_6H_5$	(243)
$CI_2{=}CI_2$	N_2O_4	$CINO_2{=}CINO_2$	(19)

TABLE 3—*Continued*

ETHYLENIC COMPOUND	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
$CCl_2{=}CCl_2$	N_2O_4	 $Cl_2\overset{\overset{NO_2}{\vert}}{C}{-}\overset{\overset{NO_2}{\vert}}{C}Cl_2$	(7, 20, 26, 96)
$CBr_2{=}CBr_2$	N_2O_4	 $Br_2\overset{\overset{NO_2}{\vert}}{C}{-}\overset{\overset{NO_2}{\vert}}{C}Br_2$	(20)
$CBr_2{=}CHBr$	N_2O_4	 $Br_2\underset{\underset{NO_2}{\vert}}{C}{-}\underset{\underset{NO_2}{\vert}}{C}HBr$	(26)
$CH_3CH{=}CHCOOH$	N_2O_4	Product on reduction with Sn and HCl gave $CH_3CHOHCHNH_2COOH$	(49)
$C_6H_5CH{=}CHCHO$	N_2O_3		(236)
$CH_2{=}CHCOOH$	N_2O_4	$C_3H_4O_2(NO_2)(OH)$, $C_3H_4O_2(NO_2)_2$	(48)
 $CH_2{=}\overset{\overset{CH_3}{\vert}}{C}COOH$	N_2O_4	Product on reduction with Sn and HCl gave  $NH_2CH_2\underset{\underset{OH}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}}COOH$	(50)

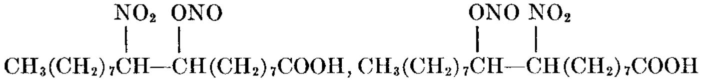
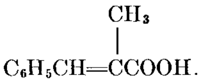
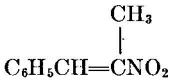
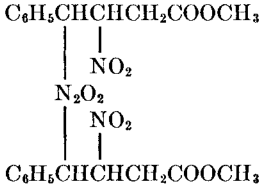
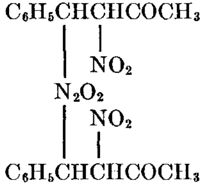
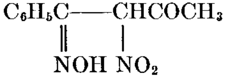
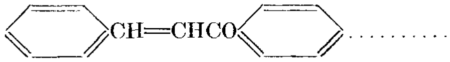
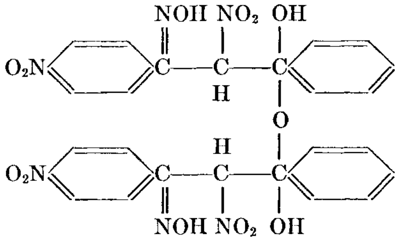
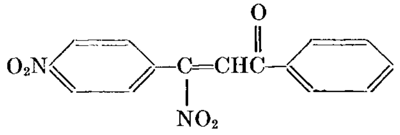
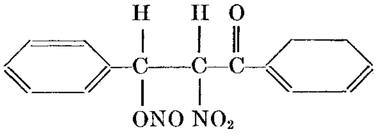
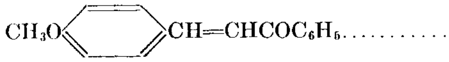
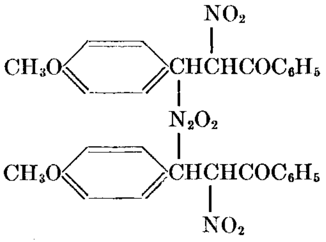
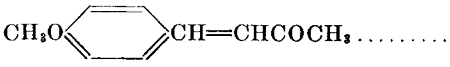
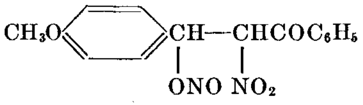
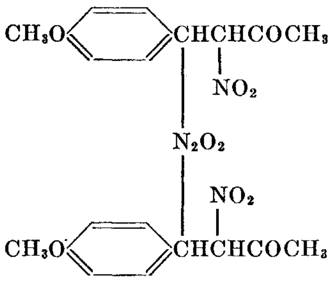
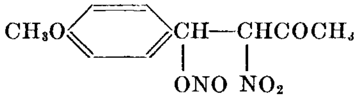
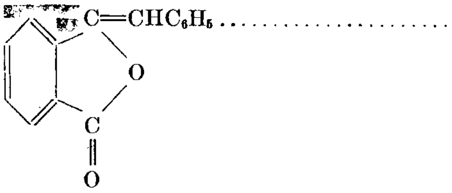
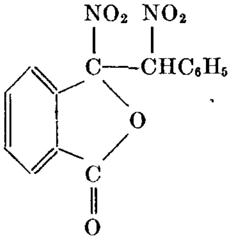
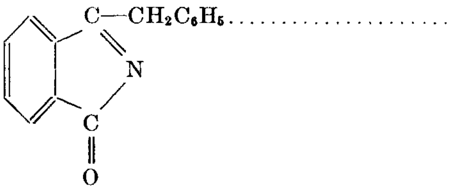
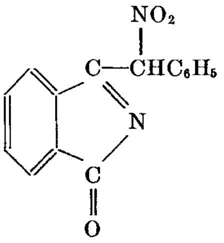
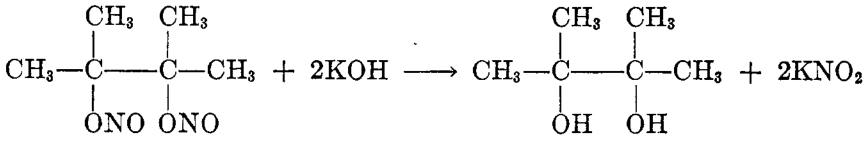
$CH_3CH{=}CHCOOH$	N_2O_4	$CH_3CHOHCHNH_2COOH$ and $CH_3CHNH_2CHOHCOOH$ formed upon reduction with Sn and HCl	(1)
$(CH_3)_2C{=}CHCOOH$	N_2O_4	$(CH_3)_2C(OH)CHNH_2COOH$ and $(CH_3)_2CNH_2CHOHCOOH$ formed upon reduction with Sn and HCl	(1)
$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	N_2O_4	 $CH_3(CH_2)_7\overset{NO_2}{CH}-\overset{ONO}{CH}(CH_2)_7COOH$, $CH_3(CH_2)_7\overset{ONO}{CH}-\overset{NO_2}{CH}(CH_2)_7COOH$	(52, 259)
$C_6H_5CH{=}CHCOOH$	N_2O_3	$C_6H_5CH{=}CHNO_2$	(56, 67)
 $C_6H_5CH{=}\overset{CH_3}{C}COOH$	N_2O_3	 $C_6H_5CH{=}\overset{CH_3}{C}NO_2$	(56)
$CH_2{=}CHCOOCH_3$	N_2O_4	$C_4H_6O_2(NO_2)(OH)$, $C_4H_6O_2(NO_2)_2$	(48)
$CH_2{=}CHCH_2CH_2COOC_2H_5$	N_2O_4	$C_7H_{12}O_2(NO_2)(OH)$, $C_7H_{12}O_2(NO_2)_2$	(51)
$C_6H_5CH{=}CHCH_2COOCH_3$	N_2O_3		(237)
$C_6H_5CH{=}CHCOCH_3$	N_2O_3	  $C_6H_5\underset{NOH}{C}-\underset{NO_2}{CH}COCH_3$	(237)

TABLE 3—*Continued*

ETHYLENIC COMPOUND	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
	N_2O_3	  	(236)
	N_2O_3		(247)

	N_2O_3	  	(247)
	N_2O_3		(66)
	N_2O_3 or N_2O_4	 $C_{15}H_{12}N_2O_4$	(66)

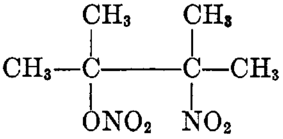


$$CH_3-\underset{ONO}{\overset{CH_3}{C}}-\underset{ONO}{\overset{CH_3}{C}}-CH_3 + 2KOH \longrightarrow CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 + 2KNO_2$$

II

III
Pinacol

that the solid compound II was the dinitrite was based on the observation that normal potassium hydroxide gave the quantity of potassium nitrite to be expected in accordance with the above reaction. The proof of the presence of pinacol was lacking. Schmidt also believed that he obtained a small amount of the dinitro derivative. Dem'yanov (41), on the other hand, believed that the main product was not the dinitrous ester but the nitronitrate (IV).



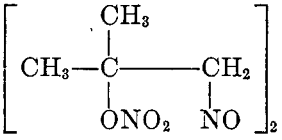
$$CH_3-\underset{ONO_2}{\overset{CH_3}{C}}-\underset{NO_2}{\overset{CH_3}{C}}-CH_3$$

IV

Dem'yanov (41) claimed the production of a very small quantity of *sym*-dinitrotetramethylethane from the reaction of nitrogen tetroxide and tetramethylethylene.

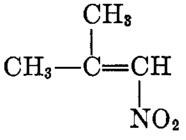
What appears to be the most thorough study of this reaction was made by Michael and Carlson (124). In ether solution they found 19.6–22 per cent of 2,3-dinitro-2,3-dimethylbutane. Without a solvent or with petroleum ether only low yields of the dinitro compound were formed. Under all experimental conditions IV was believed to be formed in various amounts depending upon the conditions. Compound IV and the dinitro derivative formed a double compound. Michael and Carlson concluded that Schmidt's dinitrous ester was not formed.

Michael and Carlson (123) also studied the products formed from isobutylene (2-methylpropene) and nitrogen tetroxide under a variety of conditions. The products from this reaction proved difficult to separate. The products believed to be formed were V, VI, VII and VIII.



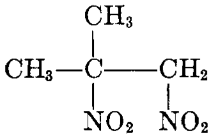
$$\left[CH_3-\underset{ONO_2}{\overset{CH_3}{C}}-\underset{NO}{CH_2}\right]_2$$

V
"Bis(α,β-nitrosonitric ester) derivative of isobutene"



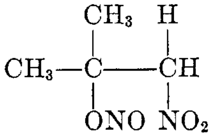
$$CH_3-\overset{CH_3}{C}=\underset{NO_2}{CH}$$

VI
"α-Nitroisobutene"



$$\begin{array}{ccc} & CH_3 & \\ & | & \\ CH_3- & C & -CH_2 \\ & | & | \\ & NO_2 & NO_2 \end{array}$$

VII
"α,β-Dinitroisobutane"



$$\begin{array}{ccc} & CH_3 & H \\ & | & | \\ CH_3- & C & -CH \\ & | & | \\ & ONO & NO_2 \end{array}$$

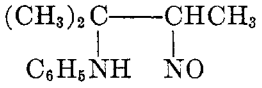
VIII
"α,β-Nitronitrous ester derivative of isobutene"

Product V was not separated when ether was used as a solvent. Without a solvent or with petroleum ether, V was formed to the extent of 13 per cent. When no solvent was used the products were largely oils. The liquid products formed in ether solution were more tractable and were distillable. The addition products in ether solution were not isolated directly but were reduced catalytically. Ammonia and β-hydroxyisobutylamine were found among the reduction products (16–23 per cent), indicating the presence of VIII; isobutylamine was produced by reduction, indicating the presence of VI (5–12 per cent); and isobutylenediamine was formed in quantities indicating at least 12 per cent of VII. This work verifies and adds to the findings of Sidorenko (207). The total yields of these products account for less than 50 per cent of the theoretical. It is probable that considerable polymerization or oxidation of the hydrocarbon took place. Again it is interesting to note the vital effect of the solvent on the course of the reaction.

Ipatieff and Ssolonima (93) reported V from the reaction of nitrogen tetroxide with "isobutene" (2-methylpropene), and analogous products from certain other ethylene derivatives.

Perhaps the reaction of trimethylethylene (amylene) with the oxides of nitrogen has been studied more than that of any other olefin. In 1861 Guthrie (79, 80) obtained a compound from amylene and nitrogen tetroxide to which he gave the formula $C_{10}H_{10}(NO_4)_2$. Translated to our present relative atomic weight system this formula would be $C_5H_{10}N_2O_4$. The latest findings indicate this to be the correct empirical formula for one of the products. Since both nitrogen trioxide and nitrogen tetroxide have been used in these studies, it would be well to consider them separately.

Wallach (229, 231, 232) obtained a 50 per cent yield of the nitric ester of 2-methyl-3-nitroso-2-butanol $(CH_3)_2C(ONO_2)CH(NO)CH_3$ (later shown to be the dimer) from trimethylethylene and "nitrous fumes" in acetic acid solution. This compound was referred to as trimethylethylene nitrosate. The presence of the $—ONO_2$ grouping was deduced from the reaction of the nitric ester with aniline to give aniline nitrate and



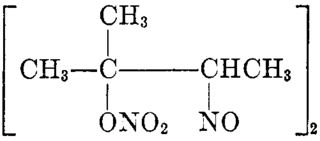
$$\begin{array}{cc} (CH_3)_2C & -CHCH_3 \\ | & | \\ C_6H_5NH & NO \end{array}$$

Similar experiments were carried out with other aromatic amines.

Schmidt (185, 186, 189) claimed yields as high as 84 per cent of what was assumed to be mainly the nitrous ester of 2-methyl-3-nitroso-2-butanol. This conclusion was reached on the basis of the color and on the gradual formation of a crystalline solid which was regarded as a dimer of the nitrous ester. On the basis of later work it is questionable if Schmidt's conclusions were correct.

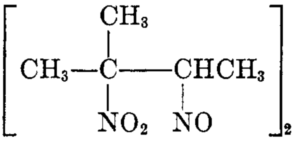
Again the most complete study of the reaction of trimethylethylene with nitrogen trioxide was carried out by Michael and Carlson (122). They made clear that the "nitrous fumes" from arsenious oxide and nitric acid were variable in composition, depending upon the concentration of the nitric acid used and upon other conditions. This discovery explains why so many researches involving nitrogen trioxide led to differing results. In fact it was found to be difficult to get consistent yields even with the best efforts to control conditions.

Most of the experiments of Michael and Carlson were carried out using ether as the solvent. The products found are represented by formulas IX, X, XI, and XII.



$$\left[CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle ONO_2}{|}}{C}}-\underset{\underset{\displaystyle NO}{|}}{CHCH_3}\right]_2$$

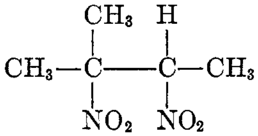
IX



$$\left[CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle NO_2}{|}}{C}}-\underset{\underset{\displaystyle NO}{|}}{CHCH_3}\right]_2$$

X

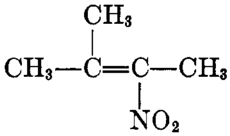
(8.6 to 17.4 per cent)



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle NO_2}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle NO_2}{|}}{C}}-CH_3$$

XI

(10 to 20 per cent)



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=\underset{\underset{\displaystyle NO_2}{|}}{C}-CH_3$$

XII

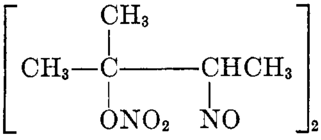
(10 to 20 per cent)

The dimeric nitric ester of 2-methyl-3-nitroso-2-butanol (IX) was shown to be present by catalytic reduction to 3-amino-2-methyl-2-butanol. Both X and XI were reduced to isoamylenediamine, and XII yielded 3-amino-2-methylbutane upon reduction (44). X was oxidized to XI with nitrous fumes or ozone.

The liquid reaction products were distilled at low pressure, giving a volatile blue oil which contained X and XII and a higher boiling green oil which contained XI.

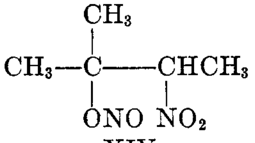
The reaction of trimethylethylene with nitrogen tetroxide was first studied by Guthrie (79, 80) and later by Tilden and Sudborough (214) and Miller (125), who obtained similar results. All subsequent investigations (95, 121, 186) agree that the solid derivative formed was the dimeric nitric ester of bis-2-methyl-3-nitroso-2-butanol. The yields of this ester have been reported from less than 1 per cent to 49 per cent depending upon the conditions.

Michael and Carlson (121) found the main reaction products to be XIII and XIV.



$$\left[CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle ONO_2}{|}}{C}}-\underset{\underset{\displaystyle NO}{|}}{CHCH_3}\right]_2$$

XIII

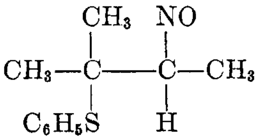


$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle ONO}{|}}{C}}-\underset{\underset{\displaystyle NO_2}{|}}{CHCH_3}$$

XIV

Very little of XIII was formed in ether, but in petroleum ether or without a solvent as high as 49 per cent of XIII was found. The liquid products from petroleum ether or without a solvent were so unstable that they were not identified. The liquid products formed when ether was used as a solvent were distillable. At least 35 per cent of this liquid product was shown to be XIV.

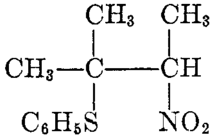
The presence of the $—ONO_2$ linkage in XIII was inferred from the reaction of XIII with sodium thiophenoxide to produce XV and sodium nitrate in quantitative yields.



$$\begin{array}{ccccc} & CH_3 & & NO & \\ & | & & | & \\ CH_3— & C & — & C & —CH_3 \\ & | & & | & \\ & C_6H_5S & & H & \end{array}$$

XV

The presence of the —ONO linkage in XIV was also demonstrated by the reaction of XIV with sodium thiophenoxide to produce a quantitative yield of XVI and sodium nitrite.



$$\begin{array}{ccccc} & CH_3 & & CH_3 & \\ & | & & | & \\ CH_3— & C & — & CH & \\ & | & & | & \\ & C_6H_5S & & NO_2 & \end{array}$$

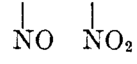
XVI

Monti (126) allowed octylene, diisobutylene, and hexadecylene to react with nitrogen trioxide and nitrogen tetroxide and obtained chiefly the nitronitrite and nitrosonitrate derivatives.

Diallyl and nitrogen tetroxide reacted in ether solution to give a substance which Henry (89) formulated as $C_6H_{10}(NO_2)_4$ and which presumably would now be written as $C_6H_{10}(NO_2)_2$. This product was not analyzed and no reactions of it were studied. Sidorenko (206) repeated this work and obtained a product which could be reduced to a diamine.

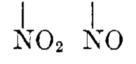
B. *Aryl ethylenes*

When styrene reacted with nitrogen trioxide (146) the product, according to Sommer (210) and Wieland (239), had the empirical formula $C_6H_5CH{=}CH_2N_2O_3$. Sommer suggested two possible structures, XVII and XVIII.



$$\begin{array}{lcc} C_6H_5 & CH— & CH_2 \\ & | & | \\ & NO & NO_2 \end{array}$$

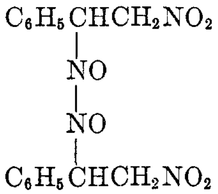
XVII



$$\begin{array}{lcc} C_6H_5 & CH— & CH_2 \\ & | & | \\ & NO_2 & NO \end{array}$$

XVIII

Wieland believed that the product was the dimeric form of XVII, or bis-1-nitroso-1-phenyl-2-nitroethane and wrote for it the formula XIX. Wieland referred to this substance as styrene pseudonitrosite, a name which has led to confusion. Compound XIX was found to be unstable.



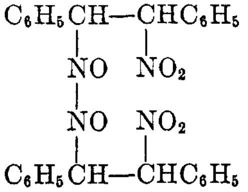
$$\begin{array}{l} C_6H_5CHCH_2NO_2 \\ \quad\;\; | \\ \quad\;\, NO \\ \quad\;\; | \\ \quad\;\, NO \\ \quad\;\; | \\ C_6H_5CHCH_2NO_2 \end{array}$$

XIX

When refluxed with ethanol it changed to the oxime of α-nitroacetophenone; with concentrated hydrochloric acid it changed to α-nitroacetophenone, which further reacted to form benzoic acid and nitromethane.

Styrene, according to Priebs (146), reacted with nitrogen trioxide to yield 1-nitro-2-phenylethylene, after steam distillation of the product.

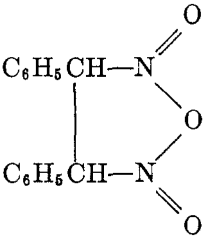
When stilbene reacted with nitrogen trioxide a solid product formed which Schmidt (183) claimed melted at 195–197°C. and Wieland (243) stated melted at 132°C. Apparently these investigators were working under different conditions; either they had different compounds or possibly they were working with mixtures. Both seemed to agree on the empirical formula $C_6H_5CH{=}CHC_6H_5N_2O_3$. Gabriel suggested the formula ($C_6H_5CH{=}CHC_6H_5N_2O_4$) (67). Schmidt regarded the product as a monomer; Wieland regarded it as a dimer and wrote for it the structural formula XX, which is analogous to XIX.



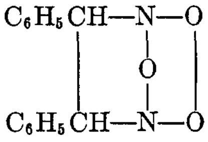
$$\begin{array}{l} C_6H_5CH{-}CHC_6H_5 \\ \quad\;\; | \qquad | \\ \quad\;\, NO \quad NO_2 \\ \quad\;\; | \\ \quad\;\, NO \quad NO_2 \\ \quad\;\; | \qquad | \\ C_6H_5CH{-}CHC_6H_5 \end{array}$$

XX

Schmidt formulated his compound as XXI or XXII.



XXI



XXII

According to Schmidt (184), stilbene reacted with nitrogen tetroxide to produce 1,2-dinitro-1,2-diphenylethane.

Shilov (204) added oxides of nitrogen to triphenylethylene and obtained a good yield of what was presumed to be the 1,2-dinitro derivative.

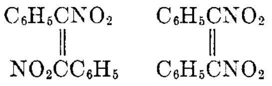
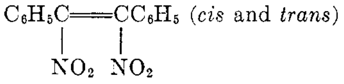
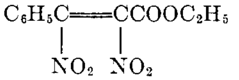
C. Acetylenic compounds (see table 4)

Several examples have been described in which nitrogen trioxide or tetroxide reacted with compounds containing acetylenic linkages, forming nitro compounds. With phenylacetylene nitrogen tetroxide formed 1,2-dinitro-1-phenylethylene; 1,2-diphenylacetylene gave 1,2-dinitro-1,2-diphenylethylene, which upon reduction with zinc and acetic acid gave 2,3,5,6-tetraphenylpiperazine (182, 188, 248). As was expected, the 1,2-dinitro-1,2-diphenylethylene existed as both a *cis* and a *trans* isomer (182, 188).

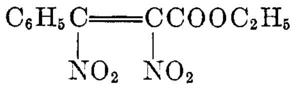
Diiodoacetylene reacted with either nitrogen tetroxide or trioxide in ether solution to produce triiodonitroethylene (19). Some doubt exists regarding the nature of this product.

TABLE 4

Acetylenic compounds

ACETYLENIC COMPOUND	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
$CI{\equiv}CI$	N_2O_3	$CI_2{=}CINO_2$	(19)
$CI{\equiv}CI$	N_2O_4	$CI_2{=}CINO_2$	(19)
$C_6H_5C{\equiv}CH$	N_2O_4	$C_6H_5C(NO_2){=}CHNO_2$	(248)
$C_6H_5C{\equiv}CC_6H_5$	N_2O_3	 $\begin{array}{c} C_6H_5CNO_2 \\ \Vert \\ NO_2CC_6H_5 \end{array}$ $\begin{array}{c} C_6H_5CNO_2 \\ \Vert \\ C_6H_5CNO_2 \end{array}$	(182, 188)
$C_6H_5C{\equiv}CC_6H_5$	N_2O_4	 $\underset{NO_2}{C_6H_5C}{=}\underset{NO_2}{CC_6H_5}$ (*cis* and *trans*)	(248)
$C_6H_5C{\equiv}CCOOC_2H_5$	N_2O_4	 $\underset{NO_2}{C_6H_5C}{=}\underset{NO_2}{CCOOC_2H_5}$	(241)

Wieland (241) reported the production of XXIII by the reaction of ethyl phenylpropiolate with nitrogen tetroxide in petroleum ether.

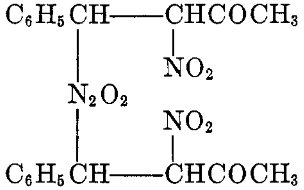


$$\underset{NO_2}{C_6H_5C}{=}\underset{NO_2}{CCOOC_2H_5}$$

XXIII

D. Ethylenic carbonyl compounds

Wieland (237, 247) studied the reaction of a series of compounds with nitrogen trioxide and in many cases obtained in low yields what he referred to as the corresponding pseudonitrosites. In this group were benzalacetone, methyl cinnamylacetate, anisalacetophenone, 2-*p*-methoxyphenyl-1-methylethylene and anisalacetone. To give a typical example, the product from benzalacetone was formulated as XXIV. Under the suggested terminology this would be called bis-1-acetyl-1-nitro-2-nitroso-2-phenylethane.

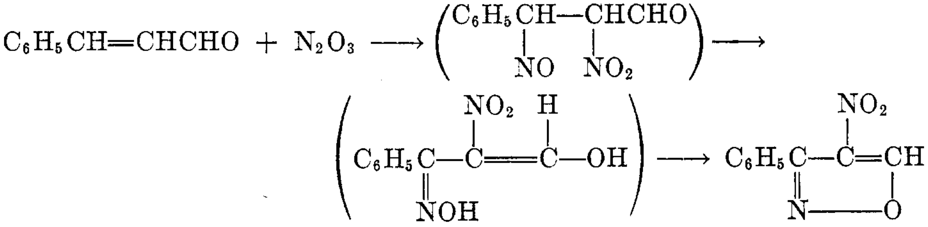


$$\begin{array}{lcl} C_6H_5CH & -\!\!-\!\!- & CHCOCH_3 \\ | & & \;| \\ | & & NO_2 \\ N_2O_2 & & \\ | & & NO_2 \\ | & & \;| \\ C_6H_5CH & -\!\!-\!\!- & CHCOCH_3 \end{array}$$

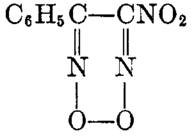
XXIV

In all cases Wieland studied several reactions of the products to substantiate his conclusions.

For cinnamaldehyde Wieland (237) regarded the first step as the formation of the monomeric nitronitroso derivative similar to XXIV. It was believed that it passed through the following sequence of changes:

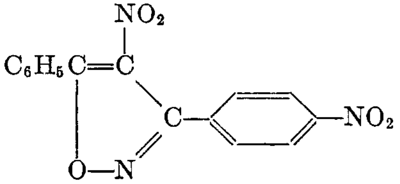


The end product was believed to be the 4-nitro-3-phenylisoxazole, which was obtained in 35 to 40 per cent yield. Wieland also reported the formation of a low yield of phenylnitroglyoxime peroxide (XXV).



XXV

From benzalacetophenone with nitrogen trioxide Wieland (236) obtained an intermediate solid which upon boiling with ethanol gave the nitroisoxazole derivative XXVI, in which nitration took place in the benzene ring as well as reaction at the double bond.



XXVI

On the basis of these experiments Wieland concluded (237, 247) that compounds of the type XXVII with nitrogen trioxide generally give the bisnitronitroso derivatives when R is positive in character, but fail to give the bisnitronitroso type when R is strongly negative.

$$C_6H_5CH{=}CHR$$

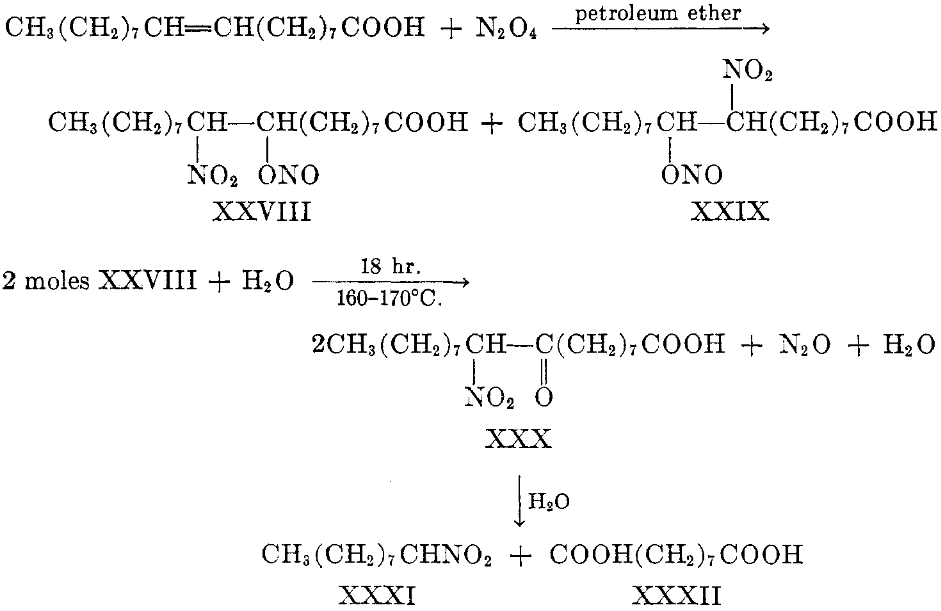
XXVII

When R is $\overset{\text{O}}{\overset{\|}{\text{—C—}}}$, either the yields of the nitronitroso derivative are low or none at all can be isolated.

Egoroff (or Yegorov: 48, 49, 50, 51, 52, 259) carried out a series of studies on the reaction of unsaturated acids with nitrogen tetroxide. In general, relatively unstable addition products formed which were usually believed to be mixtures of the dinitro, isomeric nitronitrites, and hydroxynitro derivatives. The latter type was believed to be formed *via* the nitronitrite.

Upon reduction these addition products were transformed to diamino compounds or to amino alcohols. Although the yields were generally not stated, they must have been relatively low.

Since these addition compounds could be split at the position of the double bond by water or hydrochloric acid, it was proposed that such splitting could be used as a method of locating the position of the ethylenic linkage. The example of oleic acid will suffice to illustrate. The following sequence of reactions was suggested:



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH + N_2O_4 \xrightarrow{\text{petroleum ether}}$$

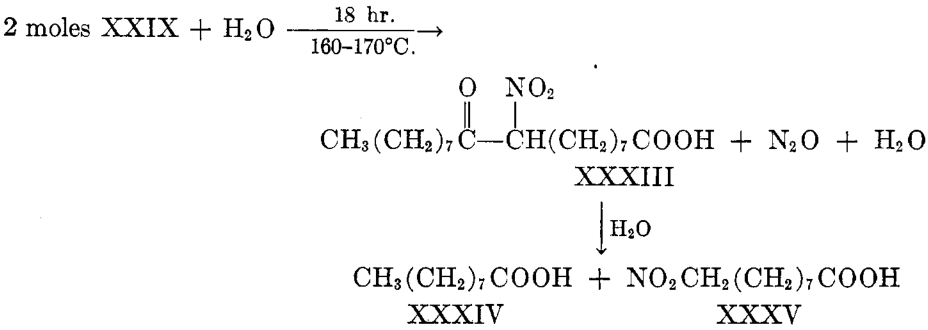
$$\underset{\text{XXVIII}}{CH_3(CH_2)_7\underset{NO_2}{\underset{|}{CH}}{-}\underset{ONO}{\underset{|}{CH}}(CH_2)_7COOH} + \underset{\text{XXIX}}{CH_3(CH_2)_7\underset{ONO}{\underset{|}{CH}}{-}\overset{NO_2}{\overset{|}{CH}}(CH_2)_7COOH}$$

$$2\text{ moles XXVIII} + H_2O \xrightarrow[160\text{–}170^\circ\text{C.}]{18\text{ hr.}}$$

$$\underset{\text{XXX}}{2CH_3(CH_2)_7\underset{NO_2}{\underset{|}{CH}}{-}\underset{O}{\underset{\|}{C}}(CH_2)_7COOH} + N_2O + H_2O$$

$$\Big\downarrow{\scriptstyle H_2O}$$

$$\underset{\text{XXXI}}{CH_3(CH_2)_7CHNO_2} + \underset{\text{XXXII}}{COOH(CH_2)_7COOH}$$

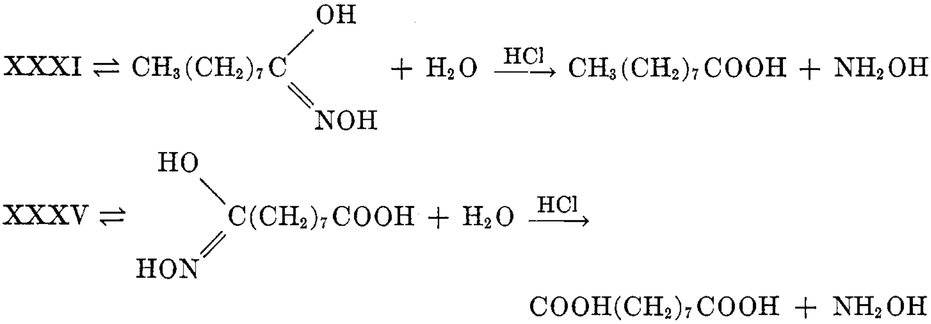


$$2\text{ moles XXIX} + H_2O \xrightarrow[160\text{–}170^\circ\text{C.}]{18\text{ hr.}} \underset{\text{XXXIII}}{CH_3(CH_2)_7\overset{\overset{O}{\|}}{C}-\overset{\overset{NO_2}{|}}{C}H(CH_2)_7COOH} + N_2O + H_2O$$

$$\downarrow H_2O$$

$$\underset{\text{XXXIV}}{CH_3(CH_2)_7COOH} + \underset{\text{XXXV}}{NO_2CH_2(CH_2)_7COOH}$$

XXVIII and XXIX when heated with concentrated hydrochloric acid in a sealed tube for 3–5 hr. were considered as first reacting as above with water to give XXX, XXXI, XXXII, XXXIII, XXXIV, and XXXV. Then XXXI and XXXV reacted further:



Accordingly, with concentrated hydrochloric acid the final products formed are azelaic and pelargonic acids, thus fixing the position of the double bond at 9,10, which is the same position as deduced by ozonolysis. This same type of bond location was done with other examples. Unfortunately the yields of the products were not stated. It may be guessed that they were discouragingly low, because apparently no one has attempted to extend the method. If conditions could be realized for obtaining reasonably good yields, this idea might be useful.

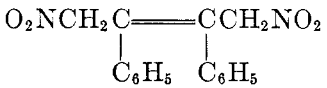
With cinnamic acid and nitrogen trioxide, Erdman (56) obtained as the only isolable product 1-nitro-2-phenylethylene. With α-methylcinnamic acid the analogous nitro derivative was obtained. Abderhalden (1) treated dimethylacrylic acid with nitrogen tetroxide and obtained results analogous to those of Egoroff.

E. Conjugated systems

Some cases of the reaction of nitrogen tetroxide with conjugated systems are recorded. Wieland (254, 255) observed the formation of 1,4-dinitro-1,4-diphenyl-2-butene when either nitrogen trioxide or tetroxide was added to 1,4-diphenyl-1,3-butadiene. The addition product could be reduced to the corresponding diamine in poor yields. Thorpe and Farmer (213) made a similar claim.

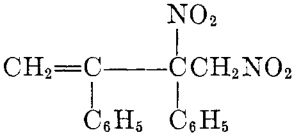
Neber and Paeschke (128) claimed 1,2-addition to 1-cyano-1,4-diphenyl-1,3-butadiene to obtain 1-cyano-1,4-diphenyl-3,4-dinitro-1-butene. Other examples studied were less conclusive with regard to 1,2- or 1,4-addition. Franklin and Wilkins (61) believed they obtained 1,4-dinitro-2-butene from the reaction of nitrogen tetroxide and 1,3-butadiene when these substances were allowed to react in various solvents or in the vapor phase. Dinitro derivatives were reported from other conjugated diolefins.

Allen *et al.* (4) observed both 1,2- and 1,4-addition of nitrogen tetroxide to 2,3-diphenyl-1,3-butadiene, giving rise to XXXVI and XXXVII.



$$O_2NCH_2\underset{C_6H_5}{\underset{|}{C}}=\underset{C_6H_5}{\underset{|}{C}}CH_2NO_2$$

XXXVI
(m.p. 151°C.)



$$CH_2=\underset{C_6H_5}{\underset{|}{C}}-\overset{NO_2}{\overset{|}{\underset{C_6H_5}{\underset{|}{C}}}}CH_2NO_2$$

XXXVII
(m.p. 192°C.)

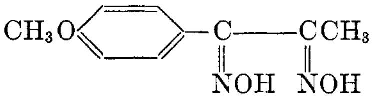
Ozonolysis of XXXVII produced formaldehyde, and oxidation with permanganate gave benzil. When XXXVII was dissolved in concentrated sodium methoxide a yellow crystalline sodium salt resulted, which upon acidification with acetic acid gave XXXVI. When the sodium salt of XXXVI was acidified, XXXVII was obtained.

F. Miscellaneous ethylenic compounds

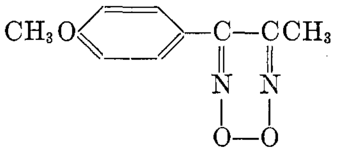
Propadiene (43) with nitrogen trioxide gave a crystalline nitrosite having the formula $C_3H_4N_2O_3$. The structural formula was not elucidated. Dimethylbutadiene gave a crystalline nitrosite, $C_6H_{10}N_2O_3$, which was reduced to an amine. The structures of these compounds were not stated.

1-Butene (40) reacted with nitrogen trioxide to give $(C_4H_8N_2O_3)_2$, which presumably was the bisnitrosonitro derivative. A residue was also formed which upon reduction gave a diamine, $C_4H_8(NH_2)_2$, and *n*-butyraldehyde.

Anethole reacted with sodium nitrite and acetic acid at 50–60°C. to give XXXVIII and XXXIX (240).

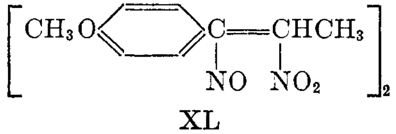


XXXVIII



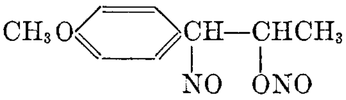
XXXIX

When the same reaction was carried out in the cold, the bisnitrosonitro compound XL was formed.



XL

Toennies (219) apparently obtained by a similar reaction a compound with the same empirical formula but preferred to consider it the nitrosonitrous compound XLI.

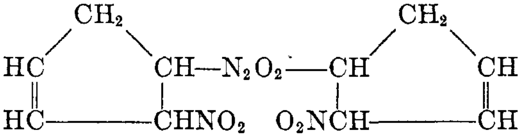


XLI

The conditions of Toennies' experiment were vaguely stated.

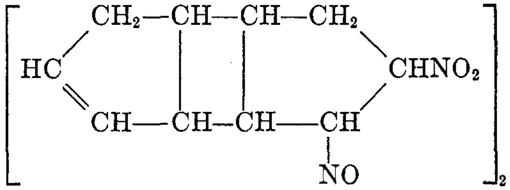
Angeli (5, 6) concluded that compounds such as apiole, safrole, and eugenole containing the grouping $—CH_2—CH═CH_2$ did not react with nitrous acid (probably nitrogen trioxide) to give solid derivatives, but that the corresponding iso-compounds containing $—CH═CH—CH_3$ did give solid derivatives, presumably of the nitronitrite type.

Wieland (255) allowed cyclopentadiene to react with nitrogen trioxide and obtained an unstable solid derivative. In spite of its instability and the difficulty of its analysis the formula XLII was suggested, probably more because of analogy with other "pseudonitrosites" obtained by Wieland.



XLII

Rule (155) and Wieland (255) studied the action of nitrogen trioxide with dicyclopentadiene. Rule gave XLIII for the formula of the product, which is



XLIII

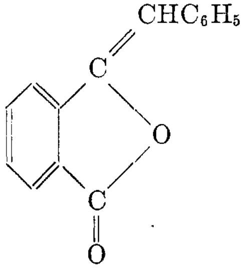
the bisnitronitroso derivative, the type so often postulated by Wieland for the addition product of nitrogen trioxide to ethylenic bonds.

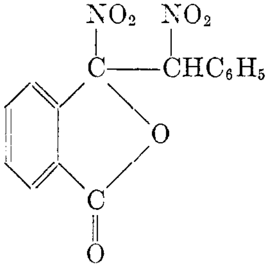
Cyclohexene (176) with dry nitrogen tetroxide in cold petroleum ether gave about a 25 per cent yield of the bisnitrosonitro derivative and oily products.

1,3-Cyclohexadiene with nitrogen trioxide in chloroform gave an intermediate which, when reduced with tin and hydrochloric acid, gave $C_6H_8(NH_2)_2 \cdot 2HCl$.

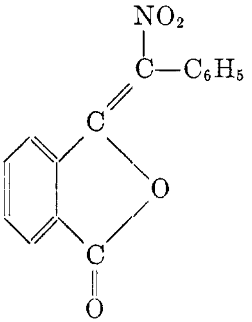
Dihydronaphthalene dissolved in acetone solution and treated with nitrogen tetroxide gave an unidentified solid, which on treatment with alcoholic potassium hydroxide yielded 2-nitro-3,4-dihydronaphthalene.

Gabriel (66, 67) allowed benzylidenephthalide (XLIV) to react with both nitrogen trioxide and tetroxide and obtained the relatively unstable XLV in both cases.

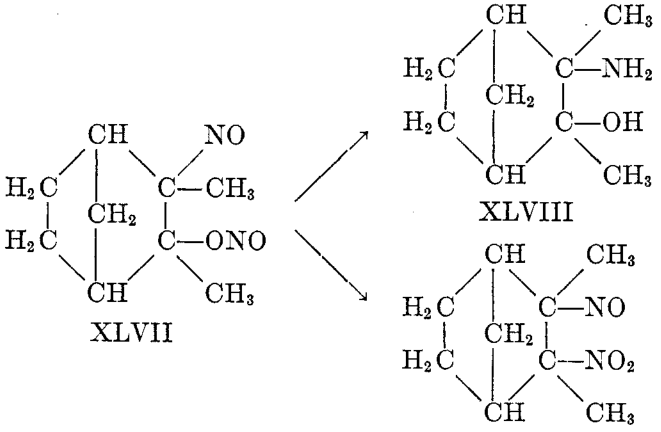

XLIV


XLV

Compound XLV lost nitrous acid in boiling benzene to give XLVI.


XLVI

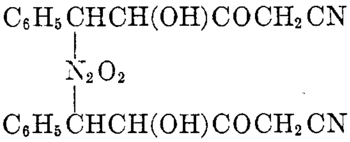
According to Dennstedt (45) indene and coumarone reacted in cold ether solution with nitrogen trioxide to form the corresponding nitrosonitrite derivatives, along with oily products. In a similar manner santene gives the santene nitrosonitrite (XLVII) (129). Compound XLVII can be converted by reduction to XLVIII and can be oxidized to XLIX.


XLVII

XLVIII

XLIX

The reaction of benzaldiacetyl monoxime with nitrogen trioxide in dry ether solution stands out as an unusual case. Diels (46) ascribed formula L to the unstable solid derivative thus obtained. A series of reactions of L were studied to elucidate its structure.



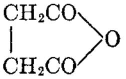
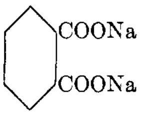
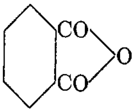
$$\begin{array}{l} C_6H_5CHCH(OH)COCH_2CN \\ \quad\quad | \\ \quad\quad N_2O_2 \\ \quad\quad | \\ C_6H_5CHCH(OH)COCH_2CN \end{array}$$

L

The only case found in which an unsaturated ether was allowed to react with nitrogen trioxide was that of methyl allyl ether. An undetermined nitronitrosopropyl ether was formed, which upon reduction gave methyl β,γ-diaminopropyl ether.

TABLE 5

Alkali metal salts of organic acids

ORGANIC ACID SALT	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
CH_3COONa	N_2O_4	$(CH_3CO)_2O$	(152, 153)
C_2H_5COONa	N_2O_4	$(C_2H_5CO)_2O$	(152, 153)
C_3H_7COONa	N_2O_4	$(C_3H_7CO)_2O$	(152, 153)
CH_2COONa CH_2COONa	N_2O_4		(151)
	N_2O_4		(151)

Considerable use of the oxides of nitrogen has been made in the separation and detection of terpenes (27, 37, 47, 58, 59, 68, 107, 228, 230). The oxides of nitrogen are added to the natural mixture to produce solid derivatives. These compounds and their reactions are usually not important except for identification purposes. The literature describing these compounds is confusing, because the structures of some terpenes previously accepted have been shown to be in error. Since this field is so confusing and since the compounds formed are not of general interest, no attempt has been made to collect and discuss the reactions of the oxides of nitrogen with terpenes.

A similar statement can be made for the studies conducted with oxides of nitrogen and rubber. After examining several papers by Harries (81, 82, 83, 84, 85) and by others (2, 3, 55, 75) and after observing the inconclusive nature of this work, no attempt was made to collect all the references on this subject.

VI. REACTIONS WITH ALKALI METAL SALTS OF ORGANIC ACIDS (SEE TABLE 5)

Rodionov and Oblitseva (152, 153) observed that good yields of acetic, propionic, and butyric anhydrides could be obtained by heating the dry sodium salts of the corresponding acids with nitrogen tetroxide. They expressed the reaction for sodium acetate as follows:

$$2CH_3COONa + 2N_2O_4 \rightarrow (CH_3CO)_2O + 2NaNO_3 + N_2O_3$$

This same technique was tried by Riebsomer and Reinecke (151), using the sodium salts of succinic and phthalic acids. The corresponding anhydrides were obtained in yields of 75 per cent or more. This approach to anhydride formation might be of interest.

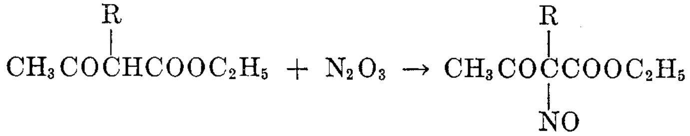
VII. REACTIONS WITH ORGANOMETALLIC COMPOUNDS (SEE TABLE 6)

Wieland (238) found that ethylmagnesium iodide in cold ether reacted very vigorously with nitrogen tetroxide. After hydrolysis and extraction with ether, diethylhydroxylamine was obtained. No analogous compound was produced from aryl Grignard reagents (249). This method might be useful for the synthesis of special hydroxylamines which are not readily obtainable by other methods.

Various aromatic organometallic compounds have been allowed to react with nitrogen trioxide or with mixtures of nitric oxide and nitrogen dioxide simultaneously (11, 97, 110, 209). In many instances good yields of the aromatic diazonium nitrates were produced. Thus diphenylmercury gave benzenediazonium nitrate with a yield of 85 per cent; tetraphenyltin, 40 per cent; tetraphenyllead, 100 per cent; phenylmagnesium bromide, 15 per cent; triphenylbismuth, 54 per cent; di-*p*-tolylmercury, 51 per cent. Aryl metal nitrates and aromatic nitroso compounds were formed simultaneously. Dimethylmercury gave an explosive crystalline product (12).

VIII. MISCELLANEOUS REACTIONS (SEE TABLE 7)

Schmidt (191, 192, 193, 194) allowed various mono-α-substituted acetoacetic esters to react with nitrogen trioxide and obtained generally the corresponding relatively unstable blue α-nitroso derivatives. The general reaction may be written:



$$CH_3CO\overset{\displaystyle R}{\overset{|}{C}}HCOOC_2H_5 + N_2O_3 \rightarrow CH_3CO\underset{\displaystyle NO}{\underset{|}{\overset{\displaystyle R}{\overset{|}{C}}}}COOC_2H_5$$

When both α hydrogens were substituted with alkyl groups no action took place.

α-Nitroso or -isonitroso compounds were also formed from ethyl propionate, isoamyl acetate, and other esters. Schmidt's general conclusion was that these

TABLE 6

Organometallic compounds

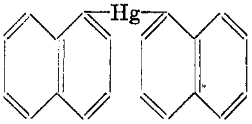
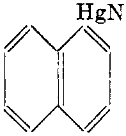
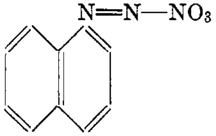
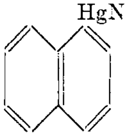
ORGANOMETALLIC COMPOUND	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
$Hg(C_6H_5)_2$	N_2O_3	$HgC_6H_5NO_3$, $C_6H_5N{=}NNO_3$, C_6H_5NO	(11, 110)
$Hg(C_6H_5)_2$	N_2O_4	$HgC_6H_5NO_3$, C_6H_5NO	(11)
(p-$CH_3C_6H_4)_2Hg$	N_2O_3	p-$CH_3C_6H_4HgNO_3$, p-$CH_3C_6H_4N{=}NNO_3$	(97)
(p-$CH_3C_6H_4)_2Hg$	N_2O_4	p-$CH_3C_6H_4HgNO_3$, p-$CH_3C_6H_4NO$	(97)
(o-$CH_3C_6H_4)_2Hg$	N_2O_3	o-$CH_3C_6H_4HgNO_3$, o-$CH_3C_6H_4N{=}NNO_3$	(97)
(o-$CH_3C_6H_4)_2Hg$	N_2O_4	o-$CH_3C_6H_4HgNO_3$, o-$CH_3C_6H_4NO$	(97)
	N_2O_3	 	(97)
	N_2O_4		(97)
$(C_6H_5)_4Sn$	N_2O_3	$C_6H_5N{=}NNO_3$	(110)
$(C_6H_5)_3SnCl$	N_2O_3	$C_6H_5N{=}NNO_3$	(110)
$(C_6H_5)_2SnCl_2$	N_2O_3	$C_6H_5N{=}NNO_3$	(110)
$C_6H_5SnCl_3$	N_2O_3	$C_6H_5N{=}NNO_3$	(110)
$(C_6H_5)_4Pb$	N_2O_3	$C_6H_5N{=}NNO_3$	(110)
$(C_6H_5)_3PbCl$	N_1O_3	$C_6H_5N{=}NNO_3$	(110)
$(C_6H_5)_3Bi$	N_2O_3	$C_6H_5N{=}NNO_3$	(110)
$(C_6H_5)_2TiCl$	N_2O_4	$C_6H_5N{=}NNO_3$	(110)
C_6H_5MgBr	N_2O_4	$C_6H_5N{=}NNO_3$	(110)
C_2H_5MgI	N_2O_4	$(C_2H_5)_2NOH$ (after hydrolysis)	(238)

TABLE 7

Miscellaneous

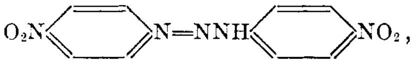
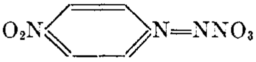
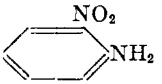
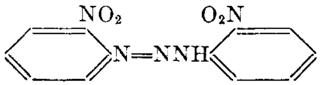
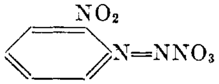
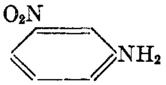
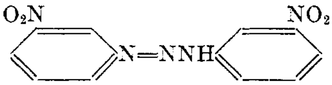
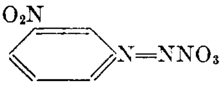
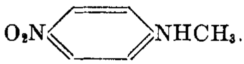
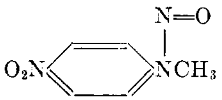
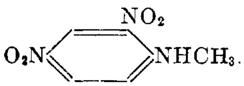
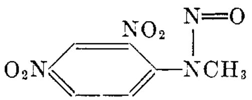
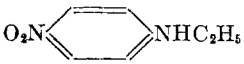
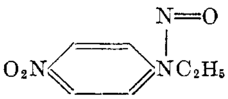
COMPOUND	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
Maleic acid	N_2O_3	Fumaric acid	(180)
Oleic acid	N_2O_4	Elaidic acid	(76, 118)
$C_6H_5NH_2$	N_2O_4	$C_6H_5N{=}NNO_3$	(256)
$C_6H_5NHCOCH_3$	N_2O_4	$C_6H_5N{=}NNO_3$, CH_3COOH	(244)
	N_2O_4	 	(91)
	N_2O_4	 	(91)
	N_2O_4	 	(91)
	N_2O_3		(211)
	N_2O_3		(211)
	N_2O_3		(211)

TABLE 7—*Continued*

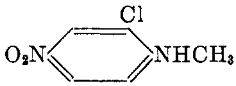
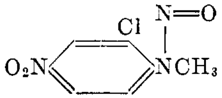
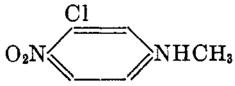
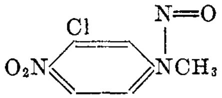
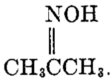
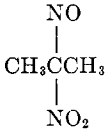
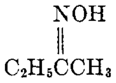
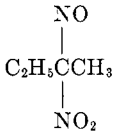
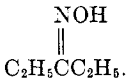
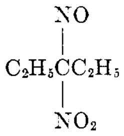
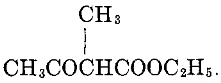
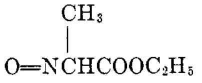
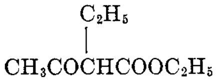
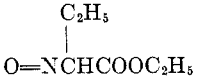
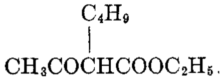
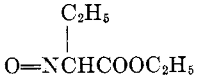
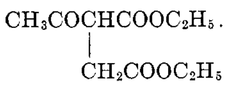
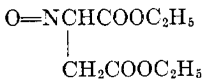
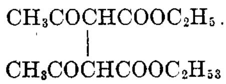
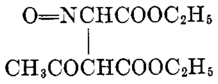
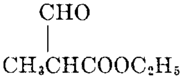
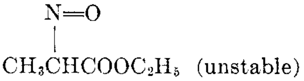
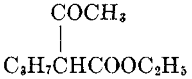
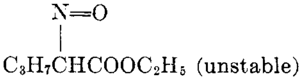
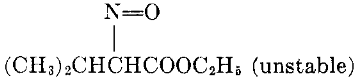
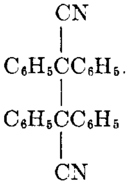
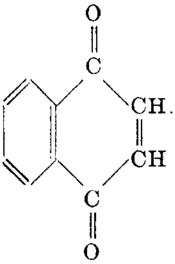
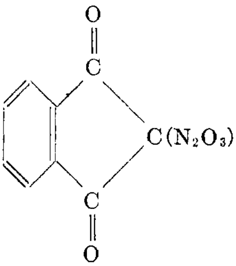
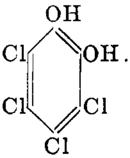
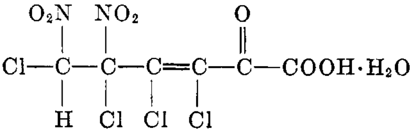
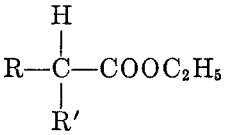
COMPOUND	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
	N_2O_3		(211)
	N_2O_3		(211)
 $\mathrm{CH_3\overset{\overset{\displaystyle NOH}{\Vert}}{C}CH_3}$	N_2O_3 or N_2O_4	 $\mathrm{CH_3\underset{\underset{\displaystyle NO_2}{\vert}}{\overset{\overset{\displaystyle NO}{\vert}}{C}}CH_3}$	(196)
 $\mathrm{C_2H_5\overset{\overset{\displaystyle NOH}{\Vert}}{C}CH_3}$	N_2O_3 or N_2O_4	 $\mathrm{C_2H_5\underset{\underset{\displaystyle NO_2}{\vert}}{\overset{\overset{\displaystyle NO}{\vert}}{C}}CH_3}$	(196)
 $\mathrm{C_2H_5\overset{\overset{\displaystyle NOH}{\Vert}}{C}C_2H_5}$	N_2O_3 or N_2O_4	 $\mathrm{C_2H_5\underset{\underset{\displaystyle NO_2}{\vert}}{\overset{\overset{\displaystyle NO}{\vert}}{C}}C_2H_5}$	(196)
 $\mathrm{CH_3CO\overset{\overset{\displaystyle CH_3}{\vert}}{C}HCOOC_2H_5}$	N_2O_3	 $\mathrm{O{=}N\overset{\overset{\displaystyle CH_3}{\vert}}{C}HCOOC_2H_5}$ (unstable)	(194)
 $\mathrm{CH_3CO\overset{\overset{\displaystyle C_2H_5}{\vert}}{C}HCOOC_2H_5}$	N_2O_3	 $\mathrm{O{=}N\overset{\overset{\displaystyle C_2H_5}{\vert}}{C}HCOOC_2H_5}$ (unstable)	(194)
 $\mathrm{CH_3CO\overset{\overset{\displaystyle C_4H_9}{\vert}}{C}HCOOC_2H_5}$	N_2O_3	 $\mathrm{O{=}N\overset{\overset{\displaystyle C_2H_5}{\vert}}{C}HCOOC_2H_5}$ (unstable)	(194)
 $\mathrm{CH_3CO\underset{\underset{\displaystyle CH_2COOC_2H_5}{\vert}}{C}HCOOC_2H_5}$	N_2O_3	 $\mathrm{O{=}N\underset{\underset{\displaystyle CH_2COOC_2H_5}{\vert}}{C}HCOOC_2H_5}$ (unstable)	(191, 193, 194)
 $\mathrm{CH_3CO\underset{\underset{\displaystyle CH_3COCHCOOC_2H_{53}}{\vert}}{C}HCOOC_2H_5}$	N_2O_3	 $\mathrm{O{=}\underset{\underset{\displaystyle CH_3COCHCOOC_2H_5}{\vert}}{N}CHCOOC_2H_5}$ (unstable)	(194)

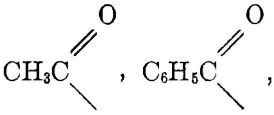
TABLE 7—*Continued*

COMPOUND	OXIDE OF NITROGEN	PRODUCTS FORMED	REFERENCE
 $CH_3\overset{\overset{CHO}{\vert}}{C}HCOOC_2H_5$	N_2O_3	 $CH_3\overset{\overset{N=O}{\vert}}{C}HCOOC_2H_5$ (unstable)	(191)
 $C_3H_7\overset{\overset{COCH_3}{\vert}}{C}HCOOC_2H_5$	N_2O_3	 $C_3H_7\overset{\overset{N=O}{\vert}}{C}HCOOC_2H_5$ (unstable)	(191)
$C_6H_5COCH(COOC_2H_5)_2$	N_2O_3	$O=NCH(COOC_2H_5)_2$ (unstable)	(191)
$(CH_3)_2CHCH_2COOC_2H_5$	N_2O_3	 $(CH_3)_2CH\overset{\overset{N=O}{\vert}}{C}HCOOC_2H_5$ (unstable)	(192)
 $\begin{array}{c} CN \\ \vert \\ C_6H_5CC_6H_5 \\ \vert \\ C_6H_5CC_6H_5 \\ \vert \\ CN \end{array}$	N_2O_4	$(C_6H_5)_2C(NO_2)CN$ or $(C_6H_5)_2C(ONO)CN$	(257)
	N_2O_3		(179)
	N_2O_4	 $Cl-\underset{\underset{H}{\vert}}{\overset{\overset{O_2N}{\vert}}{C}}-\underset{\underset{Cl}{\vert}}{\overset{\overset{NO_2}{\vert}}{C}}-\underset{\underset{Cl}{\vert}}{C}=\underset{\underset{Cl}{\vert}}{C}-\overset{\overset{O}{\Vert}}{C}-COOH\cdot H_2O$	(260)

nitroso compounds would form from nitrogen trioxide with compounds of the type



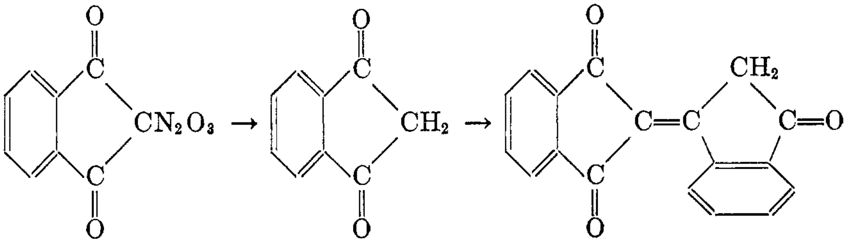
$$R{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}{-}COOC_2H_5$$



when R′ was H, CH_3C, C_6H_5C, alkyl, or —COOH.

Instances are recorded showing that nitrogen oxides are capable of transforming geometric isomers from one form to the other. Thus Schmidt (180) was able partially to convert maleic to fumaric acid. Meyer (118) and Gottlieb (76) transformed oleic to elaidic acid.

One example is recorded in which a six-membered ring compound was changed to a five-membered ring compound (179). 1,4-Naphthoquinone reacted with nitrogen trioxide to produce I, which Schmidt named α,γ-diketohydrindene nitrosite.

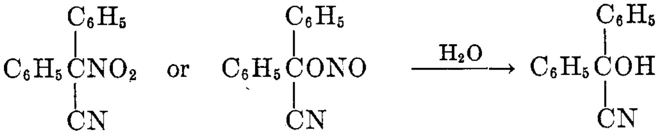


I II III

Compound I was relatively unstable and in hot water lost oxides of nitrogen to form diketohydrindene (II), which in turn gradually changed to the anhydrobisdiketohydrindene (III).

Masson (113) allowed nitrogen trioxide to react with glycerol. An unstable compound was formed to which was assigned the formula $C_3H_5(NO_2)_3$. The analytical data were not convincing. It was believed to be a nitrous ester.

Wittig (257) studied one example in which a saturated molecule was split by nitrogen tetroxide. The dinitrile of tetraphenylsuccinic acid in chloroform treated with nitrogen tetroxide gave IV or V in better than 50 per cent yield.



$$\underset{\text{IV}}{C_6H_5\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}NO_2} \quad \text{or} \quad \underset{\text{V}}{C_6H_5\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}ONO} \quad \xrightarrow{H_2O} \quad \underset{\text{VI}}{C_6H_5\overset{\overset{\displaystyle C_6H_5}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}OH}$$

IV V VI

The product hydrolyzed with water and acetic acid to produce the cyanohydrin VI, thus suggesting that structure V is to be preferred.

IX. SUMMARY

With the availability of inexpensive nitrogen tetroxide this area of research should be greatly stimulated. It would seem probable that nitrations with nitrogen tetroxide would be limited to special cases in which it might offer a peculiar advantage. The most fruitful fields of research are likely to be found in the use of nitrogen tetroxide as an oxidizing agent and in addition to compounds containing multiple bonds. The latter field is especially attractive, since the addition compounds may be reduced to amines or aminoalcohols, some of which should be useful. The reduction of these compounds has often been unfortunate because of the low yields obtained. But with the techniques now available for small- or large-scale reductions it may be possible to overcome this difficulty.

Many of the experiments which have been done with nitrogen tetroxide should be repeated under conditions controlled as accurately as possible. In those experiments in which solvents are used, a variety of solvents should be tried, because the medium in which these reactions take place often exerts a profound influence. It is possible that some inert gas could often be added with advantage when vapor-phase reactions are tried.

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