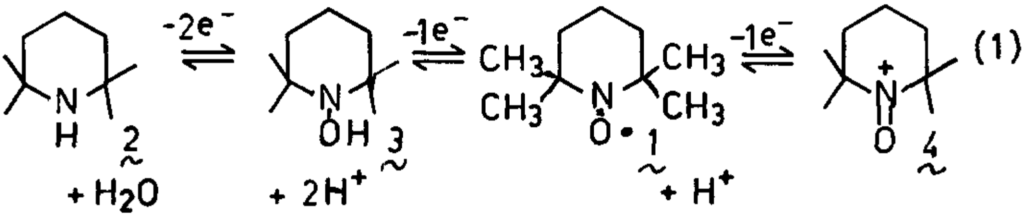
ORGANIC NITROSONIUM SALTS AS OXIDANTS IN ORGANIC CHEMISTRY

James M. Bobbitt[1] and M. Cecile L. Flores

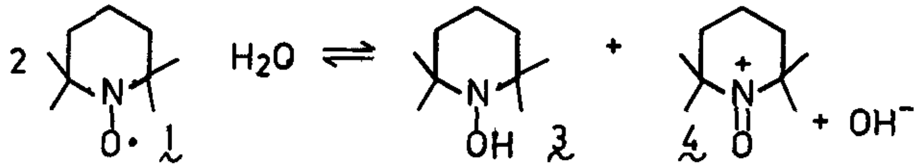
Department of Chemistry, University of Connecticut,
Storrs, Conn. 06268, U. S. A.

Abstract - *The synthesis of stable nitrosonium salts and their use as* oxidizing agents in organic chemistry will be summarized. Those systems in which nitroxides are oxidized to nitrosonium salts which, in turn, function as oxidants (mediated systems) will also be discussed. Nitrosonium salts can be used to oxidize alcohols (to aldehydes or ketones), primary amines (to aldehydes, or in certain cases, RCH_2NH_2, to nitriles), ketones (to α-diketones), and phenols (to quinones). Some dehydrogenations are also known, as well as other miscellaneous reactions.

Stable free nitroxide radicals such as 2,2,6,6-tetramethylpiperidinyl-1-oxy, **1**, often called TEMPO, have been used to place a recognizable molecule in many types of tissue, membranes, surfaces, etc.[2] The radical, however, represents only one stage in an interesting series of compounds interrelated by oxidation and reduction and shown, for TEMPO, by equation 1. These are the secondary amine, **2**, the hydroxylamine, **3**, the nitroxide, **1**, and the nitrosonium salt, **4**. Nitroxides are normally prepared by oxidation of 2 or 3, and nitrosonium salts are prepared by oxidation of either **2**, **3**, or **1**. Reagents are known for most steps in the redox series. Many radicals of diverse structural types have been *prepared as spin labels or as curiosities,*[3] *and most should have a redox* behavior similar to that shown in equation 1. Two members of the series, the nitroxides,[5] and the nitrosonium salts, are oxidizing agents, the nitrosonium salts being much more powerful. In this article, the main emphasis will be upon the nitrosonium salts and their chemistry. One review, in Japanese, has appeared on the subject.[4]



Still another redox reaction, not apparent from equation 1 is important in this chemistry. This is a reversible and acid catalyzed disproportionation of **1** to give 3 and 4 (equation 2). The equilibrium is shifted to the right in strong acid since 3 is basic enough to form a salt, and the hydroxide ion formed can be neutralized. The reverse reaction takes place in neutral or basic conditions; it was first proposed by Meyer and Reppe to explain the reactions of diarylnitroxides (for example, 5),[6] and its mechanism has been studied.[7]



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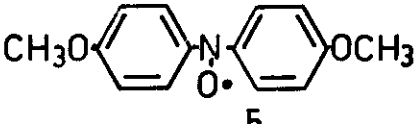
Nitrosonium salts have been used as oxidants in three different modes. First, they have been prepared, isolated, and used as pure compounds. There are relatively few examples of this, due to their reputed instability. Second, nitrosonium salts have been used as mediators in that they have been formed from radicals or even amines by a secondary oxidation system in situ. Such a system has been used extensively. The third mode depends upon the acid catalyzed disproportionation reaction (equation 2).[7] Treatment of a substrate with a radical in the presence of acid leads to oxidation by the nitrosonium salt formed by disproportionation. This mode has been observed to take place, but has not been exploited as a synthetic method. It is likely that at least some of the oxidation reactions observed for nitroxide radicals[5] take place in this latter manner.

The stability of the various radicals is attributed[3] to the fact that there are no alpha hydrogens present. If there were, nitrones would be formed from hydroxylamines by a two-electron oxidation, rather than radicals. There are some exceptions, namely some bicyclic systems such as 6 which cannot form nitrones without breaking Bredt's rule,[3c] however, there may be an alternate explanation.[3d] Presumably, nitrosonium ions are stabilized by the same phenomenon.



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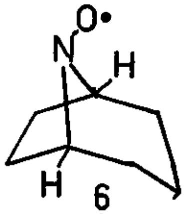

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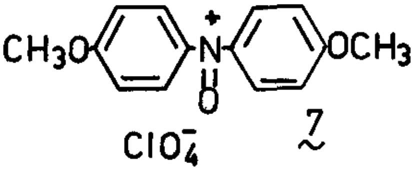

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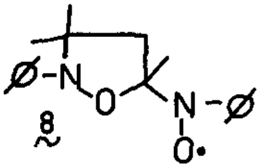
Synthesis of Nitrosonium Salts

In 1919, Meyer and Gottlieb-Billroth[8] summarized the work of many others on the nitric acid oxidation of activated aromatics and isolated pure samples of the diarylnitrosonium salts so derived. Thus, treatment of anisole with HNO_3-HOAc followed by $HClO_4$ yielded the salt, 7. In 1926, Banfield and Kenyon[9] appear to have prepared a nitrosonium salt by treatment of the radical, 8, with dry HCl (equation 2), but it was not characterized. Otherwise, most nitrosonium salts have been prepared from ditertiary nitroxides such as TEMPO. The major research group in this field has been that of V. A. Golubev in the Soviet Union. The recorded syntheses in which the salts have been isolated and characterized are given in Table 1 along with the preparation method, comments on stability (if any) melting points and references.



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Most nitrosonium salts have been prepared by oxidation of the appropriate nitroxide radicals. The most general method is oxidation with chlorine or bromine to give the respective nitrosonium chlorides or bromides; it was first used by Meyer[6] and developed extensively by Golubev.[10-15] There are three problems with this method. First, the chlorides are sometimes not very stable.[12] Second, the bromine reaction yields perbromide salts, Br_3^- except for one case, 10, R = OH, OR, in which the simple bromide is obtained.[13,16,17] Third, bromides, either simple or perbromides, tend to disproportionate in such a way as to give bromination of suitable functional groups.[14,16] Xenon fluoride has been used as an oxidizing agent to yield nitrosonium fluorides which are hygroscopic and unstable, but which can be transformed to other salts by anion exchange.[18] Nitrogen dioxide, NO_2, has been used to make a nitrosonium nitrate, 4, NO_3^-.[20] Finally, we have developed an electrochemical procedure for the oxidation of 1 to 4, BF_4^- in 84% yield.[21]

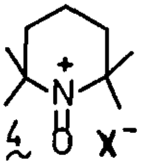
Disproportionation, equation 2, was used by Golubev[22] as an efficient method for preparing nitrosonium perchlorates, tetrafluoroborates and sulfates from various radicals. Half of the radical is converted to hydroxylamine salt which can be recovered. Treatment of radicals with a number of metal chlorides such as $SbCl_5$,[23] $SnCl_4$,[24] $PdCl_2$,[25] and $TiCl_4$[26] has given nitrosonium salts with complex anions.

The anions of nitrosonium salts can be exchanged, sometimes quite easily. This exchange has been used to convert less stable salts to more stable ones. Thus, the rather unstable chloride of 4 was easily converted to the perchlorate with $HClO_4$,[27] and a number of less stable fluorides were converted to perchlorates and tetrafluoroborates.[18]

Only two examples of dinitrosonium salts are known, 11, Br_3^- and Cl^- [12,13] but many di, tri, and even tetra radicals are known.[3] If these were oxidized to nitrosonium salts, one would have compounds with two or more oxidizing centers a measurable distance apart. Polymers containing nitroxide centers (in piperidine rings such as 16) have been prepared[32,33] and used[34] in mediated oxidations (see below). Tin oxide electrode surfaces containing nitroxide residues have been prepared and shown to be oxidizable to nitrosonium salts.[35]

Table 1. Stable and Isolated Nitrosonium Salts

General Structures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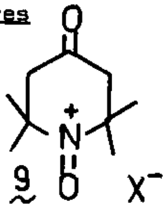
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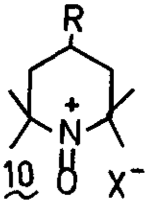
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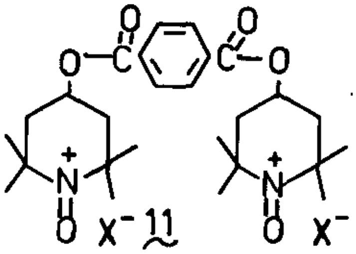
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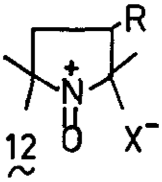
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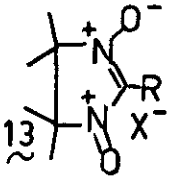
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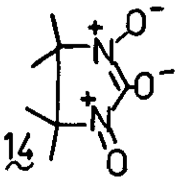
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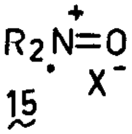

$R_2\underset{\bullet}{\overset{+}{N}}=O \quad X^-$
15

Structure, X^-	Prep. Method[a]	Prop., Yield (%), MP (°C)	Ref.
4, Cl^-	Cl_2	Stable, low t.; 98, 118-119	12,24 30
4, Br_3^-	Br_2	- , 99, 88-89	13
4, F^-	XeF_2	d. H_2O , 49, -	18
4, NO_3^-	NO_2 in NO	- , 93, 110-120	20
4, BF_4^-	**3**, F^- + BF_4	- , 84, 165-167	17
"	HBF_4, disp.[c]	d. slowly , 72, 162-163	22
"	electrooxidaation	- , 84, 164-165	21
4, ClO_4^-	**4**, F^- + $HClO_4$	- , 82, 155-157	18
"	$\phi_3{}^+ClO_4^-$ + O_2	- , 75, 157-158	26
"	$HClO_4$,disp.	d. slowly , 76, 157-158d	22
"	**4**, $SnCl_6^{--}$ + $AgClO_4$	- , - -	24
"	**4**, Cl^- + $HClO_4$	- , 90, 157-158	27
4, SO_4^{--}	H_2SO_4, disp.	d. slowly , 74, 126-127	22
4, $SbCl_6^-$	$SbCl_5$	d. slowly , 95, 156d	23
"	$\phi_3{}^+SbCl_6^-$	- , 100, 156-157	28
4, $TiCl_6^{--}$	$TiCl_4$	d. H_2O , 100, 150-200	26
"	**4**, Cl^- + $TiCl_4$	d. H_2O , - , -	26
4, $SnCl_6^{--}$	$SnCl_4$	- , -, 150-153d	24
"	**4**, Cl^- + $TiCl_4$	- , - , -	24
4, $SnBr_6^{--}$	$SnBr_4$	- , -, 137-139d.	24
4, $SnCl_5^{--}$	**4**, ClO_4^- + $SnCl_3$	- , -, 120-121	24
4, $(CH_3)_2SnCl_3^-$	**4**, Cl^- + $(CH_3)_2SnCl_2$	- , -, 103-104	24
4, $PdCl_3^-$	$PdCl_2$	- , 55, 155d	25
9, Cl^-	Cl_2	explodes r. t., -, -	12

Table 1. Cont.

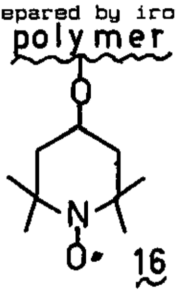
9, Br_3^-	Br_2	-	, 98,	67-68	13
9, BF_4^-	XeF_2, BF_3	-	, 40,	115-117	18
"	HBF_4, disp.	-	, 61,	116-117	22
9, ClO_4^-,	$HClO_4$, disp.	-	, 77,	120-121	22
9, $SbCl_6^-$	$SbCl_5$	d. slowly,	, 99,	131-132d	23
10, R = OH, Cl^-	Cl_2	-	, 100,	170d	10
10, R = OH, Br^-	Br_2	-	, 100,	185-190d	10
10, R = OH, Br_3^-	Br_2	-	, 93,	188-189	13
10, R = OH, $SbCl_6^-$	$SbCl_5$	d. slowly	, 99,	164-165	23
10, R = OCH_3, Cl^-	Cl_2	-	, 89,	121-123d	16,17
10, R = OCH_3, Br^-	Br_2	-	, 84,	206-207d	16
10, R = OCOϕ, Cl^-	Cl_2	stable l. t.	, 90,	86-88	12
10, R = OCOϕ, Br_3^-	Br_2	-	, 94,	96-97	13
10, R = OCOϕ, BF_4^-	HBF_4, disp.	-	, 84,	130-132	22
10, R = OCOϕ, $SbCl_6^-$	$SbCl_5$	d. slowly	, 98,	144-145	23
10, R = OCOϕ, ClO_4^-	$HClO_4$, disp.	-	, 94,	140-141	22
10, R = Cl, Cl^-	Cl_2	stable l. t.	, 95,	130-131	12
10, R = Br, Br_3^-	Br_2	-	, 95,	185	13
11, $(Br_3^-)_2$	Br_2	-	, 91,	43-45	13
11, $(Cl^-)_2$	Cl_2	decomp.	, -	-	12
12, R = CO_2H $SbCl_6^-$	$SbCl_5$	-	, 96,	155-158d	15
12, R = CO_2CH_3, Br_3^-	Br_2	-	, 97,	86-89	15
12, R = CO_2CH_3, $SbCl_6^-$	$SbCl_5$	-	, 99,	168-170	15
12, R = $CONH_2$, Br_3^-	Br_2	-	, 92,	83-89d.	14
12, R = $CONH_2$, $SbCl_6^-$	$SbCl_5$	-	, 80.	147-150	15
13, R = ϕ, Cl^-	Cl_2	-	, 93,	146-147	29
13, R = ϕ, Br^-	Br_2	only in solution			29
13, R = 2-furyl, F^-	XeF_2	-	, 31,	110-120d	18

Table 1. Cont.

13, R = 2-furyl, BF$_4^-$	13, R = 2-furyl, F$^-$ + BF$_3$	–	, 85, 150-155d.	18
13, R = 2-furyl, ClO$_4^-$	13, R = 2-furyl, F$^-$ + HClO$_4$	–	, 85, 165-170	18
14	PbO$_2$	–	, –, 198-200	31
15, R = 4-MeO-Ø, ClO$_4^-$	HNO$_3$ on aromatic + HClO$_4$	–	, 9, 155d.	8
15, R = 2-Me-4-MeO-Ø, ClO$_4^-$	"	–	, 8, 142d.	8
15, R = 4-EtO-Ø, ClO$_4^-$	"	–	, 5, 114d.	8
15, R = 2,6-di-Me-4-MeO-Ø, ClO$_4^-$	"	–	, 17, –	8
15, R = 2,4-di-MeO-Ø, ClO$_4^-$	"	–	, 39, 178d.	8
15, R = 2-Me-4,6-di-MeO-Ø, ClO$_4^-$	"	–	, –, 121	8
15, R = 2,4,6-tri-MeO-Ø, ClO$_4^-$	"	–	, 17, 189d.	8
15, R = 4-MeO-Ø, Br$_3^-$	Br$_2$	–	, 71, 116d.	6

[a] Unless noted, reagent given was used to oxidize the corresponding radical. [b] D = decomposition, r. t. = room temperature, and l. t. = low temperature. [c] Disp. = disproportionation.

A unique nitrosonium salt, 17, was prepared in solution with the idea of producing a material with properties similar to those of singlet oxygen.[36] The compound oxidized allylic alcohols to aldehydes and reacted with dienes to give adducts (for example, with cyclopentadiene to give 18). Compound 17 was prepared by iron oxidation of the corresponding radical.



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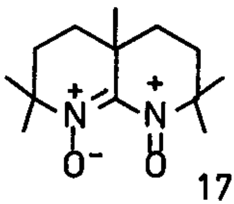

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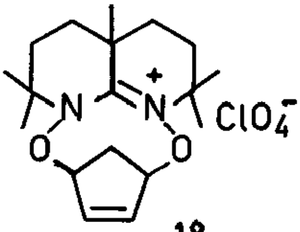

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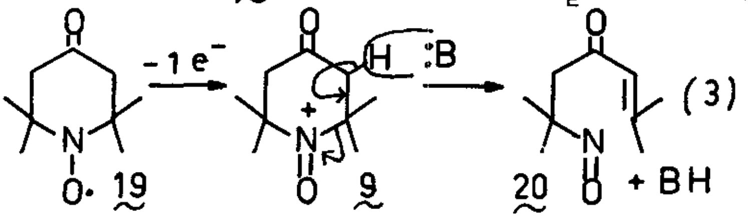
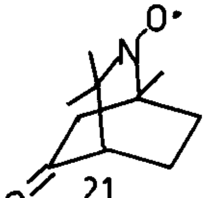
Properties of Nitrosonium Salts

Stability. Stability is a relative term, and no systematic study of the various nitrosonium salts has been made. However, there are several clearly recognizable factors.

The most obvious source of instability is the presence of a carbonyl group in the gamma position to the $>N^+{=}O$ as shown in compound 9 in equation 3. This allows a Hoffmann-type elimination which may take place in very weak base, yielding nitroso compounds. Thus, 9, Cl^- is reported to detonate at room temperature,[12] and solutions of 9 are not stable at pH's of 4.04 or above.[37] The synthesis of the radical, 19, has recently been found to be complicated by overoxidation to nitrosonium salts (9) and decomposition.[38] The chemistry in equation 3 was first observed and explained by Abakumov and Tikhonov[39] during the oxidation of 19 to 9 with Ag_2O. Similar chemistry has been noted when compounds such as 21 were oxidized with Ag_2O[40] or were pyrolyzed.[31]

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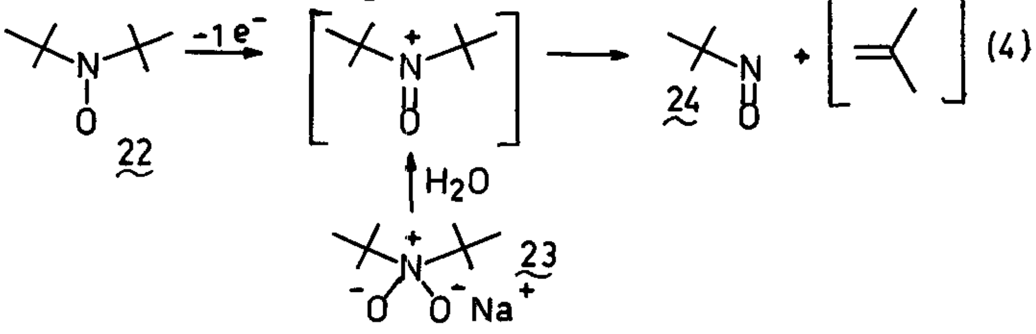
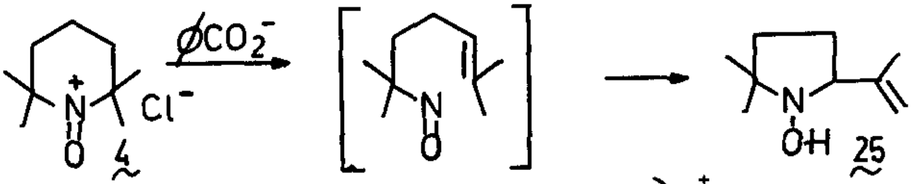
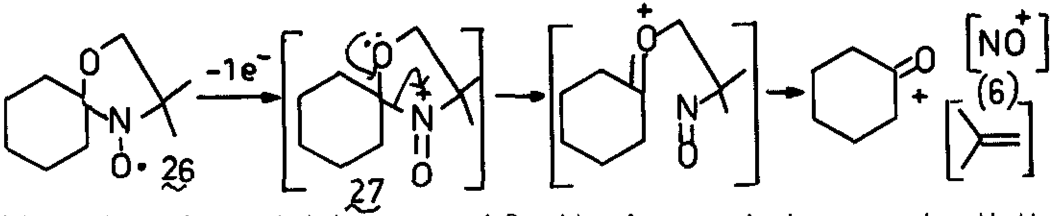
Although the elimination reaction in equation 3 is clearly enhanced by the presence of the carbonyl group, it is likely that most nitrosonium salts can decompose in a similar fashion. For example, di-tert-butyl nitroxide radical, 22, decomposes upon oxidation,[42] probably to give the same products as those formed from 23, which is, in effect, a salt of a hydrated nitrosonium ion;[43,44] (see discussion about 28 below). Although 24 was isolated along with several other compounds, the alkene by-product was not. Furthermore, it was shown[45] that 4, Cl^- is decomposed by sodium benzoate or silver benzoate to give the nitrone, 25, as shown in equation 5. Most nitrosonium salts decompose when heated in water, probably by similar routes. Since acid treatment of nitroxide radicals gives nitrosonium salts (equation 2), these mechanisms can also account for some of the decompositions of radicals.[3] Nitrosonium salts are also decomposed by excess XeF_2.[19]





(5)

Nitrosonium salts containing an oxygen beta to the $>N^+$=O are also inherently unstable. Thus, oxidation of radicals such as 26 (known as "doxyl" compounds) with NO$_2$,[20] Cl$_2$,[20] or *m*-chloroperbenzoic acid[46] produces the nitrosonium salt, 27, which decomposes, removing the doxyl group quantitatively, presumably by the route shown in equation 6. Isopropylene was trapped as its epoxide[46] when the oxidizing agent was a peracid.



Nitrosonium salts containing a second functional group which can react with the salt are obviously unstable. Thus, although a number of salts have been made of 10, R=OH (see Table 1), they would be expected to decompose slowly to form a 4-keto product through a self oxidation by the nitrosonium salt of the 4-hydroxyl group (see below). This has been observed.[10] The reaction can be blocked by making ethers or esters of the hydroxyl group of 10 as shown in Table 1.

Although never stated, it would appear that stability, at least of the crystalline salts, is a function of the anion present. Thus, while 9, Cl$^-$ detonates at room temperature,[12] its perbromide, tetrafluoroborate, perchlorate and hexachloroantimonate are not reported as unstable. Nitroxides are oxidized to nitrosonium salts by chlorine and bromine as stated above. However, iodine will not oxidize nitroxides. In fact, nitrosonium iodides readily decompose to nitroxides and iodine.[10,11]

Finally, nitrosonium salts are generally hygroscopic. We have found[21] that chlorides are very hygroscopic, but that perchlorates and tetrafluoroborates are much less so.

Assay. Nitrosonium salts have been assayed by iodometric analysis.[10,11] The salt is allowed to react with I$^-$ to give I$_2$ which is titrated with thiosulfate.

Electrochemistry. Quinones have been used for years as dehydrogenating agents and oxidants,[47] and their electrochemistry has been extensively explored.[48] It has been possible to correlate quinone structure with electrochemically measured oxidation potentials, and further, to correlate potentials with actual oxidizing properties in preparative systems. Similar correlations should be possible for nitrosonium salts, but, thus far, only fragmentary studies have appeared. In fact, there are no electrochemical studies of the nitrosonium salts themselves. The problem has been approached by studying the oxidation of nitroxides to salts and back by cyclic voltammetry (CV) (equation 1, 1 to 4 to 1).

Cyclic voltammetric data can be used in the study of the nitrosonium salts in two ways. First, one can derive information about the oxidizing *power* of various salts by measuring the oxidation potential of the nitroxide-nitrosonium salt couple. Shchukin and his coworkers[49] have measured the oxidation potentials of about 57 nitroxides, and their data as well as that of others is given in Table 2. Some anodic half-wave potentials[35,51] are also recorded in the Table. It was concluded that the potential is first a function of the ring system and second a function of the ring substituents.[49] In general, those ring atoms or substituents that tend to be electronegative or electron withdrawing raised the potential. Within some of the ring systems, mathematical relationships were derived relating Hammett functions and potential. The bicyclic systems have high potentials, and diaryl systems such as 15 have a low potential. Thus, a range of oxidizing nitrosonium salts with quite different potentials should be available. The magnitude of the oxidation potential has an important bearing on the development of mediated systems, as discussed below.

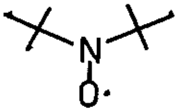
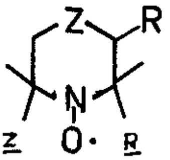
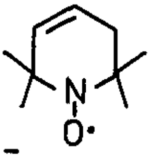
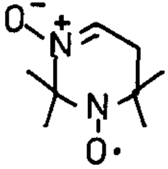
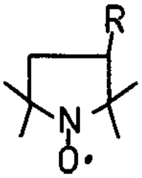
Cyclic voltammetric data can also be used to study the stability of nitrosonium salts in various environments, at least on a fairly fast time scale. This is done by studying the height of the reverse (reduction) wave in respect to the height of the forward (oxidation) wave. If the reduction wave is lower, it can be presumed that the nitrosonium salt is decomposing or reacting with its surroundings.

In at least two cases,[52,54] the electrooxidation of radicals to nitrosonium ions has been the basis for radical assay.

Acid-Base Reactions.[54,55] The nitrosonium salts are formally salts of the N-oxides of N-hydroxylamines,[55] 28, which are amphoteric. Since the parent acid, 28, is a stronger acid (pKa = 13.5) than the nitrosonium cation, 4, (pKa = 14.5), its isolation is unlikely and has not been achieved.[54] Treatment of nitrosonium salts with concentrated aqueous NaOH or KOH causes the precipitaion of the sodium or potassium salts of 29, $M^+ = Na^+$ or K^+. These salts are reported to be stable during long term storage in dry conditions and to have properties similar to nitrosonium salts. They oxidize alcohols to carbonyl compounds and, surprisingly, even oxidize dimethylformamide (to unidentified products). The metal salts are insoluble in CH_3CN and nitromethane and cannot be purified or recrystallilzed. As precipitated, they are about 83% pure, and their properties as oxidants in preparative systems have not been explored. The corresponding sodium salt of di-*tert*-butylhydroxylamine oxide, 23, had been prepared much earlier from nitroxide, 22, and sodium metal.[43]

Table 2. Oxidation Potentials of Nitroxides

Measured by Cyclic Voltammetry[a]

Compound			$E_{p/2}$[b]	Ref.
			0.21	50[c]
				
	Z	R		
1	CH_2	H	0.29	49
			0.27	50
			0.25	42
10	CHOH	H	0.34	49
			0.33	50
			0.56	37
10	$CHOCH_3$	H	0.40	49
			0.57	77
10	CHCl	H	0.40	49
9	C=O	H	0.44	"
			0.44	50
	C=O	Cl	0.60	49
			0.35	"
			0.65	"
				
	R			
12	CO_2H		0.54	37
12	$CONH_2$		0.38	49
12	CO_2CH_3		0.42	"

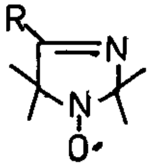
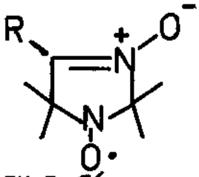
Compound	$E_{p/2}$[b]	Ref.
		
R		
CH_3	0.55	49
p-CH_3O-ϕ-	0.56	"
$CONH_2$	0.57[c]	"
p-CH_3-ϕ-	0.58	"
OCH_3	0.58	"
ϕ-	0.60	"
p-F-ϕ-	0.60	"
2-furyl	0.61	"
2-thienyl	0.61	"
CO_2CH_3	0.65	"
$CHCl_2$	0.68	"
CCl_3	0.72	"
CN	0.75	"
		
R		
p-CH_3O-ϕ-	0.80[c]	49
CH_3	0.81	"
H	0.85	"
ϕ-	0.86	"
p-F-ϕ-	0.86	"
2-furyl	0.87[c]	"
2-thienyl	0.88	"
CH_2Br	0.91	"
$CONH_2$	0.91	"
CO_2CH_3	0.92	"
p-NO_2-ϕ-	0.92	"
p-NO_2-ϕ-	0.92	"
5-NO_2-2-furyl	0.94	"
$CHBr_2$	0.95	"
5-NO_2-2-thienyl	0.95	"
CHO	0.96	"
CO_2H	1.01	"
CN	1.05	"

Table 2. Cont.

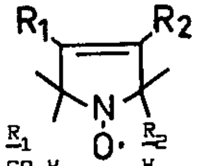
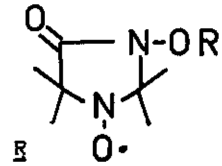
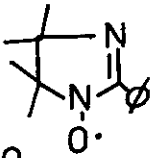
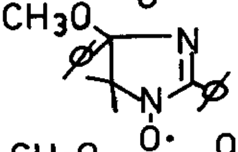
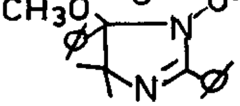
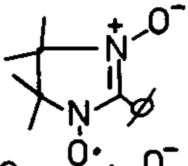
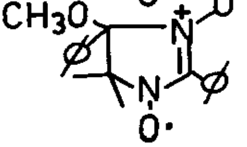
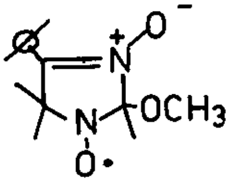
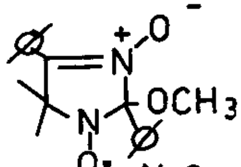
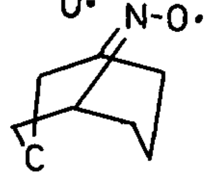
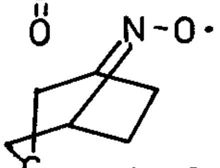
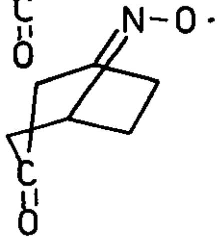
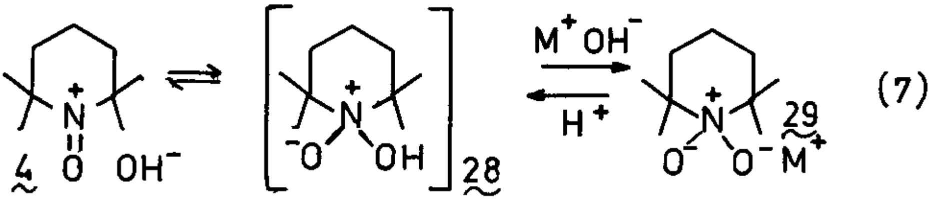
			
R_1	R_2		
CO_2H	H	0.54	37
$CONH_2$	H	0.50	49
CO_2CH_3	H	0.54	"
CO_2CH_3	Br	0.64	"
Br	Br	0.69	"
CN	Br	0.78	"
			
R			
H		0.86^c	49
CH_3		0.85^c	49
		0.84^c	49
		0.93^c	49
		1.00^c	49
13 		0.35	49
		0.54	49
		1.03	49
		1.01	49
		0.47	50
		0.45	50
		0.51	50

Table 2. Cont.

Measured From Anodic Half-Waves

Compound	$E_{1/2}$	Ref.
1	0.32	51
radical of 12	0.37	"
radical of 15, R = 4-CH_3-Ø-	0.2	"
radical of 17	about 0.73	36

[a] When compound numbers appear in the Table, they represent nitrosonium compounds that have been prepared (Table 1) from the radical in question, unless noted. [b] This is the potential at a point half-way between the anodic and cathodic peaks observed in CV. The measurements in refs. 49 and 51 were made in CH_3CN against a Ag/ 0.01 M $AgNO_3$ reference electrode. Those in refs. 42 and 50 were made in CN_3CN containing 0.4 M $LiClO_4$ against a Ag/ 0.1 M $AgNO_3$ reference electrode. Those in ref. 37 were measured in buffered aqueous solution at about pH 7 against a standard calomel electrode. Those in ref. 36 were measured in CH_3CN against a standard calomel electrode. No conditions were given for the value measured in ref. 70. [c] The oxidation reaction wave was not reversible, indicating decomposition of the nitrosonium ion.



(7)

Spectroscopy and Conformation. The various six-member ring nitrosonium salts (4, 9, 10, 11) seem to have certain consistent spectral properties. The infrared spectra all contain a band at 1600-1640 cm^{-1}, which is attributed to $>N^+=O$,[12,16,18,22,24,27,28] with the precise value depending upon substitution and the anion involved. In the case of the five-member ring compounds such as 12, the band is shifted to 1660 cm^{-1}.[14] No assignments seem to have been made for 13.

The ultraviolet spectra of most nitrosonium salts show two broad bands in the regions of 240 and 475 nm.[18,22,23,24,26,27] The perbromides (4, Br_3^-; 9, Br_3^-; 10, R = OH or $OCOC_6H_5$, Br_3^-) are exceptions in that they show bands at about 220 and 268 nm.[13,14] The 268 nm band has been assigned to a charge transfer transition involving Br_3^-.

Since the nitrosonium salts are not paramagnetic (as compared to the nitroxides), their nuclear magnetic resonance spectra are normal. However, the positively charged $\rangle N^{+}{=}O$ does cause the proton resonances to appear about 0.7-1.4 δ units downfield, at least in the piperidine series,[13,24,27,28] (shown by comparing the salt, 4, with the hydroxylamine, 2). No ^{13}C spectra seem to have been measured.

The nitrosonium salt, 4, ClO_4^-, has a twisted boat conformation, according to X-ray crystallography of the solid salt.[27] This is in contrast to the corresponding radical, 1, which has a chair conformation. The N-O bond in 4, ClO_4^- is shortened,(compared to 1) to 1.19 Å, corresponding roughly to a double bond.

Reactions of Nitrosonium Salts

The instability of nitrosonium salts may have been overemphasized in some cases, but there is little question that they are highly reactive. Golubev has stated,[27] "On the one hand, these compounds are strong oxidizing agents which react readily with alcohols, ketones, water, amines, and phosphines, undergoing reduction to radicals, hydroxylamines, and amines and acting as one-, two-, or four-electron oxidizing agents. On the other hand, they are specific electrophilic reagents, which readily add on nucleophilic reagents at the oxygen atom of the oxazonium (nitrosonium) group".

The situation is complicated by at least three factors. The most serious involves equation 2. At any time when acid and radical are present, some nitrosonium salt will be generated by disproportionation. Furthermore, at any time nitrosonium salt and hydroxylamine (4 and 2) are present together, they will react to produce a radical. This latter aspect is crucial for some of the mediated systems discussed below.

The second complication is that nitroxide radicals are often formed in the course of nitrosonium salt oxidations, and are, themselves, potent oxidizing agents.[5] Thus, the first step of a reaction series may be due to a nitrosonium salt, and a later step may be due to the radical. The third factor involves the point of attack on the $\rangle N^{+}{=}O$. Golubev states[27] that it is on the oxygen (to yield an $\rangle N{-}O{-}R$ system) rather than on nitrogen. This is not certain and is discussed in the mechanisms section below.

Mediated Reactions. The radicals used to make nitrosonium salts are expensive, and the salts have limited stability. For these reasons, a number of procedures have been developed in which catalytic amounts of radical or, sometimes, even the hydroxylamine or amine, are oxidized by a secondary, and cheaper, oxidizing agent to produce nitrosonium salts *in situ*. The nitrosonium salts react with substrate in their own unique way and are reduced back to radical or hydroxylamine. These products are then reoxidized by the secondary oxidant and so on. The nitroxide radical and its derived nitrosonium salt are therefore mediators or catalysts.

There are, however, some disadvantages to mediated systems. The main one is that the secondary oxidant must be strong enough to generate the nitrosonium salt from radical or other precursor, but must not react with the substrate itself. Thus, the electrochemically assisted system developed so successfully by Semmelhack[56,57] is quite suitable for alcohol or amine oxidation because these substrates are difficult to electrooxidize. However, the method should not work for phenols, which are more easily oxidized than the radical.[21,30,58] In some cases,[57] the mediator is appreciably decomposed during the process.

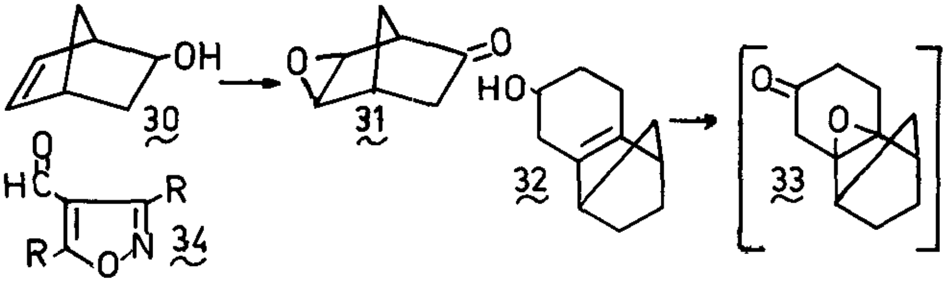
Solvents. The most commonly used solvent for nitrosonium salt oxidations has been CH_3CN, but nitromethane, acetic anhydride, and *tert*-butanol have been suggested.[30] Methylene chloride has been used with **10**, R = OCH_3, Cl^- [17], but has been reported to react slowly with **4**, Cl^-.[30] Alcohols, primary and secondary, and ketones react with nitrosonium salts. The salts are, of course, ionic and not soluble in non-polar solvents such as CCl_4, hexane, ether and ethyl acetate. They are usually recrystallized by dissolving them in a cold polar solvent such as CH_3CN and precipitating them with ether or ethyl acetate.

Oxidation of Alcohols, Non Mediated. It was noted several years ago that nitrosonium salts reacted quantitatively with simple alcohols such as methanol or ethanol to give aldehydes with no overoxidation.[10,14] However, the reaction has only been developed as a useful synthetic method in recent years.

Endo and his coworkers[16,17] prepared **10**, R = OCH_3, Cl^- and Br^- and used them to oxidize a series of alcohols to aldehydes or ketones. The methyl ether was prepared to block reaction of the 4-hydroxyl group in **10**, R = OH which was, in turn, presumably chosen for further study because it is the only cation forming a simple bromide (rather than a perbromide). In general, the chloride was found to be more effective and to have fewer side reactions. With the chloride, yields varied from 92 to 100% in most cases (as measured by gas-liquid chromatography). The chloride was found to react more rapidly with primary alcohols than with secondary alcohols, but, strangely enough, the bromide was found to react faster with secondary alcohols. Benzyl and allyl alcohols reacted faster than simple aliphatic alcohols. The bromide gave double-bond bromination of alcohols containing double bonds, but the chloride gave the expected products. A series of diols was investigated,[17] with quite interesting results. Thus, 1,4-butanediol and 1,5-pentanediol were found to yield their respective γ- and δ-lactones in isolated yields of 81 and 40%, respectively. This would indicate that, although aldehydes are not further oxidized to acids, cyclic hemiacetals are. This was also found in a mediated system.[56] 2,3-Butanediol yielded acetoin in 30% yield. The nitrosonium salt, 13, oxidizes allylic alcohols.[33]

Oxidation of Alcohols. Mediated Systems. Most of the potentially useful work on alcohol oxidation has involved mediated procedures using various secondary oxidizing systems. In 1975, Cella[59] and Ganem[60] reported the use of *m*-chloroperbenzoic acid as a secondary oxidant for the nitrosonium salt oxidation of alcohols. The mediator was the tetramethylpiperidine, 2, or its hydrochloride salt. The radical, 1, was also used.[53] Either 1 or 2 was oxidized by peracid to the nitrosonium salt, 4, which brought about the desired oxidation. Secondary alcohols yielded ketones, but primary aliphatic alcohols were oxidized to carboxylic acids (by the peracid?); some aromatic primary alcohols gave aldehydes. Yields were high. Amounts of one mole % of mediator were used by Cella, but Ganem used one mole equivalent. Ganem used two molar equivalents of peracid, but Cella used only 1.5. Cella found that acid was required, but that the HCl in the piperidine hydrochloride, 2-HCl, would suffice. Only simple piperidine derivatives were used; in the pyrrolidine series, 12 was unreactive.[46,54]

The inherent oxidizing properties of *m*-chloroperbenzoic acid were cleverly combined with those of nitrosonium salts to carry out some interesting "one-pot" syntheses. Thus, epoxidation followed by alcohol oxidation yielded 31 from 30(86%)[61] and 33 from 32.[62] Compound 33 was not isolated, but was converted to a subsequent molecule in the sequence. Alcohol oxidation followed by Baeyer-Villiger oxidation yielded benzyl acetate from 1-phenyl-2-propanol in 90% yield.[61] Other examples were given.



Oxygen oxidation of methanol in the presence of copper salts was found to be facilitated by di-*tert*-butyl nitroxide several years ago,[63] but the mechanism was not clear. The sequence could involve a nitrosonium ion, but as noted,[42] di-*tert*-butyl nitrosonium salts are not stable enough for isolation. It is interesting that HCN was a product when methanol was oxidized in the presence of ammonia.

More recently, catalytic amounts of copper ion and either **1** or the radical from **10**, R = OH have been used to promote the oxygen oxidation of allylic or benzylic alcohols to aldehydes.[64] Isolated yields were high (90-96% in most cases). In the reaction, cuprous chloride is oxygenated to give cupric ion which oxidizes the radical, **1**, to the nitrosonium salt ,**4**. The cuprous ion so formed is reoxidized by oxygen to cupric ion. The nitrosonium salt then oxidizes alcohol and is simultaneously reduced to hydroxylamine, **3**. Compound **3** reacts with **4** to regenerate the mediator,**1** (equation 2). The method was used to prepare aldehyde, **34**, from its alcohol,[65] and a good general discussion of the alcohol-aldehyde oxidation problem was given.

Stoichiometric amounts of cupric ion, as $CuCl_2$ were used to oxidize primary aliphatic alcohols to aldehydes in the presence of **1**.[64] Yields are good, but *the reaction must be carried out under anhydrous conditions* in the presence of CaH_2. Secondary alcohols are oxidized very slowly in this system.

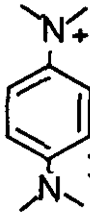
Potassium ferricyanide has been used as a secondary oxidizing agent in the mediated (with **10**, R = OCH_3)·oxidation of benzyl alcohol to benzaldehyde.[66] The reaction was carried out in a two phase system consisting of 1 *N* aqueous KOH and CH_3CN and has also been carried out using polymer-bound nitroxide units.[34]

The most promising and controllable system for nitroxide mediated oxidations is the one devised by Semmelhack[56] using anodic oxidation as a back-up oxidizing agent. The reaction is carried out in the anodic chamber of a two-compartment cell containing a Pt electrode at about +0.35 V (*vs*.Ag/0.1 M $AgNO_3$). The system is analogous to the one described above for the oxygen-copper system except that the anode is used in place of the copper and oxygen. The electrolyte was $LiClO_4$ in CH_3CN, and 5-33 mole % of nitroxide, **1**, was used. 1,2-Dibromopropane was placed in the cathode chamber. A base (2,6-lutidine) was used to pick up the acid formed. Yields were good (isolated, 40-88%), and primary alcohols were oxidized more rapidly than were secondary.

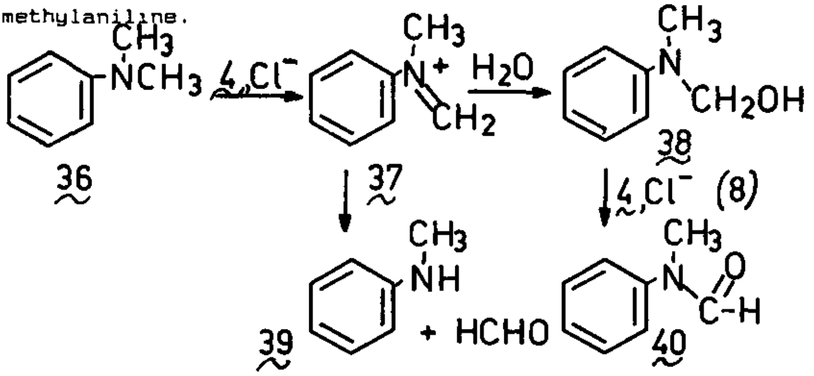
The oxidation of alcohol to aldehyde (or ketone) is a two-electron oxidation, forming hydroxylamine, **3**. In an excess of alcohol, **3** can be isolated in good yield.[10] However, under Semmelhack's conditions,[56,57,64] the hydroxylamine reacted with the generated nitrosonium salt to yield nitroxide (equation 2).

Oxidation of Amines-Non Mediated. In 1965, Golubev[10] showed that nitrosonium salts react with amines. He allowed **10**, R = OH, Br^- to react with N,N,N',N'-tetramethyl-*p*-phenylenediamine to yield the well known cation radical, Würster's blue, **35**, in a presumably one-electron reaction. He showed that triethylamine decomposed nitrosonium salts to radicals but was unable to isolate any product from amine oxidation.

This work has been reinvestigated recently.[30] Several tertiary aliphatic amines (conanine, triethylenediamine, and ethyldiisopropylamine) were allowed to react with **4**, Cl^- at -80° C. As in the earlier work, radical, **1**, could be isolated, but no amine products were obtained. However, oxidation of N,N-dimethylaniline, **36**, yielded N-methylformanilide, **40**, and N-methylaniline, **39**, (equation 8). It was suggested that the intermediate, **37**, was formed first. In the presence of small amounts of water, intermediate **37** would be converted to **38** which could be further oxidized to the formanilide. In the absence of water, the intermediate would be hydrolyzed during workup to give formaldehyde (trapped) and N-methylaniline.



35



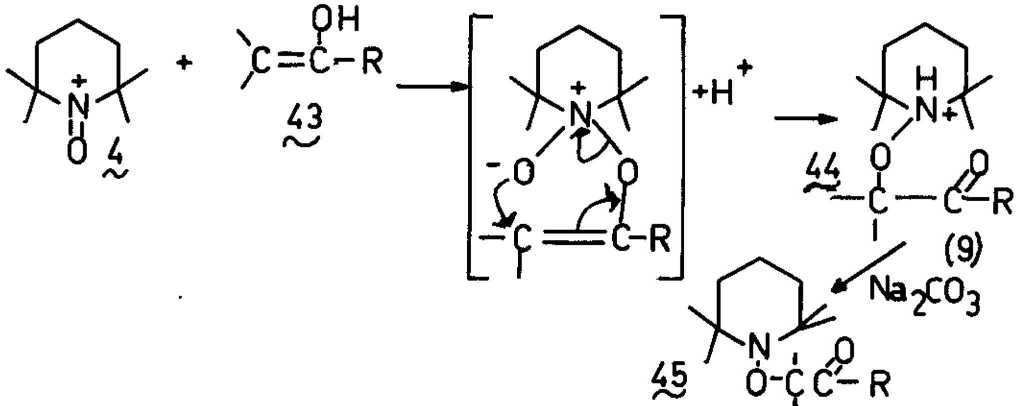
Oxidation of Amines-Mediated. Semmelhack has applied his electrochemical method to amines, using **1** as a mediator.[57] The products from primary amines were aldehydes or ketones in good yield, as long as some water was present. Under anhydrous or near anhydrous conditions, nitriles were the major products from primary amines on primary carbons (RCH_2NH_2). Yields were reasonable to good. One secondary amine, N-benzylaniline, gave benzaldehyde. It was found that the mediator decomposed more rapidly in the amine series than in the alcohol series, and in some cases, two equivalents of the nitrosonium salt were preformed in solution before the amine was added. The reaction is similar to that shown above for N,N-dimethylaniline. The first product formed would be a Schiff base corresponding to **37**, but, of course, uncharged. Water present would cause the hydrolysis to aldehyde or ketone. In the absence of water, the Schiff base would be further oxidized to nitrile. In one case, a Schiff base, **42**, was actually isolated from the oxidation of bis-(diphenylmethyl)-amine, **41**. The formation of nitriles is reminiscent of the nitroxide-catalyzed oxygenation of methanol to HCN noted above.[63] It is of interest that Schiff bases, as opposed to aldehydes, seem to be oxidized by nitrosonium salts.

$$\underset{\mathbf{41}}{\varnothing_2CH\text{-}NHCH\varnothing_2} \longrightarrow \underset{\mathbf{42}}{\varnothing_2C{=}NCH\varnothing_2}$$

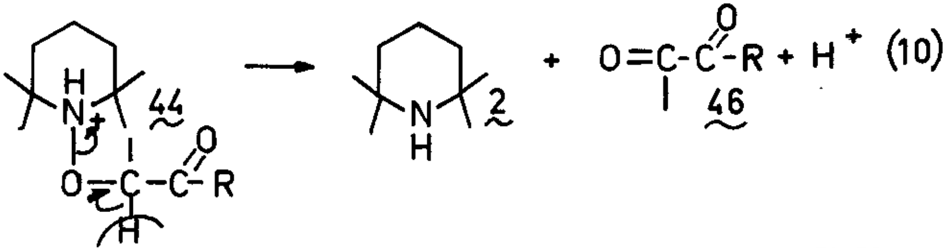
Oxidation of Ketones. Nitrosonium salts react with ketones containing an α-hydrogen. Both piperidine (**4**, **9**, **10**)[25,30,67-70] and pyrrolidine (**12**)[14] salts react. The products depend upon the anion portion of the salt.

When the anion is Br_3^-, the product is an α-bromoketone.[14,68] This does not appear to be a product of reaction with the nitrosonium salt. It results from the reaction of ketone with small amounts of Br_2 released by equilibration of nitrosonium perbromide to give nitroxide and halogen. Since one of the products of bromination is HBr which causes a disproportionation of nitroxide to hydroxylamine and nitrosonium bromide again, (equation 2), the ultimate product is hydroxylamine as its hydrobromide.

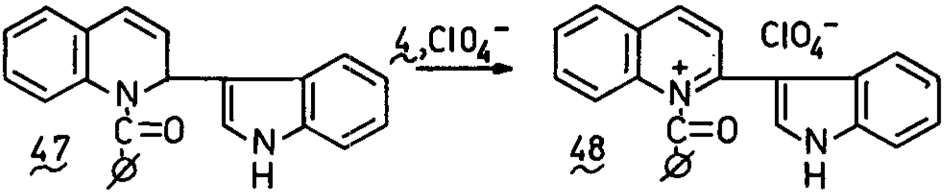
With other anions such as Cl^-, ClO_4^-, and $PdCl_3^-$, N-alkoxyamine salts such as **44** are formed (equation 9). The ethers, **45**, can be isolated after neutralization. The reaction appears to take place through the enol, **43**, and, in fact, has been used for the spectrometric analysis of the enol content of ethyl acetoacetate and acetylacetone.[67] It is of further interest that methyl ethyl ketone reacts at the methylene group, not at the methyl group.[69]

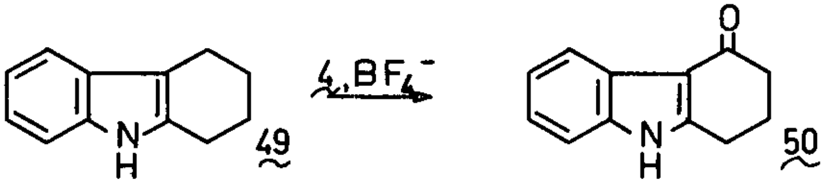


These alkoxy ether salts, **44**, decompose on heating to give α-dicarbonyl compounds in a remarkable reaction that appears as a four-electron oxidation (equations 9 and 10). A number of nitrosonium salts have been investigated,[69] and yields of dicarbonyl products are good.[70] Some of this work has been repeated recently,[30] and the reaction was found to be improved by the addition of 2 mole % of p-toluenesulfonic acid. Cholestan-3-one was oxidized to give chlestan-2,3-dione which was isolated in 35 % yield as a mixture of enol benzoates.

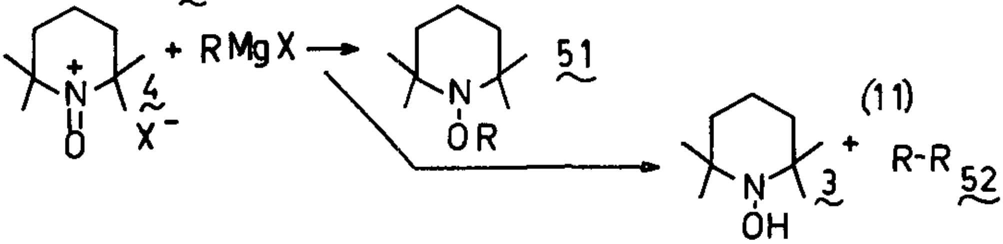


Miscellaneous Oxidations. Nitrosonium salts react with phenols,[21,30] but only two reactions have actually been published. α-Naphthol gave a 95 % yield of 1,2-naphthoquinone, and β-naphthol gave a mixture of 1,2- and 1,4-naphthoquinones.[30] It should be noted that phenols also react with nitroxide radicals to give quinonoid products.[5a, 5f] Triphenyl phosphine was converted to its oxide by 4, Cl^- in 91 % yield.[30] Certain partially reduced aromatic systems containing nitrogen can be dehydrogenated with nitrosonium salts.[71] Thus, 47 gave 48 on treatment with 4, ClO_4^-, probably through a hydride transfer.[72] It is possible that the indole ring plays an important role in the reaction. We have used 4, BF_4^- to convert 1,2,3,4-tetrahydrocarbazole, 49, to 4-keto-1,2,3,4-tetrahydrocarbazole, 50, in 62% yield.[21] Benzyl ethers react with 10, R = OCH_3, Br^- and Cl^-. The product from the benzyl portion is benzaldehyde; the product from the other portion is an alkyl halide in low yield or, in the case of dibenzyl ether, benzaldehyde also.[73]





When suspended in ether, the nitrosonium salts react with Grignard reagents to give, primarily, the alkoxy ethers, 51.[74] This reaction was visualized as taking place by Grignard addition to $>N^+=O$ where the polarity is such that the oxygen is more positive than N. A secondary and minor product, the hydrocarbon, 52, resulting from a coupling of the Grignard reagent was also noted. (equation 11). Other organometallic compounds such as dibenzylmercury or trimethylbenzylstanane also react with nitrosonium salts to give alkoxy ethers such as 51, but this was shown to be a radical reaction.[75]



Compound 17, as noted above, reacts with dienes to give addition compounds such as 18.[36] The radical corresponding to 10, R = Cl, disproportionates in acid to yield 10, R = Cl which was shown, spectrometrically, to react with N,N,N',N'-tetramethyl-p-phenylenediamine, thianthrene, phenothiazine, N-methylphenothiazine, and carbazole to yield cation radicals.[76] Triphenylamine was thought to be converted to N,N,N',N'-tetraphenylbenzidine which then gave a cation radical. The interesting internal salt, **14**, also produced by an acid disproportionation (CF_3CO_2H in CH_2Cl_2), was shown[31] to oxidize 9,10-diphenylanthracene, perylene, and tetraphenylethylene to their respective cation radicals.

Nitrosonium ions, for example, **10**, R = OCH_3, Br^-, react with hydroxide ion to yield hydrogen peroxide[77] as hydroxyl radical, a reaction also noted for **13**, R = phenyl, Br^-.[29] Similar reactions were noted for the salts with water.[10,43] Nitrosonium salts have also been shown to react with hydrogen peroxide to give oxygen.[78] Nitrosonium salt, **4**, was generated electrochemically and shown to react with iron wire.[79]

Nitrosonium salt, **4**, Cl^-, was specifically found not to react with camphor, 1-methoxynaphthalene, diphenylether, diphenylsulfide, benzylphenylsulfide, benzylphenylsulfone, Δ^2-cholestene and 3-acetoxy-Δ^2-cholestene.[30]

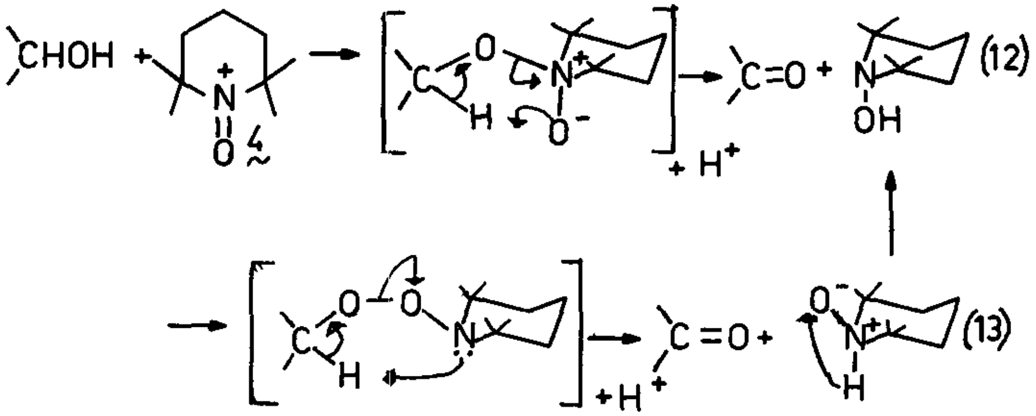
Mechanism of the Reactions

One-electron Oxidations. These reactions presumably come about by an electron transfer from substrate to salt. The best evidence for this is the formation of Würster's blue, **35**, a well known cation radical[10] and the various cation radicals observed spectrometrically.[31,76] The oxidation of benzyl ethers is thought to proceed by way of two one-electron transfers.[73]

Two-electron Oxidations. These reactions are the most interesting synthetically, and most of the reported mechanistic work has been done with them. It was suggested[30] that -OH or, presumably $>$NH in amines, is necessary for successful oxidation with nitrosonium salts. This would be logical for two- and four-electron oxidations and could be a factor in determining a reasonable mechanism. It is of interest that tertiary amines are reactive while ethers (except for benzyl ethers[73]) and thioethers are not.[30]

In an extensive kinetic study, Golubev[80] established the following facts concerning alcohol oxidation. First, the reaction was two-electron, yielding the aldehyde or ketone and hydroxylamine. When the pH was below 2, the hydroxylamine could be isolated. Second, at pH values above 2, the initially formed hydroxylamine reacted with excess nitrosonium salt to yield nitroxide (equation 2). Third, the oxidations involved a hydride transfer from what amounted to an alcoholic anion (in a complex or intermediate with nitrosonium ion). However, he made little attempt to propose a transition state or intermediate. Ganem[60] noted the probable presence of an intermediate in the reaction, but was unable to isolate it. He suggested the structure given in equation 12.

Semmelhack and his students have recently made a more thorough study of the mechanism of alcohol oxidation.[81] Two pathways were rejected; simple electron transfer followed by loss of H$^+$ to give nitroxide radical and alkoxy radical, and simple hydride transfer from the carbon bearing the hydroxyl group. The radical mechanism was presumably rejected because the product from the nitrosonium salt is clearly hydroxylamine, not nitroxide[80] and there are no obvious radical products from an alkoxy radical. Simple hydride transfer was rejected because it could be demonstrated that little positive charge was built up on the carbon bearing the hydroxyl group during the reaction. This leaves two pathways as shown in equations 12 and 13.



The authors favored equation 12 although 13 could not be ruled out. The crucial matter is whether initial reaction takes place on nitrogen (as in 12) or oxygen (as in 13). There is only one clear example where reaction is on oxygen. This is the reaction of the salts with Grignard reagents and other organometallics (equation 11),[74,75] but it is possible[75] that some of these reactions take place by radical coupling.

Reactions with primary or secondary amines could take place in a manner similar to alcohols as, in fact, could reactions of primary amines to nitriles. No evidence has been given on these mechanisms. It is not posssible to comment on the reactions of tertiary aliphatic amines since none of the products are known. A reaction scheme is given above (equation 8) for the oxidation of N,N-dimethylaniline.

Four-electron Oxidations. The reactions of nitrosonium salts with ketones, and probably phenols, is an overall four-electron oxidation. However, it certainly takes place in steps. These are shown above in equations 9 and 10. The reaction with phenols is less clear. It could be a four-electron reaction, but the observed quinonoid products are also formed by nitroxide radicals[5a,5g] and quinones,[47] both widely recognized as being one-electron reagents.

Summary

Several conclusions can be drawn from the relatively sparce published data on nitrosonium salts. First of all, there is a question of stability. There would appear to be a wide range of stabilities for various salts, depending upon *both* the cation and the anion present. Some should be sufficiently stable for commercial exploitation. Second, the salts exhibit a wide range of reactivities toward several functional groups in organic chemistry.

Finally, almost all of the preparative work has been done with the chloride salts of two or three of the piperidine derivatives, because they are relatively inexpensive and easy to make. However, the chlorides are probably the least stable and most hygroscopic of the known salts. Based upon the various electrochemical parameters that have been measured, it should be possible to formulate a series of nitrosonium salts with various oxidation potentials. If the transition states as shown in equations 12 and 13 have any validity, it should also be possible to construct nitrosonium salts with *specific steric configurations for specific purposes.*

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Russian references will be given in English if they have been translated, and page numbers will refer to the English translations.

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