

Oxoammonium Salt Oxidations of Alcohols

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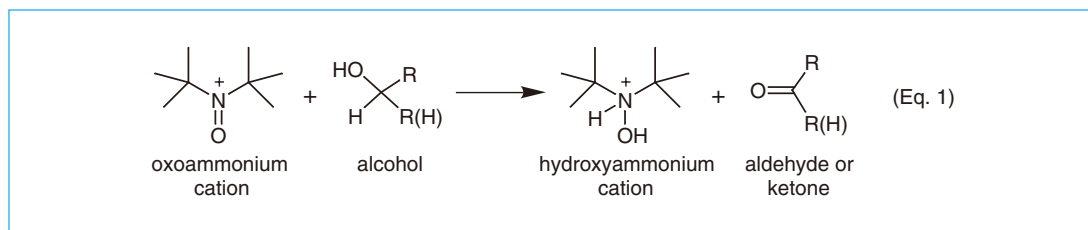
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1 Introduction

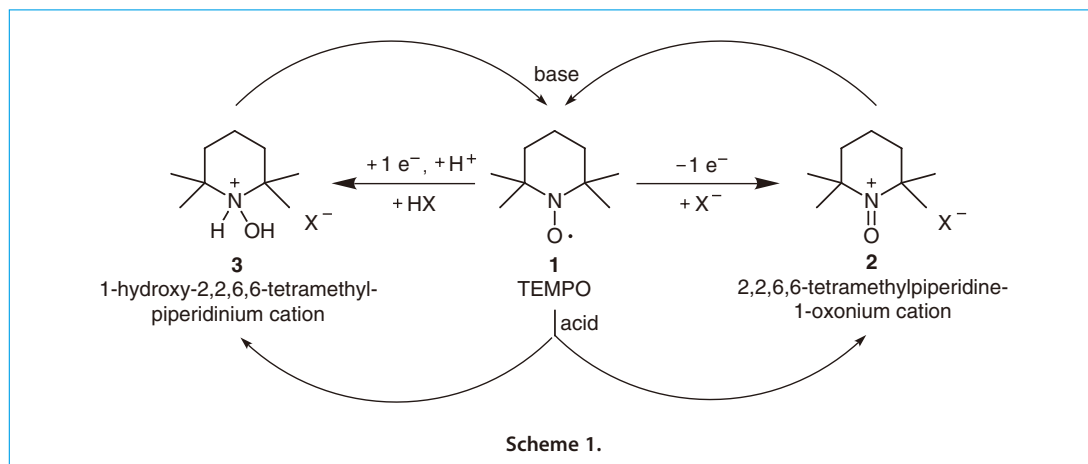
Much of the material in this article has been taken from a recent comprehensive review entitled "Oxoammonium and Nitroxide-Catalyzed Oxidations of Alcohols".¹ Two previous reviews on oxoammonium chemistry² and on the experimental methods used in this work³ have also been used.

The oxidations (mostly of alcohols) outlined in this report involve the remarkable selectivity of an oxoammonium cation. Rarely, if ever, are isomerizations observed, either of double bonds (*cis-trans*) or of chiral centers, and carbon-carbon bonds are not cleaved. Furthermore, the reagents are "green" in that no heavy metals such as chromium or manganese are involved.

The reaction is shown schematically in Eq. 1.



For oxoammonium cations to be stable, there can be no hydrogens on the carbons attached to nitrogen (α -hydrogens), or it must be impossible to form a double bond between nitrogen and one of the adjacent carbons for some other reason.⁴ There are many examples of these salts,² but the most common ones are based on a piperidine nucleus as shown in Scheme 1. In Scheme 1, the redox properties of nitroxides, **1**, oxoammonium salts, **2**, and hydroxyamines or their salts, **3**, are summarized, as are the general methods of preparation and decomposition.

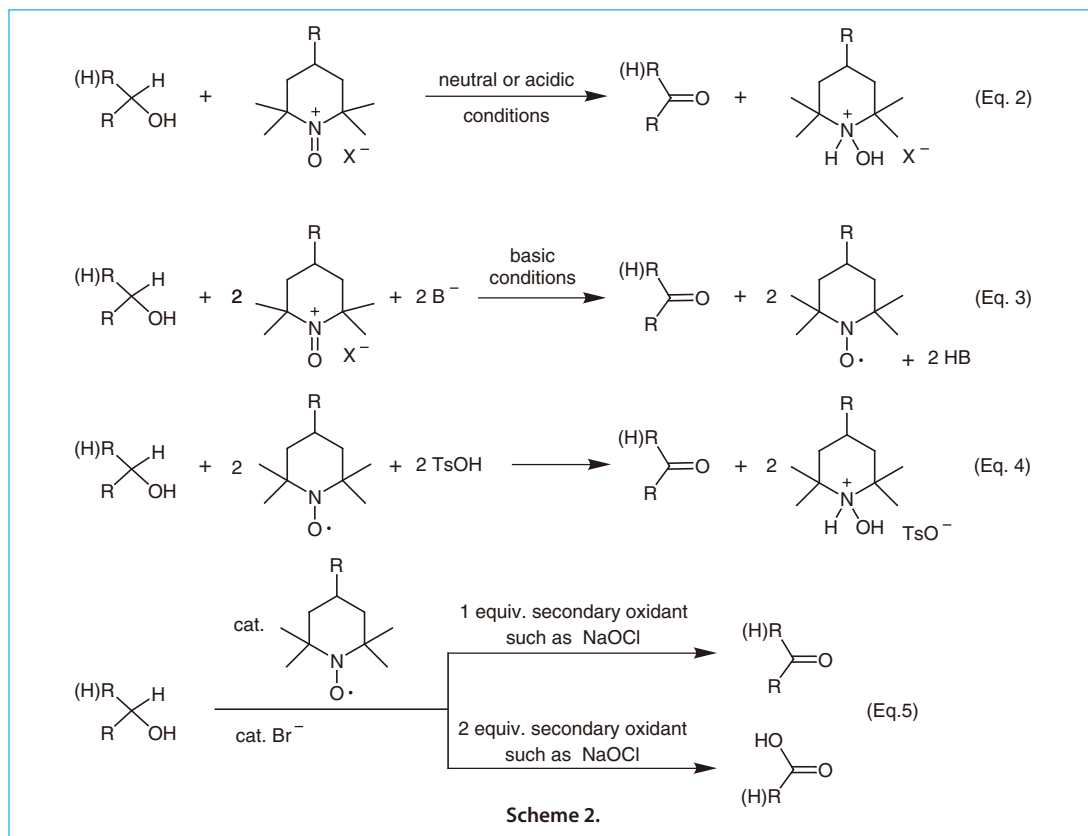


The best-known compound of any portion of this work is TEMPO or 2,2,6,6-tetramethylpiperidine-1-oxyl, **1**. TEMPO is a stable oxygen free radical, discovered in 1962.⁵ The removal of one electron from TEMPO in the presence of a suitable anion yields the oxoammonium salt, **2** (2,2,6,6-tetramethylpiperidine-1-oxonium or 2,2,6,6-tetramethyl-1-oxopiperidinium salt). The addition of one electron with a suitable anion and acid to TEMPO gives the hydroxyamine salt, **3** (1-hydroxy-2,2,6,6-tetramethylpiperidinium salt). In a remarkable disproportionation reaction in strong acid, TEMPO is converted to one molecule of **2** and one molecule of **3**. This reaction was discovered by Golubev and is one of the methods for the preparation of oxoammonium salts.⁶ The driving force for this reaction is almost surely the formation of ionic products from the neutral TEMPO. A corresponding comproportionation takes place if a mixture of **2** and **3** is made basic, thus converting the compounds back to **1**.

Combining Eq. 1 with Scheme 1, it is apparent that an alcohol oxidation involves a two-electron reaction in which the oxoammonium salt, **2**, is converted to a hydroxyammonium salt, **3**.

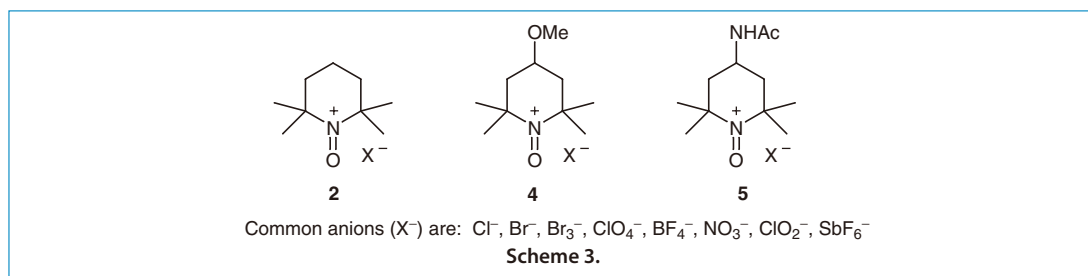
Oxoammonium ion oxidations can be used in four ways (Scheme 2); in stoichiometric oxidations, either in acid (Eq. 2) or base (Eq. 3), or using the acid-disproportionation reaction (Eq. 4) described in Scheme 1, and in nitroxide-catalyzed oxidations using some secondary oxidant such as sodium hypochlorite (bleach) (Eq. 5). Of these, the acid-disproportionation method using a nitroxide and acid (Eq. 4) has been less studied.^{7,8} The nitroxide-catalyzed reactions (Eq. 5) have been extensively studied and widely used with many different secondary oxidants,¹ but will not be considered in this article. In Equations 2-5, the R group can be hydrogen or several other groups.

We are primarily interested in stoichiometric reactions, that is reactions wherein preformed oxoammonium salts are used in a one mole/one mole manner with the alcohol or other compound being oxidized. These reactions can be carried out in neutral or slightly acidic conditions and in the presence of bases, as in Eqs. 2 and 3. The acid disproportionation procedure described in Eq. 4 is also a stoichiometric reaction in that the nitroxide and *p*-toluenesulfonic acid (two equivalents of each) are used in stoichiometric amounts.

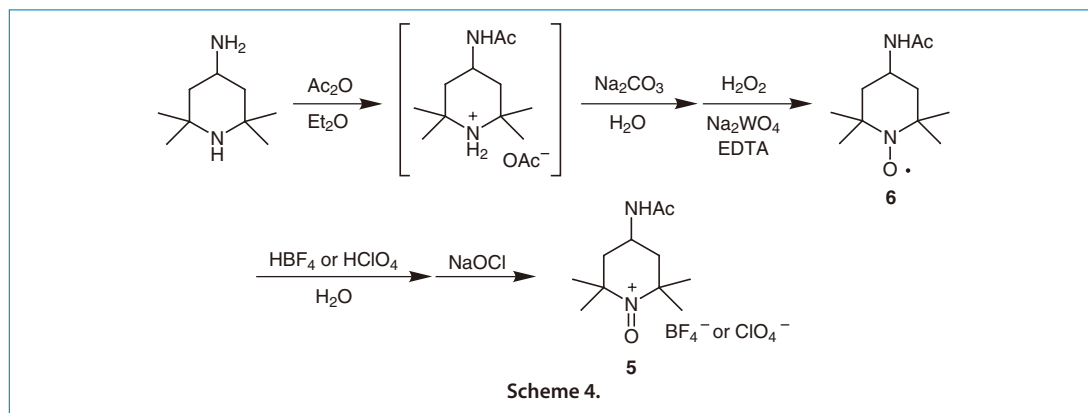


2 Preparation and Properties of Oxoammonium Salts

Oxoammonium salts are prepared by the further oxidation of nitroxides such as **1**. In turn, nitroxides are prepared by the oxidation of amines which contain no α -hydrogens or cannot form a double bond. There are many known nitroxides with many different structures,⁹⁻¹¹ and thus many *possible* oxoammonium salts.² However, essentially all of the reported oxidations have been carried out by nitroxides (as catalysts or salts) derived from 2,2,6,6-tetramethylpiperidines. This is largely due to their commercial availability. The most used salts are shown in Scheme 3. The corresponding nitroxides are used in acid-disproportionation or nitroxide-catalyzed reactions.



The general overall synthesis of the only commercially available oxoammonium salt (**5** as the tetrafluoroborate) is shown in Scheme 4. Specific instructions for the preparation of **5** BF_4^- are given in a paper by Bobbitt¹² and described in *Organic Synthesis*.¹³

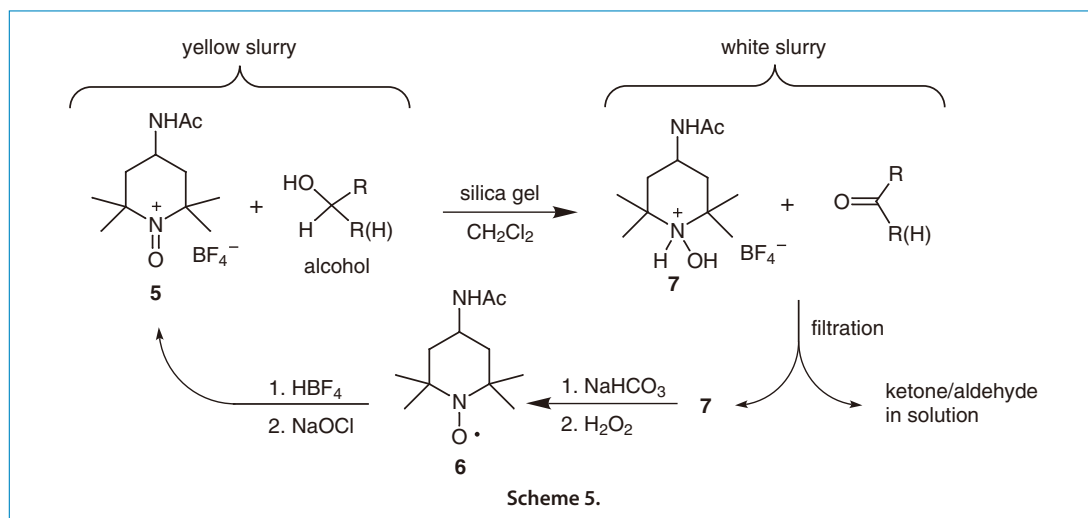


The reactions in Scheme 4 are essentially based on the work of Golubev⁶ as summarized in Scheme 1. The other major method for the synthesis of oxoammonium salts involves the oxidation of nitroxides with halogens to give the halogen salts.¹⁴

Compound **6** (4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxyl) requires special comment, particularly in comparison to TEMPO. It melts at 143-145 °C as opposed to 36-38 °C for TEMPO and is much more stable. It is easily prepared from 4-amino-2,2,6,6-tetramethylpiperidine (Scheme 4) and is used extensively in nitroxide-catalyzed oxidations instead of TEMPO. It also has interesting solubility properties, being very soluble in methylene chloride, partially soluble in water and only slightly soluble in diethyl ether. Thus, it can be extracted from water with methylene chloride or from diethyl ether with water. It can be recrystallized from ethyl acetate or water (with some loss).

3 Oxidations of Alcohols in Acidic or Near Neutral Conditions

The oxidation of a series of alcohols with **5** ClO_4^- was reported by Bobbitt¹² before the instability of the perchlorate salt was discovered; it detonated.¹⁵ However, the tetrafluoroborate, which was reported in the same paper and is commercially available, seems to work equally well. The overall reaction scheme for an alcohol oxidation using silica gel as a catalyst is shown in Scheme 5.



A slurry of alcohol, the bright yellow oxoammonium salt and silica gel in methylene chloride is stirred until the slurry turns white. The mixture is filtered, and the filtrate is passed through a thin pad of silica gel and evaporated to dryness. Usually, no further purification is needed. Yields are high, and the methylene chloride solution is quite suitable for a number of follow-up reactions (Grignard reactions, Wittig reactions, Baylis-Hillman reactions and many others) without product isolation. The method is ideal for the preparation of low molecular weight or unstable aldehydes or ketones.

The reaction has a number of advantages. It is carried out in methylene chloride at room temperature, and stringent anhydrous conditions are not required. The reaction is colorimetric in the sense that the reaction mixture goes from a bright yellow slurry to a white slurry. The salt is sufficiently soluble to allow reaction in the solvent, but the reduced oxidant, **7**, is quite insoluble. The mixture of silica gel and **7** can be processed to give recovered **6**.^{12,13}

While the normal oxidation is from an alcohol to a carbonyl compound, diols sometimes give lactones, especially when a five or six member ring can be formed.^{16,17} In the presence of pyridine (base reactions) lactones can also be formed, some with large rings.^{18,19}

The reaction rates of various alcohol oxidations are, from fastest to slowest; benzyl or allyl alcohols, secondary aliphatic alcohols and acetylenic alcohols and, finally, primary aliphatic alcohols.¹² The rates of all of the reactions are increased markedly in the presence of silica gel.

The reasons for silica gel catalysis are not known, but can possibly be explained by imagining that the polar silica gel attracts polar molecules to its surface, thus increasing the local concentration of the reacting species. A similar catalysis is noted with alumina, but not with the less polar charcoal.¹² From a practical view, the reactions can be carried out with a 50-50 blend of salt and silica gel ground together. The grinding of this blend or even the salt, if it is used by itself, seems to increase the reaction rates. This may be because the reaction is a surface reaction or simply that the finely divided reagent goes into solution faster. The silica gel may also aid in the isolation of product by adsorbing small amounts of by-products.

The main disadvantage of the method is that alcohols having a β oxygen function oxidize so slowly as to be unreactive.^{7,12} While the reasons for this inhibition are unknown, such molecules can hydrogen bond internally to make a five-member ring, and this may inhibit the formation of the hydrogen bonded intermediate visualized in the mechanism of this reaction (see Mechanisms in Acidic or Neutral Media section).

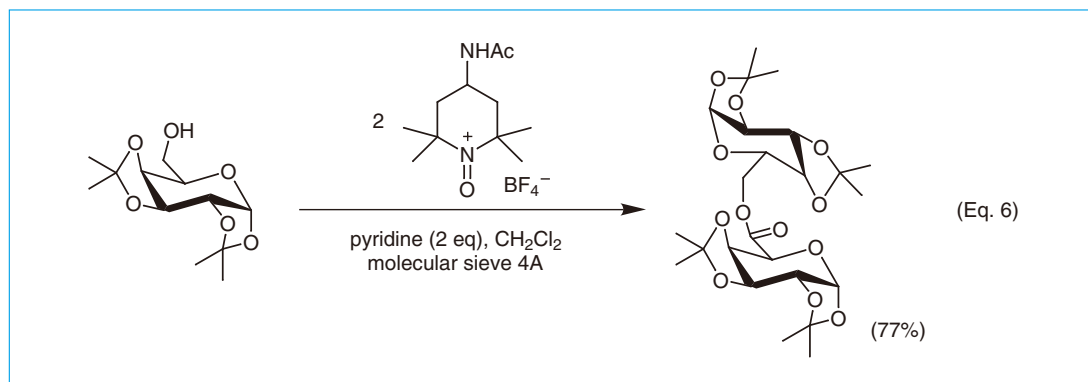
With a few exceptions (see Non-Alcohol Oxidations), amines react with oxoammonium salts to give unrecognizable products and are best avoided; although amides are quite stable. Molecules having a trisubstituted double bond, a benzyloxy group or an acetal group react slowly with the reagent. The blocking group, *tert*-butyldimethylsilyloxy (TBDMS) is slowly cleaved, but *tert*-butyldiphenylsilyloxy (TBDPS) is stable.¹² Reactions with trisubstituted alkenes in acetonitrile have been further studied,²⁰ as have reactions with benzyloxy groups.^{21,22} These side reactions are problems only with aliphatic alcohols; benzylic or allylic alcohols in methylene chloride react so rapidly that there is no problem. The various nitroxide-catalyzed reactions, which are usually carried out in basic media apparently do not have these disadvantages.

4 Oxoammonium Salt Oxidations in Basic Conditions

Oxoammonium salts react slowly in water under basic conditions to give peroxides and nitroxides.²³ It is important to note, however, that almost all of the various nitroxide-catalyzed oxidations take place in basic media in the presence of water.¹

Reactions in methylene chloride in the presence of pyridine bases, however, do take place, although they have been little studied.^{18,19,24} Whereas alcohols having a β oxygen do not react with oxoammonium salts

under neutral or acidic conditions, they give good yields of dimeric esters when carried out in the presence of pyridine.¹⁸ A specific example of this is shown in Eq. 6 for a sugar derivative. The reaction tolerates the presence of allylic double bonds, acrylic esters, benzyloxy groups, cyclopropyl ethers and sulfides.



The reactions seem to depend on the nature of the pyridine base, since, in the presence of 2,6-lutidine, aldehydes are formed.²⁵ These reactions are under study.

5 Oxidation by the Acid-Disproportionation Method

In the acid-disproportionation reaction, as shown in Eq. 4, one equivalent of substrate, two equivalents of nitroxide, **6**, and two equivalents of *p*-toluenesulfonic acid are stirred in methylene chloride.⁷ The nitroxide disproportionates to give one equivalent of oxoammonium tosylate and one equivalent of hydroxylamine tosylate as in Scheme 1. The oxoammonium salt tosylate, carries out the oxidation and is converted to a second equivalent of hydroxylamine tosylate which precipitates. The mixture is filtered, and the filtrate is washed with water and brine, and dried. Further purification may be necessary. Like the oxoammonium salt oxidation, the reaction is colorimetric in that the orange nitroxide is converted to a white slurry. Yields are high.⁷ Also, as in the oxoammonium salt reactions, the spent oxidant can be regenerated to give the nitroxide.

The method has been extensively developed by the Banwell group in Australia.^{8,26} In the Banwell work, 1,2-diols are readily oxidized to hydroxy ketones or 1,2-diketones (Scheme 8). Apparently, there is no β oxygen inhibition in these reactions.

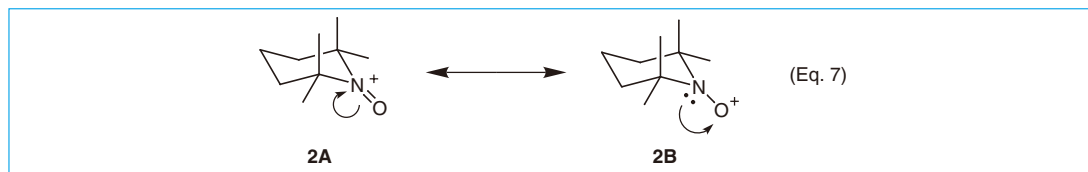
6 Mechanisms

The oxidation of an alcohol to an aldehyde or ketone is a deceptively simple transformation. A number of studies have been published concerning the mechanism of oxoammonium oxidations and nitroxide-catalyzed oxidations of alcohols, although the details of this formal two proton and two electron process (Eq. 1) are not totally clear.²⁷⁻²⁹

In this section, we will be concerned only with the mechanisms involving oxoammonium cations and various substrates. The catalytic mechanisms are described elsewhere.¹

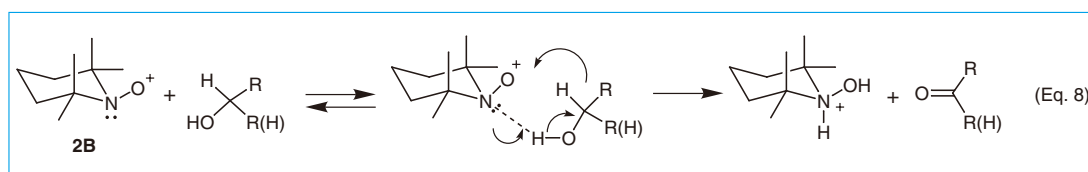
Some of the uncertainties of the mechanism arise from the fact that the oxoammonium cation can be formulated as two reacting resonance forms, **2A** and **2B** (Eq. 7). Form **2A** has a full electron octet on both oxygen and nitrogen, with a positive charge on nitrogen as the less electronegative atom. Hence, it should

contribute most towards its reactivity. However, the existence of form **2B** cannot be ruled out and represents a rare example of an electrophilic oxygen.^{30,31} Form **2B** has been invoked to explain reactions of oxoammonium salts with Grignard reagents³² and activated double bonds (to be discussed in the Miscellaneous Side Reactions section),^{7,20,31,33} and could well be more important in alcohol oxidations than hitherto realized.



Mechanisms in Acidic or Neutral Media In the original discovery of stoichiometric oxoammonium-salt oxidations of aliphatic alcohols, it was stated that the relative reactivity of the substrates was in the order secondary alcohol > primary alcohol > MeOH,^{27,34} and that the relative reaction rates are in accord with the known strengths of the carbon-hydrogen bonds on the hydroxyl-bearing carbon. A hydride abstraction was suggested. This type of mechanism, which is supported by B3LYP/6-31+G* energy calculations, is consistent with the fact that isopropyl alcohol is oxidized faster than methanol.²⁹

A cyclic intermediate, possibly aided by hydrogen bond formation between the hydrogen of the alcohol and the nitrogen electron pair from structure **2B** may facilitate this reaction (Eq. 8).



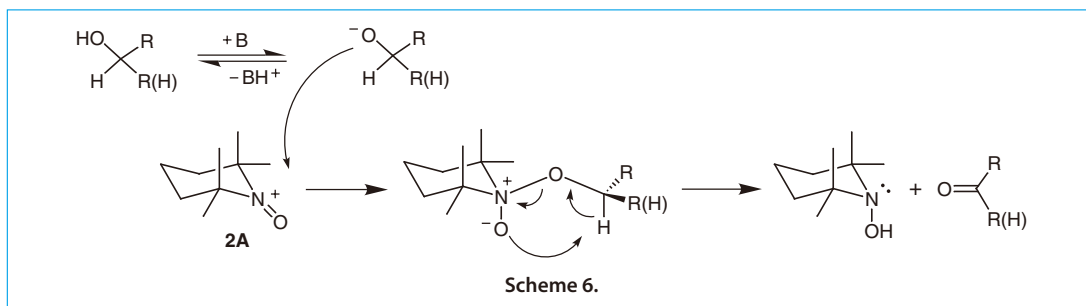
The counter anions of the oxoammonium salts have an effect on the rate of the oxidation.^{14,35} Chloride ions appear to cause much faster reaction rates than do perchlorate or tetrafluoroborate ions, which, in turn, cause faster reactions than bromide ions. The intermediate as shown in Eq. 8 disregards any anion effect and cannot account for the observed rate differences. The reaction rates using perchlorate or tetrafluoroborate salts are appreciably enhanced in the presence of silica gel.¹²

The lack of reactivity of alcohols containing a β oxygen toward oxoammonium salts in acidic media, referred to above may involve hydrogen bonding.^{7,12,36} If hydrogen bonding between the hydroxyl group being oxidized and the oxidant is inhibited by intra-molecular hydrogen bonding with the β oxygen in β oxygen compounds (and many other compounds), the reaction would be prevented or significantly retarded. On the other hand, whether such a mechanism would prevail in strongly acidic or aqueous media is problematic. This problem does not seem to occur in the catalyzed reactions, which are primarily carried out in basic media.

The results obtained with oxoammonium salts that are generated in acid-disproportionation reaction add to the confusion. In oxidations using nitroxides with *p*-toluenesulfonic acid as the disproportionation reagent (Eq. 4), the β oxygen inhibition is present with simple molecules,⁷ although it certainly does not apply in more complex cases.⁸ All in all, the β oxygen effect remains a mystery.

Mechanisms in Basic Media Almost all of the nitroxide-catalyzed oxidations have been carried out in basic media. Oxoammonium salts react slowly with dilute, aqueous base to give nitroxide and hydrogen peroxide.^{37,38}

Oxidations of alcohols in base are thought to involve an alcoholate as the nucleophilic species.²⁷⁻²⁹ The formation of alcoholate and the further details of the reaction are shown in Scheme 6. This mechanism has also been supported by computational results.²⁹

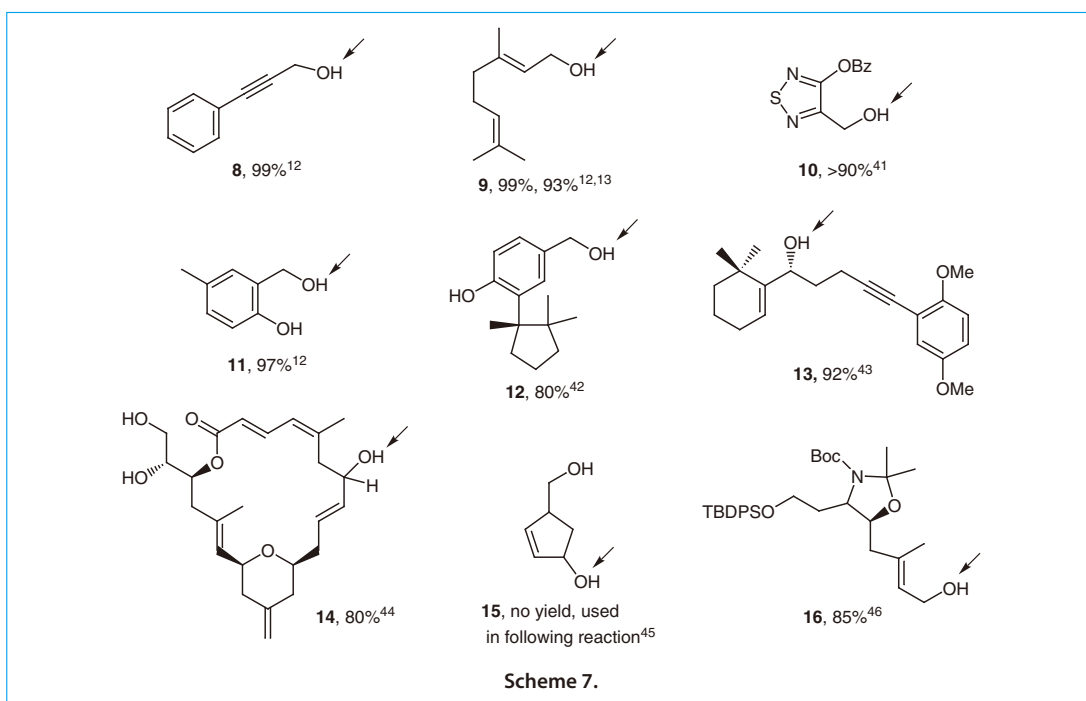


The equilibrium constants for the formation of these complexes decrease as the steric bulk of the alkoxide increases, and the differences in complex stability serve to explain the observation that primary alcohols are oxidized more rapidly than are secondary alcohols. This is observed experimentally²⁷ and is especially important in the nitroxide-catalyzed reactions.¹ Studies of stoichiometric oxidations in the presence of pyridine bases have been reported, but the mechanisms are not clear.^{18,24}

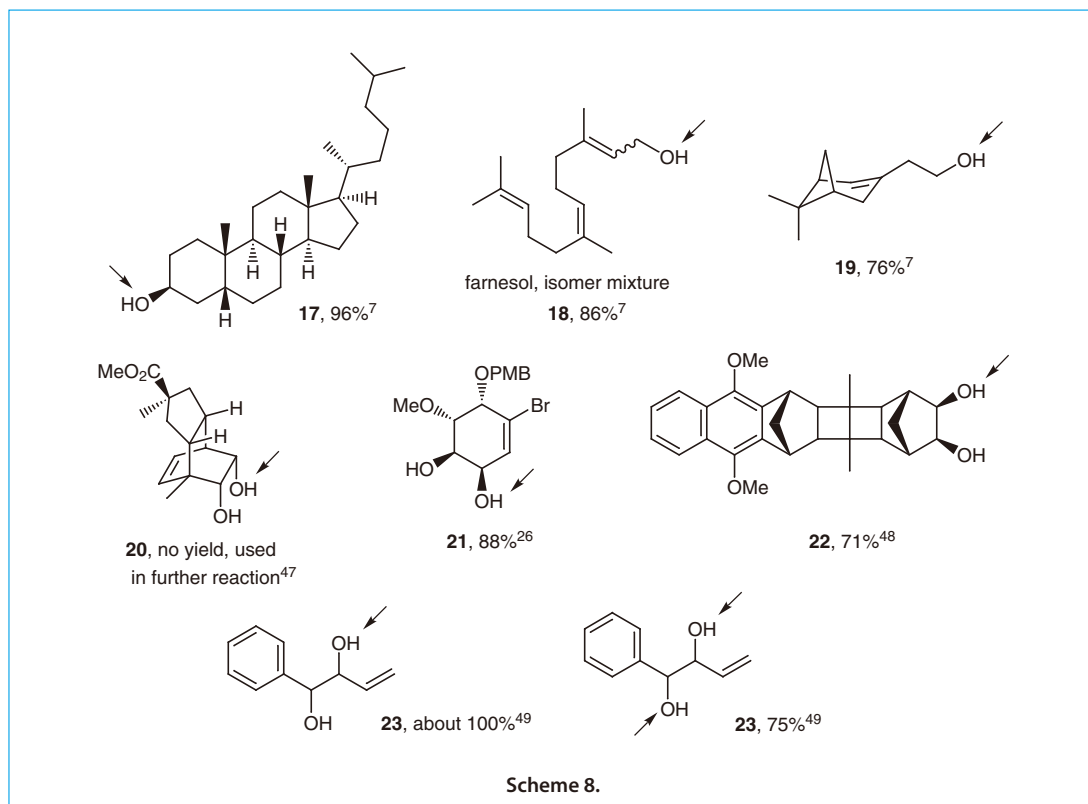
7 Specific Examples of Oxidations

A number of oxoammonium salt oxidations (at least 1,500), both stoichiometric and catalytic, have been reported.^{1,2,39,40} We have cataloged about 270 examples of stoichiometric oxidations (Eqs. 2-4) up until about July of 2008 in our *Organic Reactions* chapter.¹ Since the perchlorates are subject to detonation,¹⁵ we recommend the tetrafluoroborate salts.

Oxoammonium Salt Oxidations (Eqs. 2 and 3) In Scheme 7, the structures of a few of the more complex substrates are given. The site of oxidation is shown by an arrow, and the oxidations yield a carbonyl, either an aldehyde or a ketone. The reactions show some of the selectivity observed in oxoammonium oxidations.



Nitroxide-Acid Disproportionation Oxidations (Eq. 4) Several examples of the disproportion-type oxidations are given in Scheme 8. The acid used is *p*-toluenesulfonic acid, and the reactions are carried out in methylene chloride.

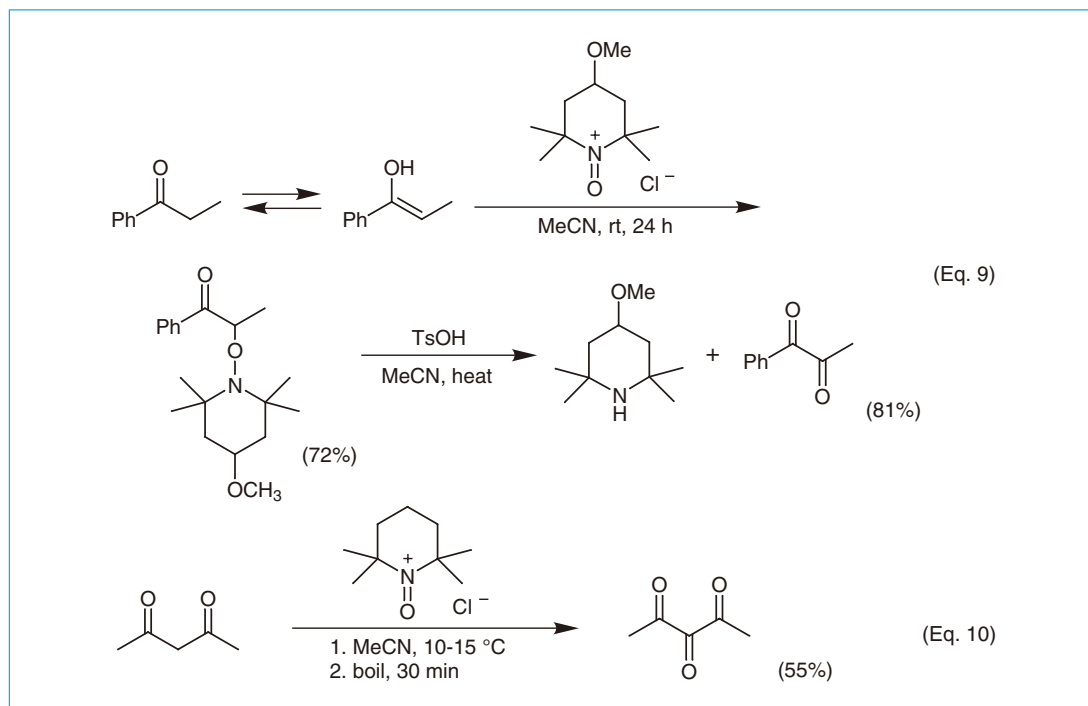


8 Stoichiometric, Non-Alcohol Oxidations

There are several reactions of oxoammonium salts which are not alcohol oxidations. In some cases, they may cause problems with alcohol oxidations, but most take place in another solvent, acetonitrile, and are slow in methylene chloride.

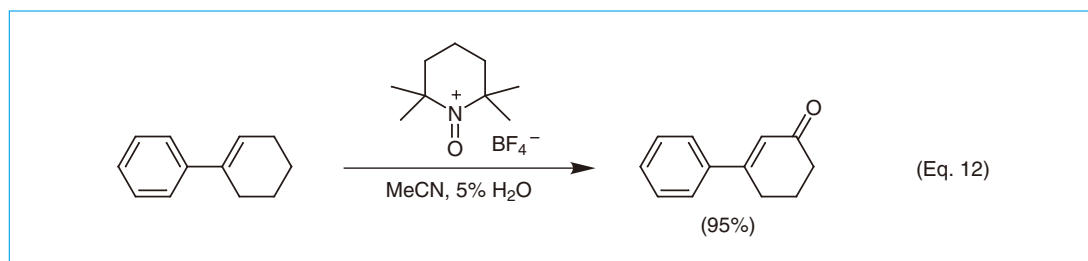
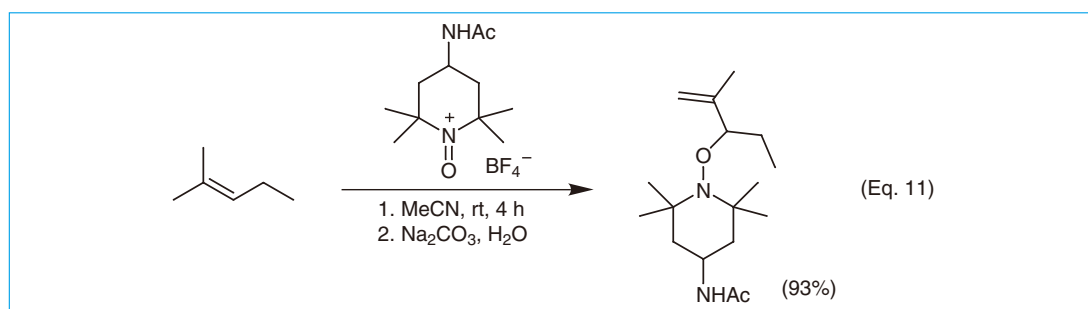
Amines react with oxoammonium salts, but the reactions are best avoided and are not very useful.^{34,50,51} Much more work needs to be done.

Monoketones can be oxidized to α -diketones (Eq. 9),^{33,52-55} and 1,3-diketones can be oxidized to 1,2,3-triketones (Eq. 10).⁵³ The latter reaction yielding 1,2,3-tricarbonyl compounds without carbon-carbon bond cleavage is unique and has not been further developed.

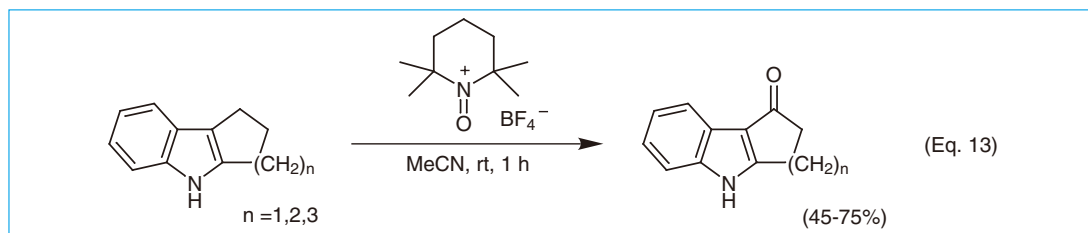


Enol ethers and enamines react with oxoammonium salts to give addition products.^{56,57}

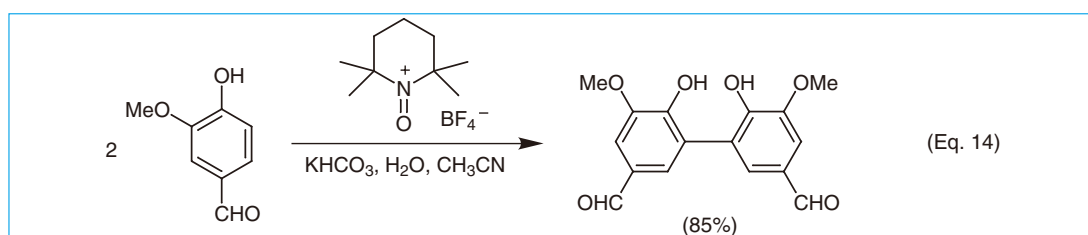
Trialkyl and tetraalkyl alkenes react slowly with oxoammonium salts in methylene chloride, but more rapidly in acetonitrile to give addition products (Eq. 11).²⁰ In a unique reaction, an activated double bond gives rise to an unsaturated ketone (Eq. 12).⁵⁸ This reaction should be further explored.



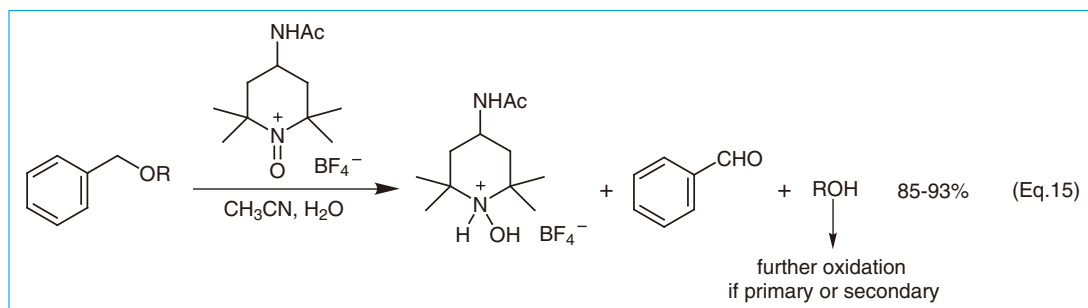
In another unique reaction, an oxoammonium salt oxidizes a carbon attached to the 3 position of an indole (as in tetrahydrocarbazole and its analogs) to a ketone (Eq. 13).⁵⁹ This reaction may involve the addition of a water molecule, but this is uncertain.



Phenols and phenyl ethers react with oxoammonium salts to yield quinones or carbon-carbon coupled dimers (Eq. 14).^{51,60-63}



Benzyl ethers react fairly rapidly in acetonitrile to give benzaldehyde and an alcohol which is further oxidized (Eq. 15).^{21,22} The reaction is much slower in methylene chloride. Oxidations of benzyl alcohols in methylene chloride are fast enough that benzyl ethers (if present) are not affected.



Reactions of sulfur compounds with oxoammonium salts are controversial. Mercaptans react with oxoammonium salts to give disulfides.⁵⁶ Sulfides are reported to be resistant to oxidation.⁶⁰ Dimethyl sulfoxide reacts rapidly with an oxoammonium salt (as in an NMR tube), but the products are not known.⁶⁴

9 Summary

Oxoammonium salt oxidations and acid-disproportionation oxidations represent facile oxidations of alcohols featuring high yields and simple product isolations. Furthermore, the reactions do not require stringent experimental conditions, are “green” in that no heavy metals are involved, and allow one to follow the reactions colorimetrically as they take place. Many of the oxidations allow one to continue with further reactions in a sequence without product isolation.

The reactions are especially suitable when a volatile or unstable product is required. All of the nitroxides and one oxoammonium salt are commercially available.

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執筆者紹介

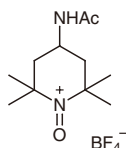
James M. Bobbitt Professor Emeritus, University of Connecticut

James M. Bobbitt was born in Charleston, West Virginia in 1930. He studied at West Virginia University, receiving the B. S. degree in chemistry in 1951. He attended the Ohio State University, receiving the Ph. D. degree in 1955 under the supervision of Professor M. L. Wolfrom. After a year of postdoctoral work at Wayne University with Professor Carl Djerassi, he accepted an instructorship at the University of Connecticut in 1956. He rose through the ranks, reaching the rank of Professor in 1967. In 1959, he received a National Science Foundation Postdoctoral Fellowship to study with Professor Hans Schmid in Zürich, Switzerland, and in 1964-65 was a guest professor at East Anglia University in England with Professor Alan Katritzky. He was a guest professor at La Trobe University in Australia in 1971-72 and at The University of Adelaide, Australia in 1986. From 1973 until 1993, he had research projects with Professor Tetsuji Kametani and Professor Tetsuo Osa at the Pharmaceutical Institute of Tohoku University and with Professor Koichi Tokuda at the Tokyo Institute of Technology. Bobbitt retired in 1992, but has remained active at the University of Connecticut since that time.

Bobbitt's research has ranged from natural product chemistry (the iridoid glycosides), chromatography, heterocyclic chemistry (isoquinoline synthesis), and electroorganic oxidations of heterocyclics. For the last 25 years it has been centered on oxoammonium salt oxidations of alcohols and other compounds. In 1991, he received the University of Connecticut Alumni award for teaching.

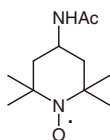
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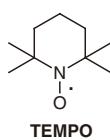


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1-oxopiperidinium Tetrafluoroborate
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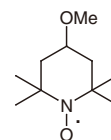
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