126 J. Org. Chem. 1989, 54, 126-131

Oxidation of Imines to Nitrones by the Permanganate Ion

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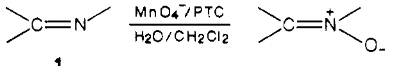
Received November 25, 1987

A series of imines have been oxidized to nitrones in reasonable yields with the permanganate ion under phase-transfer conditions. The influence of the amount of permanganate, solvents, phase-transfer catalysts, and acidity of the aqueous phase on the reaction course have been investigated. It has been found that the presence of water is necessary for the formation of the nitrone. The best phase-transfer catalysts are quaternary ammonium salts with long aliphatic carbon chains. The mechanism for the permanganate oxidation of imines to nitrones is discussed from a frontier orbital point of view. It is suggested that the reaction proceeds via an interaction of the oxygen ligands in the permanganate ion to carbon and nitrogen in the imine. The electronic and geometrical structures of the permanganate–imine complex are discussed.

Introduction

The permanganate ion, MnO_4^-, is one of the classic oxidation reagents in organic and inorganic chemistry. Within the organic field the permanganate ion is able to oxidize a variety of compounds as e.g. saturated and unsaturated carbon compounds, alcohols, aldehydes, nitrogen, and sulfur containing systems.[1] Here, we want to present a new permanganate ion oxidation reaction: the oxidation of imines, **1**, to nitrones, **2**, under phase transfer catalyst (PTC) conditions (i).



1 **2** (i)

Nitrones, **2**, are highly versatile synthetic intermediates and spin trapping reagents.[2] Nitrones, **2**, are usually prepared by either condensation of aldehydes with hydroxylamines or oxidation of the corresponding hydroxylamines.[2] The difficulty of these methods is often the preparation of the starting hydroxylamines.

Oxidation of imines with peracid leads to oxaziridines as the main product.[3] It has also been found that $MoCl_5$ or $Mo(CO)_6$ catalyze the oxidation of imines to oxaziridines with *tert*-amyl hydroperoxide as oxygen donor, but no nitrones were found.[4] Recently it has been shown that nitrones can be prepared from secondary amines with selenium dioxide[5a] or sodium tungstate[5b] as catalysts and hydrogen peroxide as oxygen donor.

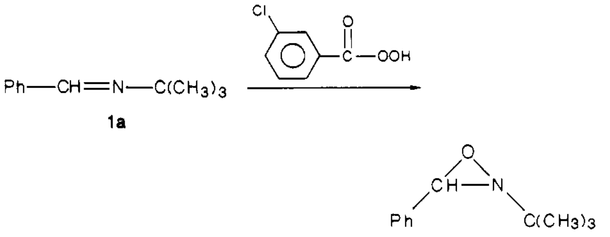
In this paper we report the oxidation of imines, **1**, to nitrones, **2**, with the permanganate ion as the oxidation reagent.[6] The influence of the amount of permanganate, solvents, different PTC's, and acidity of the water phase on the reaction course will be investigated. The mechanism of the oxidation is analyzed from both an experimental and theoretical point of view.

I. Oxidation of Different Nitrones. The efficiency of the permanganate ion to oxidize various imines, **1a–f**, was investigated under a standard set of conditions: imine (2.5 mmol), $KMnO_4$ (5 mmol), $(CH_3(CH_2)_3)_4N^+Cl^-$ (PTC) (0.5 mmol), H_2O (pH 4.1) (5 mL), and CH_2Cl_2 (5 mL) for 24 h at room temperature (for more details see the Experimental Section). The results are listed in Table I.

It appears from Table I that the imines **1a–f** are oxidized to the nitrones **2a–f** in reasonable yields, except in the cases where a phenyl group is attached to the nitrogen in the imine function where yields under 40% are found. The main byproducts formed under the reaction are the corresponding amide together with some aldehyde. In the case of **1a–c,e** the aldehyde is observed as traces (<3%). Spectroscopic data for the nitrones **2a–f** as well as the byproducts are found in the Experimental Section.

The permanganate ion oxidation of imines to nitrones is very dependent of the reaction conditions. The influence of the amount of permanganate, solvents, PTC's, and acidity of the aqueous phase on the reaction course will be presented in the following. We have mainly used benzylidene-*tert*-butylamine, **1a**, for these purposes.

If **1a** is oxidized with *m*-chloroperbenzoic acid the corresponding oxaziridine, **3a**, is formed (ii): It is observed that beside the oxaziridine **3a**, traces (<3%) of the nitrone **2a**, amide **4a**, and benzaldehyde are also formed. The permanganate ion and *m*-chloroperbenzoic acid oxidize then probably the imine by two different mechanisms.



1a **3a** (ii)

II. Amount of Permanganate. We have found that an imine:permanganate ion ratio of 1:2 gives the best yield of the nitrone under the conditions studied; increasing the

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(1) See e.g.: (a) Stewart, R. In *Oxidation in Organic Chemistry*; Wiberg, K. B., Ed.; Academic: New York, 1965; Part A, p 2. (b) Arndt, D. *Manganese Compounds as Oxidizing Agents in Organic Chemistry*; Open Court: La Salle, IL, 1981; p 183. (c) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981. (d) Augustine, R. L. *Oxidation*; Marcel Dekker: New York, 1969. (e) Lee, D. G. *The Oxidation of Organic Compounds by Permanganate Ion and Hexavalent Chromium*; Open Court: La Salle, IL, 1980. (f) Boyer, J. H. *Chem. Rev.* **1980**, *80*, 495. (g) Fatiadi, A. J. *Synthesis* **1987**, 85.

(2) See e.g.: (a) Sandler, S. R.; Karo, W. *Organic Functional Group Preparations*; Academic: New York, 1972; Vol. 3, p 301. (b) Tennant, G. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Ed.; Pergamon: New York, 1979; Vol. 2, p 500. (c) Breuer, E. *The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives*; Patai, S., Ed.; Wiley: New York, 1982; p 459. (d) Torssell, K. B. G. *Nitrile Oxides, Nitrones and Nitronates in Organic Synthesis*; Verlag Chemie: Weinheim, 1988.

(3) Patai, S. *The Chemistry of the Carbon-Nitrogen Double Bond*; Wiley: New York, 1970.

(4) Tolstikov, G. A.; Jemilev, U. M.; Jurjev, V. P.; Gershanov, F. B.; Rafikov, S. R. *Tetrahedron Lett.* **1971**, 2807.

(5) (a) Murakashi, S.; Shiota, T. *Tetrahedron Lett.* **1987**, *28*, 2383. (b) Mitsui, H.; Zenki, S.; Shiota, T.; Murahashi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 874.

(6) Amides have been obtained in a few cases where imines are oxidized the permanganate ion: see ref 1e, p 97.

(7) (a) Pews, R. G. *J. Org. Chem.* **1967**, *32*, 1628. (b) It should also be noted that nitrones have been formed in these reactions: Bjørgo, J.; Boyd, D. R.; Neill, D. C.; Jennings, W. B. *J. Chem. Soc., Perkin Trans. 1* **1977**, 254.

0022-3263/89/1954-0126$01.50/0

Table I. Oxidation of Imines 1 to Nitrones 2 with Potassium Permanganate under Phase-Transfer Conditions (See the Experimental Section for More Details)

imine	nitrone 2, yield, %	other products (yield, %)
1a, $C_6H_5CH{=}NC(CH_3)_3$	89	$C_6H_5C(O)NHC(CH_3)_3$ (11) **4a**
1b, $C_6H_5CH{=}NC_6H_5$	36	$C_6H_5C(O)NHC_6H_5$ (15) **4b**
1c, p-$NO_2C_6H_4CH{=}NC(CH_3)_3$	81	p-$NO_2C_6H_4C(O)NHC(CH_3)_3$ (19) **4c**
1d, p-$CH_3OC_6H_4CH{=}NC(CH_3)_3$	66	p-$CH_3OC_6H_4\overline{CH\text{-}O\text{-}N}C(CH_3)_3$ (3) **3d** p-$CH_3OC_6H_4C(O)NHC(CH_3)_3$ (15) **4d** p-$CH_3OC_6H_4CHO$ (16)
1e, $(CH_3)_2CHCH{=}NC(CH_3)_3$	76	$(CH_3)_2CHC(O)NHC(CH_3)_3$ (24) **4e**
1f, $(CH_3)_3CCH{=}NC_6H_5$	13	$(CH_3)_3CCHO$ (4)

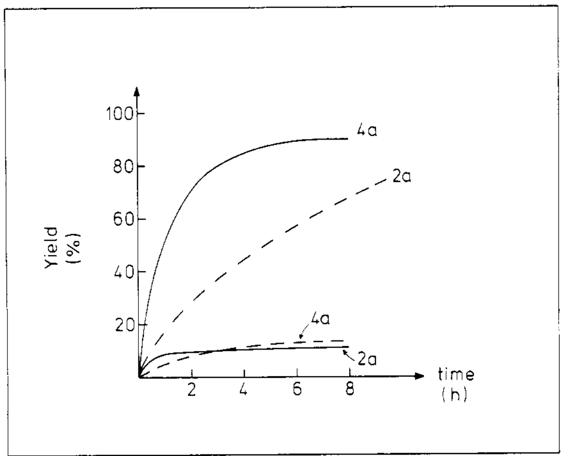

Figure 1. The variation of the yield of **2a** and **4a** as a function of time for the reaction of **1a** with potassium permanganate in acetonitrile/water (solid line) and under standard conditions (dotted line).

ratio to 1:3 or 1:4 leads to a small decrease in the yield of the nitrone **2a** (80%) and a small increase in the amount of the formed amide **4a** (20%). A reduction of the imine:permanganate ion ratio to 1:1 leads to a drastic decrease in the yield of the nitrone **2a** (17%) and also in the amount of amide **4a** formed (7%).

III. Solvents. If **1a** is oxidized with potassium permanganate in dry organic solvents (acetone, methanol, acetonitrile, or methylene chloride), no significant oxidation was found after 24 h. If a small amount of water (pH 4.1) is added to the reaction in methylene chloride, 60% of the nitrone **2a** and 19% of the amide **4a** are formed after 24 h. If the reaction takes place in acetonitrile in the presence of a small amount of water (pH 4.1), a faster reaction takes place with the formation of both **2a** and **4a**. Figure 1 shows the variation of **2a** and **4a** as a function of time for the reaction of **1a** with potassium permanganate in acetonitrile/water (solid line) as well as under the standard conditions (dotted line). It appears from Figure 1 that the oxidation of **1a**, in an acetonitrile/water solution, is faster than the procedure used to obtain the results listed in Table I. But in the acetonitrile/water solution no selectivity for the nitrone formation in the oxidation is found; after 1 h the nitrone **2a** is formed in 10% yield and the amide **4a** is present in 65%. After 3 h reaction time no significant increase in the nitrone yield is found, but the amide is now present in 87%. The reason for the faster reaction in acetonitrile/water might be that potassium permanganate is soluble in acetonitrile. It appears from our results that water is necessary for this oxidation reaction.

Table II. Oxidation of $C_6H_5CH{=}NC(CH_3)_3$, 1a, with Potassium Permanganate Using Different Phase-Transfer Catalysts[a]

phase-transfer catalyst	products (yield, %)
$(CH_3CH_2CH_2CH_2)_4N^+Cl^-$	**2a** (89), **4a** (11)
$(CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2)_4N^+Br^-$	**2a** (80), **4a** (20)
$(CH_3)_4N^+Cl^-$	**2a** (69), **4a** (19), C_6H_5CHO (11)
$C_6H_5CH_2(CH_3CH_2)_3N^+Cl^-$	**2a** (76), **4a** (23)
$C_6H_5CH_2(CH_3)_3N^+BF_4^-$	**2a** (66), **4a** (16), C_6H_5CHO (17)
$(C_6H_5CH_2)_2(CH_3)_2N^+Cl^-$	**2a** (68), **4a** (30)
$C_6H_5(CH_3)_3N^+IO_3^-$	**2a** (26), **4a** (33), C_6H_5CHO (34)
$(C_6H_5)_3CH_3P^+I^-$	**2a** (50), **4a** (18), C_6H_5CHO (32)

[a] The same reaction conditions as in Table I.

Table III. Oxidation of $C_6H_5CH{=}N(CH_3)_3$, 1a, with Potassium Permanganate at Different Acidities[a]

pH	products (yield, %)	pH	products (yield, %)
2.0	**2a** (64), **4a** (24)	8.0	**2a** (74), **4a** (10)
4.1	**2a** (89), **4a** (11)	10.4.	**2a** (73), **4a** (25)
6.2	**2a** (76), **4a** (18)	12.0	**2a** (74), **4a** (20)

[a] The same reaction conditions as in Table I.

IV. Phase-Transfer Catalysts (PTC's). PTC's are known to play an important role in the permanganate ion oxidation of alkenes.[1,8] We have found that these PTC's also are important for the permanganate ion oxidation of imines to nitrones. Without PTC present under the reaction a slow oxidation is observed. The influence of different PTC's on the reaction course of the permanganate ion oxidation of **1a** have been studied and the results are listed in Table II. It has been found that long-chained tetraalkylammonium salts are the best PTC's. Tetrabutylammonium chloride and tetraoctylammonium bromide give under the conditions studied high yields of the nitrone **2a**. When tetramethylammonium chloride is used as PTC the yield of the nitrone is lower and benzaldehyde is found, too. Benzylalkylammonium salts are not found to be as effective as tetrabutylammonium chloride and tetraoctylammonium bromide as PTC under the conditions used here. Changing an alkyl group to a benzyl group (benzyltriethylammonium chloride) in the PTC reduces the yield of the nitrone **2a**, and the amide **4a** is formed in higher amount compared with the tetrabutylammonium salt as PTC. If benzyltrimethylammonium tetrafluoroborate is used instead of benzyltriethylammonium chloride (changing the ethyl to methyl groups in the PTC), further reduction in the yield of the nitrone **2a** is observed, and benzaldehyde is also formed. Using dibenzyldimethylammonium chloride as PTC gives

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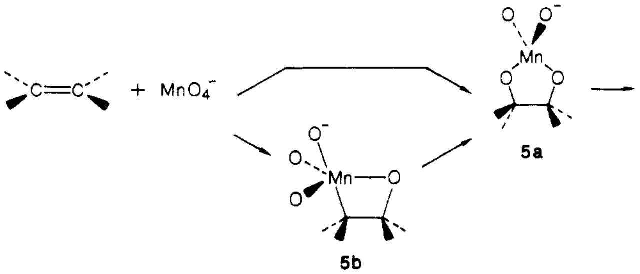
(8) Weber, W. P.; Shepherd, J. P. *Tetrahedron Lett.* **1972**, 4907.

Scheme I



similar results as with benzyltriethylammonium chloride.

V. Acidity and Basicity of the Water Phase. Table III shows the variation of the amount of nitrone **2a** and amide **4a** formed by oxidation of **1a** with the permanganate ion at different pH values of the water phase.

It appears from Table III that relatively good yield of the nitrone **2a** is formed under both acidic, neutral, and basic conditions in the water phase. The highest yield of **2a** is obtained at pH 4.1; at lower pH values less nitrone is formed, but more amide and benzaldehyde are formed, whereas under neutral and basic conditions a constant amount of **2a** (~75%) and **4a** (~20%) is formed. In all the cases small amounts of benzaldehyde is also formed. The change in the amount of **2a** and **4a** formed at pH 2 relative to the other pH values lead us to study the stability of **2a** under acidic conditions. At a 10^{-1} M DCl solution in $CDCl_3$ it has been found that the nitrone rearranges to the amide (15% of **4a** after 24 h) and is hydrolyzed to benzaldehyde in about 5% after 24 h. This rearrangement might account for the formed amide **4a** and for the benzaldehyde found.

VI. Mechanistic Section. The permanganate ion, MnO_4^-, belongs to the class of d^0 transition metal oxo complexes, which also includes osmium tetraoxide, OsO_4, and ruthenium tetraoxide, RuO_4. The mechanism for the oxidation of alkenes by this type of transition metal oxo complexes has been a subject of debate.[1c,9] Two mechanisms have been invoked:[1c] A concerted [3 + 2] cycloaddition of the alkene to the oxygen ligands in the transition metal oxo complex, **5a**,[1c,10] and a [2 + 2] addition of the alkene π bond to one of the metal oxo bonds leading to a metallocyclooxatane, **5b**.[1c,11] This asymmetric intermediate, **5b**, rearranges then to the symmetric manganese(V) ester intermediate, **5a** (Scheme I).[11,12]

The metallocyclooxatane **5b** has been suggested as an intermediate in many oxygen transfer reactions. It has, e.g., been suggested as an useful explanation for the increase of the rate of formation of the osmium(VI) ester complex, which is formed in the reaction between osmium tetraoxide and an alkene when pyridine is present.[11,13] The metallocyclooxatane intermediate has received support from both an experimental and theoretical point of view.[1c,9,14] But there has also, based on the frontier orbital approach in the case of the osmium tetraoxide oxidations, been argued for a concerted [3 + 2] cycloaddition of the alkene to the oxygens in osmium tetraoxide.[10,15] The [3 + 2] cycloadditions lead to an explanation on the effect of pyridine on the reaction rate as well as the structure of some of the osmium tetraoxide–alkene complexes.

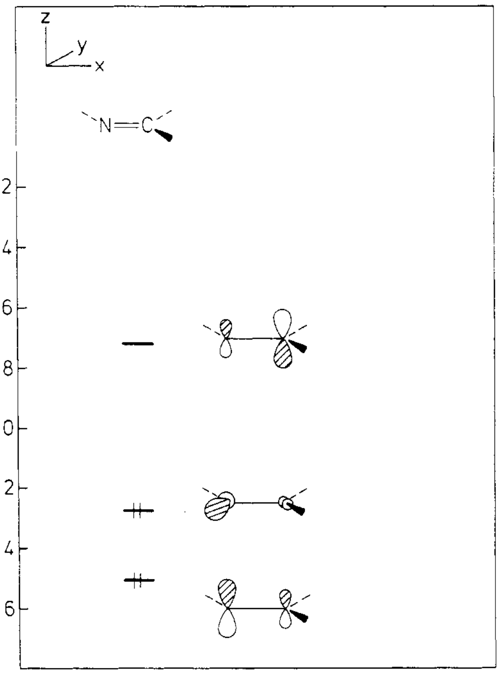
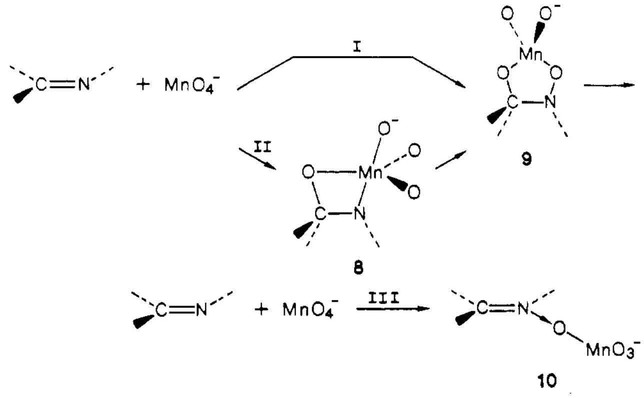


Figure 2. The frontier orbitals of an imine.

Scheme II



In an attempt to explain the permanganate ion oxidation of imines to nitrones we will here also try to use the frontier orbital approach,[16] extended Hückel,[17] and INDO[18] calculations. The extended Hückel calculations are used when interactions between the imine and the permanganate ion are studied and INDO calculations when structural information of possible intermediates involved is needed.

Let us start with the frontier orbitals of an imine shown in Figure 2. The highest occupied molecular orbital (HOMO) in the imine is mainly located on nitrogen (the lone pair electrons) and is a combination of p_x and p_y in the imine plane. About 2 eV below the HOMO is the second HOMO located a π_{N-C} orbital with the largest amplitude at nitrogen. The lowest unoccupied molecular orbital (LUMO) of the imine is located at −7.3 eV and is the π_{N-C}^* orbital, with the largest amplitude at carbon.

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[9] Jørgensen, K. A. *Chem. Rev.*, in press.

[10] Jørgensen, K. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1986**, *108*, 1867.

[11] (a) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120. (b) Hentges, S. G.; Sharpless, K. B. *Ibid.* **1980**, *102*, 4263.

[12] See e.g.: Freeman, F.; Kappos, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6628.

[13] (a) Schröder, M.; Constable, E. C. *J. Chem. Soc., Chem. Commun.* **1982**, 734. (b) Casey, C. P. *Ibid.* **1983**, 126.

[14] Rappé, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1980**, *102*, 5114; **1982**, *104*, 3287.

[15] Osmium tetraoxide is isoelectronic with the permanganate ion.

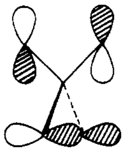
[16] See e.g.: Fujimoto, H.; Fukui, K. In *Chemical Reactivity and Reactivity Paths*; Klopman, G., Ed.; Wiley: New York, 1974; p 23.

[17] Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

[18] (a) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw Hill: New York, 1970. (b) Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta* **1979**, *53*, 21 and references therein.

The difference in the frontier orbitals when moving from an alkene to an imine is mainly that in the imine the nitrogen lone pair electrons are put in between the well-known π and π^* orbitals of the alkene.

We will not go in detail with the frontier orbitals of the permanganate ion (T_d symmetry) as similar types of orbitals have recently been described in the case of the isoelectronic osmium tetraoxide.[10] We will here mainly draw the attention to one of the HOMO's and two of the LUMO's of the permanganate ion. This HOMO, located at −14.50 eV, is of t_1 symmetry and is 2p atomic orbitals on oxygen, shown in **6**. The LUMO's, **7a**,**b**, are of e symmetry and are mainly 3d orbitals on manganese mixed in with a small amount of 2p on oxygen located at −8.59 eV.



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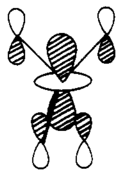
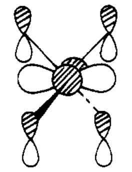


7a



7b

At least three mechanisms (I–III) can account for the permanganate ion oxidation of the imine to the nitrone. These are outlined in Scheme II.

Mechanisms I and II are similar to those outlined in Scheme I for the reaction between the permanganate ion and alkenes. From **9** the nitrone can be formed by breaking the carbon–oxygen bond and the manganese–oxygen (the oxygen bound to nitrogen) bond. In mechanism III the lone pair at nitrogen located in the imine plane attacks one of the oxygens in the permanganate ion and the nitrone is formed by breaking the manganese–oxygen bond. The latter mechanism should probably operate without water present as no intermediate is present that needs to be hydrolyzed, but it appears from our experimental results that water is necessary for the nitrone formation. We have tried to calculate the electronic changes of the system as the permanganate ion approach to the nitrogen in the imine as shown in **10**. The overlap population between the nitrogen in the imine and the oxygen in the permanganate ion increases as the permanganate ion approaches the imine, indicating that an nitrogen–oxygen bond is formed. But simultaneously the overlap population between oxygen and manganese in the permanganate ion is increased, too, also indicating that this bond is increased in strength by this reaction path. The total energy for the system increases also by this approach mainly because of electron–electron repulsion. On the basis of these results we will therefore not pursue mechanism III, but we cannot exclude this mechanism as a possibility.

The outcome of mechanism I and II is intermediate **9**, a result of a [3 + 2] cycloaddition between two oxygens in the permanganate ion and the imine.

From the symmetry and shape of the frontier orbitals of the permanganate ion it appears that the oxygens are better set up for an interaction with the imine via a [3 + 2] cycloaddition reaction rather than via a [2 + 2] cycloaddition of the imine to one of the manganese–oxo bonds in the permanganate ion. If the imine adds to the permanganate ion to give **8**, a geometrical distortion of the permanganate ion would have to take place followed by a second deformation back to **9**.[19] One can also argue against this mechanism from the principle of least motion. We will therefore in the following draw the attention to a [3 + 2] cycloaddition reaction between the imine and the permanganate ion. We cannot exclude **8** as an intermediate on these grounds, but as it will be seen below, intermediate **9** can explain the oxidation of imines to nitrones.

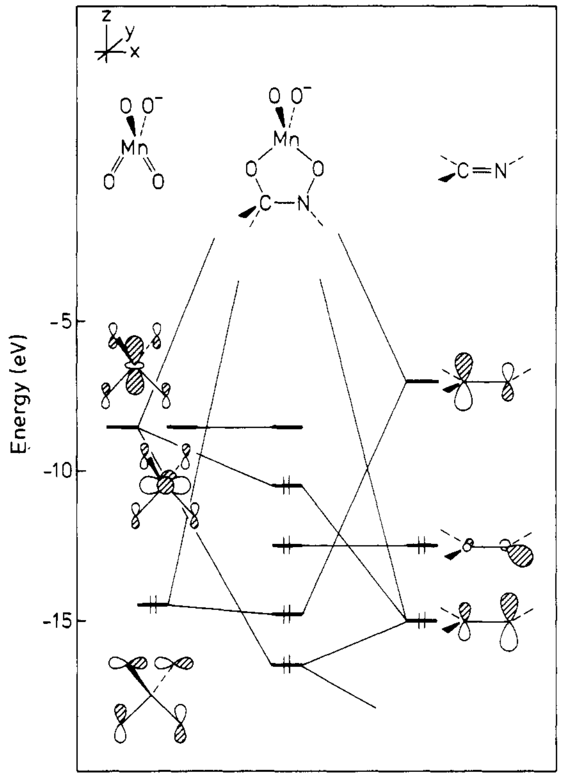


Figure 3. Interaction diagram for the formation of the permanganate ion–imine complex, **9**, from the permanganate ion to the left and the imine to the right.

The interaction between an imine and the permanganate ion leading to **9** is an interaction of the LUMO of π^* symmetry of the imine with **6** and an interaction of the second HOMO of π symmetry of the imine with **7a**. Figure 3 shows an interaction diagram for an imine to the right and the permanganate ion to the left. In the center are the energy levels of **9**. Only the orbitals related to those shown in Figure 2 and **6**, **7a**, and **7b** are shown in Figure 3.

The HOMO of the imine, which is mainly the lone pair electrons at nitrogen, is not involved in any interaction with the permanganate ion. The LUMO of the permanganate ion, mainly d_{z^2} at manganese interacts with both the second HOMO and a lower located orbital in the imine. These interactions lead to a HOMO of **9**, which now is mainly d_{z^2} mixed in with a small amount of $d_{x^2-y^2}$, π_{N-C} and σ_{N-C}. The LUMO in **9** is mainly $d_{x^2-y^2}$ at the manganese atom. These interactions lead to a reduction of manganese. The electrons that reduce the metal come mainly from the p orbital of the imine.

The LUMO orbital of metal character at manganese is consistent with attack of the water nucleophile at this site in the hydrolysis process leading to the nitrone.

Let us now focus on the electronic and geometric structure of **9**. The overlap population between manganese and the two oxygens bound to carbon and nitrogen in the imine are 0.598 and 0.498, respectively. In the per-

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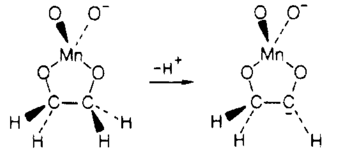
(19) From the LUMO of the permanganate ion an interaction with the HOMO of an alkene leading to an octahedral or a trigonal-bipyrimidal organometallic complex as suggested by Freeman et al.[12] seems not unrealistic.

(20) See ref 14 for a discussion of this type of interaction.

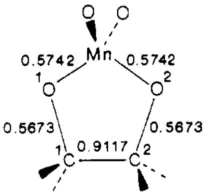
(21) Hoffmann, R., personal communication.

manganate ion the overlap population between manganese and oxygen is 0.797. These results indicate that the weakest manganese–oxygen bond in **9** is the one to which the oxygen is bound to nitrogen. Within the extended Hückel model it is not possible to compare the overlap population between nitrogen–oxygen and carbon–oxygen in **9**.[22] Instead we will use **5a′** as a model intermediate

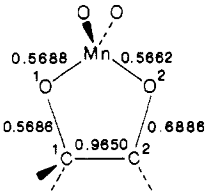


5a **5a′**

for **9**, because a removal of a proton from **5a** will lead to an isoelectronic species to **9**. We will then compare the overlap populations in **5a** and **5a′**. These are shown below.



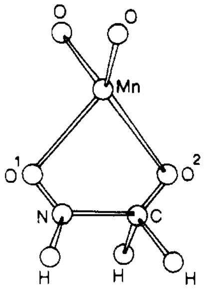
5a



5a′

A removal of a proton from **5a** leads to an increase in overlap population between the two carbons, which mainly comes from the presence of the lone pair electrons at carbon 2. The overlap population between carbon 1 and oxygen 1 remains more or less unchanged by the removal of the proton, whereas the overlap population between carbon 2 and oxygen 2 increases significantly. These results indicate that the presence of the lone pair electrons on nitrogen in the imine leads to an increase of the bond between nitrogen and oxygen, whereas the carbon–oxygen bond is not affected by the presence of these lone pair electrons.

The structure of the hypothetical intermediate, **9**, has been optimized by using the INDO procedure[18] and is shown below. The overlap population trends discussed above are easily seen in **11**. The nitrogen–oxygen bond is 1.31 Å, whereas the carbon–oxygen bond is 1.58 Å. The manganese–oxygen 1 bond is as expected longer than the manganese–oxygen 2 bond. Nitrogen–carbon–oxygen 2–oxygen 1 are not lying in the same plane in **11**, oxygen 1 is tilted out of plane. The formation of the nitrone from **11** takes thus place by breaking the manganese–oxygen 1 and carbon–oxygen 2 bonds. Our experimental results and theoretical considerations indicate thus that an intermediate of the type **9** might be present along the reaction path for the formation of nitrones from imines and the permanganate ion.



11

Summary

We have in this paper shown that imines can be oxidized to nitrones in reasonable yields by using the permanganate ion under phase transfer catalyst conditions. This permanganate ion oxidation of imines to nitrones needs water. The best type of phase-transfer catalysts have been found to be quaternary ammonium salts containing long aliphatic carbon chains whereas introduction of benzylgroups in the quatrinary ammonium salts lower the yield of the nitrone. The byproduct usually found in this oxidation reactions is the amide. We have tried to elucidate the mechanism for the oxidation using our experimental results and theoretical considerations, and we suggest that it proceeds via a [3 + 2] cycloaddition of two oxygen ligands of the permanganate ion to the imine bond. The frontier orbitals of the permanganate ion have the right symmetry to react with the π and π^* orbitals of the imine. Calculations of the overlap populations in this and a model intermediate indicate that the oxygen from the permanganate ion is strongest bound to nitrogen.

Experimental Section

^{1}H NMR spectra were recorded on a Varian Gemini 200 spectrometer. TMS was used as internal standards. IR spectra were recorded on a Beckman IR18 spectrometer. Mass spectra were recorded on a MicroMass 7070F or Trio-2 spectrometer operating at 70 eV with a direct inlet.

Materials. All the imines were synthesized according to the literature.[22] The potassium permanganate, PTC's, and solvents were used as received from the companies.

General Procedure for the Permanganate Ion Oxidation of Imines to Nitrones. First, 2.5 mmol of the imine was dissolved in 2 mL of CH_2Cl_2 and 2 mL of H_2O (pH 4.1) at room temperature; 5 mmol of $KMnO_4$ was then added. After 1 h 0.25 mmol of $(CH_3CH_2CH_2CH_2)_4N^+Cl^-$ was added over half an hour; 3 h later 3 mL of CH_2Cl_2 and 3 mL of H_2O (pH 4.1) were added. The reaction was stopped after 24 h. Then, 50 mL of 0.4 M aqueous water solution of $NaHSO_3$ was added to reduce the different oxidations species present in the reaction mixture, and the solution was stirred until it became colorless. This reaction mixture was filtered and extracted several times with CH_2Cl_2. The extractions have to be done very carefully to get a satisfactory total yield. The organic phase was dried over Na_2SO_4. To remove the remaining ammonium salt from the organic phase the CH_2Cl_2 phase was stirred with two times 50 mL of 0.1 M KI aqueous. Upon the addition of ether to the residue, the $(CH_3CH_2CH_2CH_2)_4N^+I^-$ crystallized. The ether phase was evaporated to give the products. The products can then be separated by column or preparative thin-layer chromatography or directly analyzed by spectroscopic methods. The products were checked by ^{1}H NMR, MS, and IR analyses. The ^{1}H NMR data are given below.

2a: mp 73–74 °C; δ 1.62 (s, 9 H) $C(CH_3)_3$, 7.55 (s, 1 H) $CH{=}N$, 7.40–7.43, 8.27–8.32 (m, 5 H) Ph.

4a: mp 130 °C; δ 1.48 (s, 9 H) $C(CH_3)_3$, 5.95 (br s, 1 H) NH, 7.41–7.48, 7.70–7.75 (m, 5 H) Ph.

2b: mp 112 °C; δ 7.88 (s, 1 H) $CH{=}N$, 7.36–7.46, 7.56–7.78, 8.31–8.42 (m, 10 H) 2 Ph.

4b: δ 9.00 (br s, 1 H) NH, 7.10–7.90 (m, 10 H) 2 Ph.

2c: δ 1.61 (s, 9 H) $C(CH_3)_3$, 8.10 (s, 1 H) $CH{=}N$, 8.12 (d, 2 H) Ph, 8.20 (d, 2 H) Ph.

4c: δ 1.48 (s, 9 H) $C(CH_3)_3$, 5.93 (br s, 1 H) NH, 7.83 (d, 2 H) Ph, 8.22 (d, 2 H) Ph.

2d: δ 1.60 (s, 9 H) $C(CH_3)_3$, 3.81 (s, 3 H) OCH_3, 8.01 (s, 1 H) $CH{=}N$, 6.85 (d, 2 H) Ph, 8.06 (d, 2 H) Ph.

3d: δ 1.17 (s, 9 H) $C(CH_3)_3$, 3.80 (s, 3 H) OCH_3, 4.64 (s, 1 H) CHN, 6.90 (d, 2 H) Ph, 7.38 (d, 2 H) Ph.

4d: δ 1.46 (s, 9 H) $C(CH_3)_3$, 3.84 (s, 3 H) OCH_3, 5.91 (br s, 1 H) NH, 6.90 (d, 2 H) Ph, 7.69 (d, 2 H) Ph.

2e: δ 1.34 (d, 6 H) $(CH_3)_2$, 1.62 (s, 9 H) $C(CH_3)_3$, 2.64 (m, 1 H) CH, 5.78 (d, 1 H) $CH{=}N$.

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[22] (a) Campbell, K. N.; Sommers, A. H.; Campbell, B. K. *J. Am. Chem. Soc.* **1944**, *66*, 82. (b) Emmons, W. P. *Ibid.* **1957**, *79*, 5739. (c) Pews, R. G. *J. Org. Chem.* **1967**, *32*, 1628.

4e: δ 1.12 (d, 6 H) $(CH_3)_2$, 1.34 (s, 9 H) $C(CH_3)_3$, 2.23 (m, 1 H) *CH*, 5.25 (br s, 1 H) N*H*.

2f: δ 1.22 (s, 9 H) $C(CH_3)_3$, 4.33 (s, 1 H) C*H*=N, 7.43–7.56, 7.89–7.96 (m, 5 H) Ph.

4f: δ 1.32 (s, 9 H) $C(CH_3)_3$, under aryl peaks (1 H) N*H*, 7.27–7.36, 7.50–7.55 (m, 5 H) Ph.

The mass spectra of the nitrones show all M^+ for the molecular ion and then $M^+ - 16$ followed by further decomposition.

Oxidation in Organic Solvents. First, 2.5 mmol of **1a** was dissolved in 4 mL of organic solvent (acetone, acetonitrile, or methanol); 5 mmol of $KMnO_4$ was then added. The reaction was stopped after 24 h and worked up as above. The products were identified by ^1H NMR spectroscopy. When water was present **1a** was dissolved in 2 mL of organic solvent and 2 mL of H_2O otherwise as above.

Oxidation with Different Phase-Transfer Catalysts. The general procedure was used but with the different PTC's in the same molar amount as above.

Oxidation under Acidic and Basic Conditions in the Water Phase. The pH in the water phase was adjusted to the appropriate pH (see Table III) with HCl or NaOH, and the general procedure was used.

Calculations. The extended Hückel calculations[17] were used for the calculation of the frontier orbitals, interaction schemes, and overlap population analysis. The geometries for **5a**, **5a′**, and **9** were approximated to the osmium tetraoxide–alkene system.[10] The calculations for **1** were performed for an imine (C=N, 1.27 Å; C—H, 1.09 Å; N—H, 1.05 Å and all angles involving C—H or N—H 120°) to which the permanganate ion (T_d symmetry, Mn—O, 1.64 Å) approaches with an oxygen to the imine nitrogen in the imine plane. The geometry of **9** was optimized with the INDO procedure.[18]

Acknowledgment. Thanks are expressed to Professor Kurt Torssell for fruitful discussions, to Lise Ravn-Petersen for technical assistance, to Hanne Kirkegaard for typing the manuscript, and to Arne Lindahl for the draft work.

Registry No. **1a**, 6852-58-0; **1b**, 538-51-2; **1c**, 718-36-5; **1d**, 15875-74-8; **1e**, 6852-60-4; **1f**, 26029-60-7; **2a**, 3376-24-7; **2b**, 1137-96-8; **2c**, 3585-88-4; **2d**, 40117-28-0; **2e**, 85664-55-7; **2f**, 75351-06-3; **3a**, 43052-01-3; **4a**, 5894-65-5; **4b**, 93-98-1; **4c**, 42498-30-6; **4d**, 19486-73-8; **4e**, 7472-49-3; $KMnO_4$, 7722-64-7; $(CH_3CH_2CH_2CH_2)_4N^+Cl^-$, 1112-67-0; $[CH_3(CH_2)_7]_4N^+Br^-$, 14866-33-2; $(CH_3)_4N^+Cl^-$, 75-57-0; $C_6H_5CH_2(CH_3CH_2)_3N^+Cl^-$, 56-37-1; $C_6H_5CH_2(CH_3)_3N^+BF_4^-$, 35820-01-0; $(C_6H_5CH_2)_2(CH_3)_2N^+Cl^-$, 100-94-7; $C_6H_5(CH_3)_3N^+IO_3^-$, 117678-56-5; $(C_6H_5)_3CH_3P^+I^-$, 2065-66-9; *p*-$CH_3OC_6H_4CHO$, 123-11-5; C_6H_5CHO, 100-52-7; $(CH_3)_3CCHO$, 630-19-3.

Thermal and Photochemical Reactions of Triarylmethyl Peroxides[1]

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Received April 28, 1988

The thermal and photochemical decomposition products of *p*-benzoyltriphenylmethyl peroxide (I), of *m*-benzoyltriphenylmethyl peroxide (II), and of isotopically labeled analogues indicate rapid radical 1,2-migrations precluding other radical processes such as β-elimination from the incipient radical. The mechanism of these processes is interpreted in terms of these rearrangements as well as reversible elimination of O_2 from the starting peroxide. Differences in the two isomeric peroxides are assessed.

Cited as evidence for the intervention of the free triphenylmethyl radical in the reaction of triphenylmethyl halides with mercury and silver,[2,3] the observation of triphenylmethyl peroxide contributed enormously to early mechanistic and structural theory. Triphenylmethyl peroxide decomposes at the melting point[4] to benzpinacol diphenyl ether, benzophenone, and tetraphenylethylene,[5] a result claimed as evidence for 1,2-migration of phenyl[6] to give α-hydroxy(*O*-phenyl)diphenylmethyl. Benzophenone derives in this context it is said from β-cleavage of phenyl, though diphenylphenoxymethyl cannot be isolated and gives no peroxide in the presence of oxygen.[4] Schmidlin and Hodgson were the first to observe this product, along with the formation of phenol from the "distillate" of triphenylmethyl peroxide at 240 °C. Tetraphenylethylene may result either by α-cleavage of the rearranged radical to the carbene followed by dimerization or by elimination of two phenoxy radicals from benzpinacol diphenyl ether. Though Gomberg also reported that many triarylmethyl radicals such as α-naphthyldiphenylmethyl[7] and β-naphthyldiphenylmethyl[8] are unstable to light, the products as such were identified in these early papers, and there have been no reported studies of the photochemistry of triarylmethyl peroxides containing absorbing chromophores. Product studies were limited to thermolysis reactions.[4,5]

As part of a program established to search for more efficient UV photoinitiators, we have investigated the thermal and photodecomposition of the benzoyltriphenylmethyl peroxides *p*-benzoyltriphenylmethyl peroxide (I), and *m*-benzoyltriphenylmethyl peroxide (II). In view of the thermal decomposition results,[4,5] and our own results with *tert*-butyl per-4-benzoylbenzoate,[9] efficient radical formation by O–O cleavage was anticipated when the compounds were irradiated at, or near, the n-π* maximum. The resulting triarylakoxy radical is a masked bis(benzophenone) if the β-cleavage expected to predom-

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[1] Contribution no. 36 from the Center for Photochemical Sciences.

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