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One-Flask Transformation of Secondary Amines to Nitrones by Oxidation with Hydrogen Peroxide Mediated by Triscetylpyridinium Tetrakis Oxodiperoxotungsto-phosphate (PCWP). Some Mechanistic Considerations

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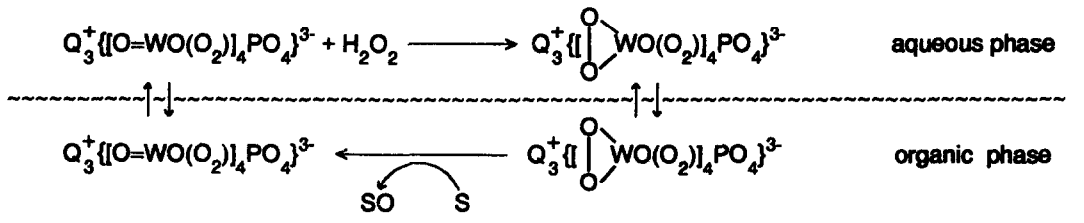
Abstract: *Acyclic and cyclic secondary amines are oxidized to nitrones by H_2O_2/PCWP system in water/chloroform under phase transfer catalysis conditions. The different acidities of the protons of the carbon atoms α to the nitrogen might be responsible for the identity and of the stereochemistry of the formed nitrone. The presence of an aromatic ring such as benzene directly linked to the nitrogen represents a limitation, since in this case many oxidation products are observed. As far as the mechanistic aspects are concerned, it is suggested that the oxidation process might be started by a nucleophilic attack of the amine to the peroxidic oxygens of the peroxometal complex or by a single electron transfer from the amine to the oxidant.*

Metal catalyzed oxygen transfer processes, which employ dilute hydrogen peroxide as oxygen source, meet an increasing interest in the field of synthetic organic chemistry owing to the development of phase transfer techniques.[1-8] The procedure involves the formation of a peroxidic derivative in the aqueous phase by hydrogen peroxide reaction with a metal compound, its transfer into the organic phase by a suitable phase transfer agent and subsequent reaction with the organic substrate to yield the oxidized products.

Recent papers report that some Mo(VI) and W(VI) peroxopolyoxocomplexes of general formula $Q_3^+\{PO_4[MO(O_2)_2]_4\}^{3-}$ have been employed as catalysts in such oxidation reactions.[5-7,9-12] One of the advantages in using these salts as oxidants comes from the possibility that the countercation Q^+ itself acts as a phase transfer agent as in the case in which Q^+ represents convenient ammonium salts (Scheme 1).

Scheme 1



Furthermore such peroxocomplexes, which have been shown to be very versatile oxidants, can be readily obtained from commercially available reactants as molybdates or tungstates salts and dilute hydrogen peroxide.

It is worth mentioning that the oxidation chemistry of peroxopolyoxocomplexes is becoming richer and richer, since it involves oxygen tranfer to a large variety of organic substrates as alkenes,[9-11] alkynes,[5-7] alcohols,[9,15] diols,[9,13] sulphides,[12,14] and sulphoxides.[14]

To enlarge the synthetic scope of this class of oxidants we explored extending their use to amines to yield nitrones.

The importance and the versatility of nitrones as synthons in organic synthesis is well known,[15-21] e.g. cycloaddition reactions in obtaining nitrogeneous natural products, or as radical traps[22] expecially in biomedical fields.

Some methods reported in the literature to synthesize nitrones employ hydroxylamines as key intermediates, but these procedures suffer from the drawbacks that the preparation of hydroxylamines is not a trivial task. On the other hand, there are a few procedures which are based on the oxidation of secondary amines with different kinds of oxidants, as for the recently described systems which employ dimethyldioxirane[23] or hydrogen peroxide-sodium tungstate.[8]

Results and discussion

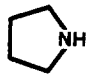
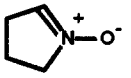
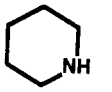
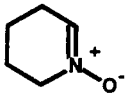
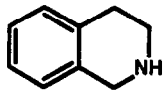
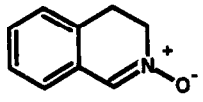
In the procedure reported here acyclic and cyclic secondary amines are oxidized in a single step to yield nitrones, as the main or the exclusive oxidation product (eq. 1), in water-chloroform upon treatment with nearly 3 molar equiv. of diluted hydrogen peroxide (35%) in the presence of 1mol% of $[C_5H_5\overset{+}{N}CH_2(CH_2)_{14}CH_3]_3\{PO_4[WO(O_2)_2]_4\}^{3-}$(PCWP) at 40°C.

$$R^1R^2CHNHR^3 \xrightarrow[H_2O/CHCl_3]{H_2O_2,\ PCWP} R^1R^2C{=}N^+(O^-)R^3 \qquad (1)$$

The relevant data are reported in table 1. Benzylalkylamines, dibenzylamine and diisopropylamine give the nitrone derivative as the sole (runs 2, 3, 5) or the main (runs 1, 4) reaction product. The more branched is the alkyl chain, the more selective is the reaction towards the nitrone formation. Also five and six membered cyclic amines (runs 7,8) yield the nitrone in good yields and the presence of a fused ring, 1,2,3,4-tetrahydroisoquinoline, does not represent a limitation (run 9).

Generally the yields obtained in this procedure are comparable or quite better than those obtained by sodium tungstate-hydrogen peroxide[8] (e.g. N-tert-butylbenzylamine gives 100% yield in our case *vs* 83% or dibenzylamine 75% *vs* 71%).

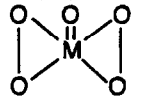
Table 1. Oxidation of Secondary Amines with Dilute Hydrogen Peroxide[a] at 40°C in $CHCl_3/H_2O$ in the Presence of Tris-cetylpyridinium Tetrakis(diperoxotungsto)phosphate (PCWP)[b].

Run	Substrate(mmol)	Time(min)	Conv.(%)	Products(yields,%)[c,d]
1	$PhCH_2NHCH_3$ (3.0)	45	94	$PhCH{=}N^+(O^-)CH_3$(37) PhCHO(7) PhCH=NOH(36)
2	$PhCH_2NHCH(CH3)_2$ (3.0)	120	100	$PhCH{=}N^+(O^-)CH(CH_3)_2$(98) PhCHO(2)
3	$PhCH_2NHC(CH_3)_3$ (3.0)	60	50	$PhCH{=}N^+(O^-)C(CH_3)_3$(100)
4	$PhCH_2NHCH_2Ph$ (3.5)	180	91	$PhCH{=}N^+(O^-)CH_2Ph$(75) PhCHO(19) PhCH=NOH(6)
5	$(CH_3)_2CHNHCH(CH_3)_2$ (3.0)	360	50	$(CH_3)_2C{=}N^+(O^-)CH(CH_3)_2$(100)
6	$PhCH_2NHPh$ (3.5)	150	100	$PhCH{=}N^+(O^-)Ph$(2) PhCH=NPh(6) PhCOOH(6) PhCHO(46) PhNO(17) PhNO2(11)
7	 (3.0)[e]	60	80	 (63)
8	 (3.0)[e]	60	80	 (55)
9	 (3.1)[e]	120	80	 (79)
10	(S)-(-)-$PhCH_2NHCH(CH_3)Ph$ (3.5)	90	95	(S)-(+)-$PhCH{=}N^+(O^-)CH(CH_3)Ph$(90)

[a]$[H_2O_2]$=20 mmol. [b][PCWP]=0.03 mmol. [c]Isolated yields. [d]Identities of compounds were obtained by comparison of their MS and ^1H NMR spectra with those of autenthic samples. [e]t=0°C.

By contrast, the presence of an aromatic ring such as benzene, directly linked to the nitrogen atom (run 6), changes the scenario dramatically. In such a case, very small amounts of nitrone are obtained, whereas many other reaction products are present. Although of no synthetic value, it is quite interesting from a mechanistic point of view and provides useful hints about the limitation of the method.

Murahashi et al.[8] suggested that in the oxidation of secondary amines to nitrones by Na_2WO_4-H_2O_2, the oxidant species are the peroxytungstates $HOOWO_3^-$ and $HOOWO_6^-$. We believe that this mechanistic hypothesis is not correct on the basis of the following facts:

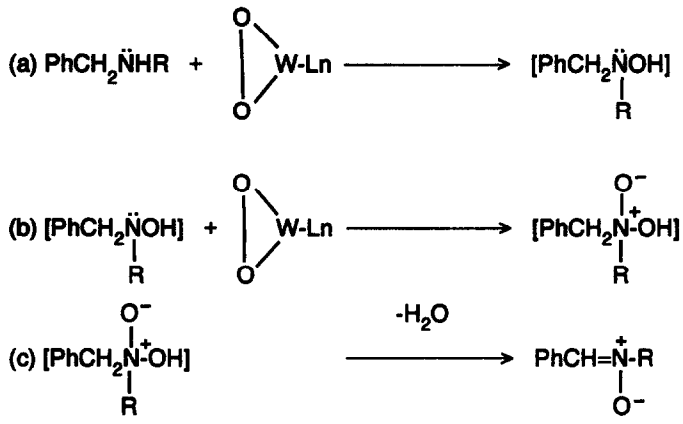
(i) it is known that the oxidant activity of Na_2MO_4-H_2O_2 (M=Mo(VI) or W(VI)) is due to the generation in situ of "side-on" peroxo complexes  which have been also isolated and structurally charecterized by X-rays.[24-28]

(ii) organic substrates possessing lone pairs or π electrons, usually behave as nucleophiles towards such peroxo complexes which, therefore, are defined electrophilic oxidants.[12,24,30,33] Peroxopolyoxo complexes, such as PCWP, have been shown to belong to the class of "side-on" complexes[29,12] and, therefore, their reactivity should be rationalized on such basis.

X-ray structural determination of W peroxopolyoxo complexes[29] indicated the presence of four

peroxidic bridges $W(O_2)_2$, joined to a central PO_4 group. Therefore, it might be reasonable to assume, that the amine can attack the peroxidic oxygen of the peroxopolyoxo complex nucleophilically[30] to yield the hydroxylamine, which, after further oxidation followed by elimination of a molecule of water, yields the nitrone (Scheme 2).

Scheme 2



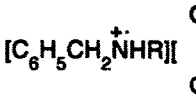
On the other hand, the oxidation of $C_6H_5CH_2NHCH(CH_3)C_6H_5$ (1.4 mmoles) performed in $CHCl_3$ by isolated (in absence of H_2O_2) PCWP (0.24 mmoles, $[O_{active}]=8[PCWP]=1.9$ mmoles) gives the nitrone $C_6H_5CH=N^+(O^-)CH(CH_3)C_6H_5$ (0.86 mmoles, 90% yield based on the oxidant consumption) according to the following stoichiometry (eq. 2):

$$4\ PhCH_2NHCH(CH_3)Ph + [C_5H_5N^+(CH_2)_{15}CH_3]_3\{PO_4[WO(O_2)_2]_4\}^{3-} \longrightarrow$$
$$4\ PhCH=N^+(O^-)CH(CH_3)Ph + 4H_2O + 4WO_3 + [C_5H_5N^+(CH_2)_{15}CH_3]_3PO_4^{3-} \quad (2)$$

This result would indicate that, at least formally, two oxygen atoms, one from each peroxidic bridge $W(O_2)$, are required in the formation of a molecule of nitrone; furthermore, it would support the involvement of the PCWP, as the active oxidant species, also in the catalytic oxidation, where the role of hydrogen peroxide might be to regenerate "in situ" the PCWP (scheme 1).

Step (c) of scheme 2 is crucial because it determines the location of the double bond in the nitrone. In fact in the case of methylbenzylamine (run 1) we obtained the nitrone with double bond located between the nitrogen and the benzyl carbon. However, in principle, it might be possible to have the nitrone with the double bond located between the nitrogen and the alkyl carbon. The selectivity of this step might be governed, inter alia, by the different acidities of the protons of the carbon atoms in position α to the nitrogen atom. In this respect, oxidation of (S)-(-)-N-benzyl-α-phenylethylamine, (run 10), is very intriguing. The selective formation of the chiral nitrone (S)-(+)-$C_6H_5CH=N^+(O^-)CH(CH_3)C_6H_5$, was observed with retention of configuration, where the proton of the leaving water molecule was removed from the benzyl carbon atom rather than from the benzyl

carbon atom bearing a methyl group (more basic). Therefore this kind of acidity[31] might be a parameter which allows to control the identity and the stereochemistry of the nitrone.

On the other hand, dealkylation products observed in runs 1 and 4, as well as in run 6, cannot be accomodated within a single reaction mechanism. The possibility that the oxidation process might be triggered by an electron transfer from the amine to the oxidant should be envisaged.[32] Generally amines are good electron donor substrates and peroxopolyoxo complexes such as PCWP have been shown to behave as acceptors in suitable conditions.[33] The transfer of a single electron might lead to the formation of a radical ions pair, i.e. an aminium radical cation and an oxidant radicalanion,  , which then collapses probably to form hydroxylamine, which is further oxidized to products.[34]

However, if the aminium radical cation is sufficiently long-lived to be able to escape from the radical pair cage, it undergoes fragmentation and the resulting radicals are oxidized to different products. This might be the case with benzylaniline (run 6), where formation of a relatively stable aminium radical cation (stabilized by resonance), breakage of the C-N bond, and subsequent oxidation of the fragments may account for the observed oxidation products, such as Ph-NO, Ph-NO_2 or Ph-COOH. That organic radicals are generated in run 6 is supported by e.s.r. experiments, which reveal the presence of radical species (18 lines, $a_H^{o,p}$=3, a_N=12, a_{CH_2}=9).

Similarly, in the case of dibenzylamine, e.s.r. measurements gave a spectrum of 15 lines (a_H=9.4, a_N=15.0) which, according to literature reports, might be indicative of the presence of the corresponding nitroxide.[35]

It is apparent from previous considerations that a rationalization of the reactivity of "side-on" peroxopolyoxometal complexes is required and some mechanistic work is warranted to clear up the chemistry of these processes.

Conclusion

The results reported in this paper indicate that secondary amines are efficiently oxidized to nitrones by H_2O_2/PCWP system under phase transfer catalysis conditions. It seems that the identity and the stereochemistry of the formed nitrone is governed, inter alia, by the different acidities of the protons of the carbon atoms α to the nitrogen atom. The oxidation process might occur through a nucleophilic attack of the amine to the peroxidic oxygens or might be started by a single electron transfer from the amine to the oxidant. E.s.r. measurements reveal in some cases the incursion of radicals. The presence of an aromatic nucleus directly linked to the nitrogen represents a limitation for the substrates which can be oxidized by this procedure.

Acknowledgements. We thank prof. R. Bonomo, University of Catania, for e.s.r. experiments. Financial support by MURST and by CNR is also gratefully acknowledged.

EXPERIMENTAL SECTION

Materials. All reactions were run under helium atmosphere. Amines (Aldrich) were distilled over

calcium hydride prior to use.
Chloroform (Carlo Erba, RPE) was distilled over P_4O_{10}, whereas H_2O_2 (35%) (Carlo Erba, RPE) was used without further purification.

Preparation of triscetylpyridinium tetrakis(diperoxo-tungsto)phosphate(PCWP).
PCWP was prepared according to Ishii et al.[10] To a solution of cetylpiridinium chloride (1.1 gr, 3.1 mmoles) in 35% H_2O_2 (40 mL) was added $H_3PW_{12}O_{40}$ .nH_2O (3.0 gr) in 35% H_2O_2 (10 mL), and the mixture was stirred at 40°C for 4-5h. The white precipitate, after filtration, was washed with water until H_2O_2 disappeared and then dried in vacuo over P_4O_{10},([O_{active}]=8[PCWP]>97%, iodometric titre).
The IR spectrum (KBr) corresponds to that reported in the literature.
Instrumentation
Proton NMR spectra were obtained on a Bruker WP-80 and 200 MHz spectrometer.
GC/MS analyses were performed by a Hewlett-Packard model 5890 gas chromatograph (using an HP-1 dimethylpolysiloxane 25m capillary column), equipped with a Hewlett-Packard MS computerized system Model 5971A, ionization voltage 70 eV, electron multiplier 1700 V, ion source temp. 280°C.
E.s.r. spectra were measured with a conventional X-band spectrometer (Bruker Model 220 D) operating at 9.3-9.5 GHz and using 100-KH field modulation and a 10-in. electromagnet.
GLC analysis was carried out on a Perkin-Elmer 8420 gas chromatograph equipped with a flame ionization detector and program capability. A 25 m capillary column DB-1 was used for products determinations.
Optical rotation was measured on a Perkin-Elmer 141 polarimeter.

N-Benzylidenmethylamine-N-oxide
(General procedure for synthesis of nitrones). To a warm (40°C) solution containing 68 mg of PCWP (0.03 mmoles) in 5 mL of chloroform was added a solution containing 360 mg of N-methylbenzylamine (3.0 mmoles) in 5 mL of chloroform, and 1.8 mL of H_2O_2 35% (20 mmoles).
After the addition was complete, the mixture was stirred for an additional 45 min at 40°C, then the organic layer was separated, washed with a 10% of aqueous solution of sodium bisulphite and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure to leave behind a thick oil, which was subjected to silica gel chromatography using a 30% ethyl acetate-cyclohexane mixture as eluent.
The first eluted fraction gave 124 mg of benzaldoxime. Mass spectrum (E.I. 70 eV): m/z 121 (M^+, 95), 103 (base peak). Further elution gave 142 mg of pure nitrone as white needles m.p. 85°C (lit.[36] m.p. 81-82°C).^{1}H NMR: δ ($CDCl_3$) 3.68 (s, 3H, N-CH_3), 7.36-7.46 (m, 3H, aromatic protons), 7.52 (s, 1H, CH=N), 8.24-8.34 (m, 2H, aromatic protons). Mass spectrum (E.I., 70 eV): m/z 135 (M^+, 100), 119 (30). Benzaldehyde (20 mg) was identified by GC/MS from crude reaction and determined by GLC analysis.[37]
N-benzylideneisopropylamine-N-oxide[37]
N-isopropylbenzylamine (445 mg, 3.0 mmoles) was oxidized according to the general procedure. Removal of the solvent gave 480 mg of nitrone. ^{1}H NMR: δ ($CDCl_3$) 1.38 (d, 6H, CH_3, J= 6.5 Hz), 4.38 (hept , 1H, CH-N, J= 6.5 Hz), 7.35-7.46 (m, 3H, aromatic protons), 7.56 (s, 1H, CH=N), 8.24-

8.36 (m, 2H, aromatic protons). Mass spectrum (E.I., 70 eV): m/z 163 (M^+, 100), 147 (5), 120(8), 104(20).

Benzaldehyde (6 mg) was identified by GC/MS from crude reaction and determined by GLC analysis.

N-Benzylidene-tert-butylamine-N-oxide[8,23]

Oxidation of 500 mg of N-tert-butylbenzylamine (3.0 mmoles) gave 270 mg of pure nitrone. ^{1}H NMR: δ ($CDCl_3$) 1.60 (s, 9H, CH_3), 7.29-7.48 (m, 3H, aromatic protons), 7.52 (s, 1H, CH=N), 8.09-8.40 (m, 2H, aromatic protons).Mass spectrum (E.I. 70 eV): m/z 177 (M^+, 15), 146 (5), 125(16), 78(7), 57(100).

N-Benzylidenbenzylamine-N-oxide[8,23]

700 mg of N-dibenzylamine(3.5 mmoles) was oxidized by the general procedure. Removal of the solvent after reaction gave 510 mg of nitrone, 64 mg of benzaldehyde and 24 mg of benzaldoxime. Nitrone: ^{1}H NMR: δ ($CDCl_3$) 5.02 (s, 2H, $PhCH_2$), 7.30-7.55 (m, 9H, aromatic protons and CH=N), 8.10-8.32 (m, 2H, aromatic protons).

N-(1-methylethylidene)-1-methylethylamine-N-oxide[8]

Oxidation of 302 mg of diisopropylamine (3.0 mmoles) gave 175 mg of pure nitrone. ^{1}H NMR: δ ($CDCl_3$) 1.39(d, 6H, CH_3, J= 6.5 Hz), 2.18 (s, 6H, $N=C(CH_3)_2$), 4.45 (hept, 1H, CH-N, J= 6.5 Hz).

N-Benzylidenphenylamine-N-oxide

Oxidation of 638 mg of N-phenyl-N-benzylamine (3.5 mmoles) gave 14 mg of nitrone, 38 mg of N-benzylidenphenylimine, 26 mg of benzoic acid, 171 mg of benzaldehyde, 64 mg of nitrosobenzene and 47 mg of nitrobenzene. All compounds were identified by GC/MS from the crude reaction and determined by GLC analysis.

1-Pyrrolin-N-oxide[8]

(General procedure for synthesis of cyclic nitrones)

To a cold (0°C), magnetically stirred solution of 213 mg of pyrrolidine (3.0 mmoles) in 5 mL of chloroform was added a solution of 5 mL of PCWP (68 mg) and 0.6 mL of H_2O_2 (35%, 6.9 mmoles) in 5 min. After the addition was complete, the mixture was stirred for 1h, then flash chromatographied over silica gel. Elution with 30% ethylacetate-cyclohexane mixture gave 128 mg of the nitrone. ^{1}H NMR (200 Mz) : δ ($CDCl_3$) 2.20-2.32 (m, 2H, CH_2), 2.70-2.81 (m, 2H, CH_2), 3.91-4.00 (m, 2H, CH_2), 6.87-6.93 (m, 1H, CH=N). Mass spectrum (E.I., 70 eV): m/z 85 (M^+, 100), 55(47).

2,3,4,5-Tetrahydropyridine-N-oxide[8]

The general procedure was used with 256 mg of piperidine (3.0 mmoles) and 131 mg of nitrone were obtained. ^{1}H NMR (200 Mz): δ ($CDCl_3$) 1.6-1.8 (m, 2H, $-CH_2-$), 1.9-2.1 (m, 2H, $-CH_2-$), 2.4-2.5 (m, 2H, $-CH_2C=$), 3.75-3.85 (m, 2H, $-CH_2N-$), 7.15-7.25 (m, 1H, -CH=N-). Mass spectrum (E.I., 70 eV): m/z 99 (M^+, 100), 83 (10), 55 (23), 41 (28).

3,4-Dihydroisoquinoline-N-oxide[8]

Oxidation of 400 mg of 1,2,3,4-tetrahydroisoquinoline (3.0 mmoles) gave 280 mg of pure nitrone. ^{1}H NMR (200 Mz): δ ($CDCl_3$) 3.18 (t, 2H, $ArCH_2$, J= 7.8 Hz), 4.11 (dt, 2H, CH_2N, J= 1.1 and 7.8 Hz), 7.10-7.31 (m, 5H, aromatic protons), 7.71 (m, 1H, CH=N). Mass spectrum (E.I., 70 eV): m/z 147 (M^+, 88), 129 (100), 103 (38), 91(50), 77(46), 51(47).

(S)-(+)-C-phenyl-N-α-phenylethylnitrone[38]

Oxidation of 740 mg of (S)-(-)-N-benzyl-α-phenylethylamine[39] (3.5 mmol) gave 670 mg of pure nitrone. ^{1}H NMR: δ (CDCl3) 1.51 (d, 3H, CH_3, J=6.60 Hz), 5.19 (q, 1H, CH, J=6.60 Hz), 7.43-7.68 (m,

9H, aromatic protons and CH=N), 8.18-8.43 (m, 2H, aromatic protons). $[a]^{20}_{578}$ (c1, CH_2Cl_2) +83.6. Anal. Calcd for $C_{15}H_{15}NO$: C, 80.00; H, 6.66; N, 6.20%. Found: C, 79.89; H, 6.64; N, 6.15%.

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