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HYDROPEROXIDE OXIDATION OF SOME NITROGEN-CONTAINING COMPOUNDS CATALYSED BY METALS

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We have established that the tert-amyl hydroperoxide (HPTA) oxidation of Schiff bases in the presence of $MoCl_5$ or $Mo(CO)_6$ leads to oxaziridine formation. In benzene solution the reaction proceeds rapidly and oxaziridine yields are as a rule high (see table 1). The procedure for obtaining oxaziridines is preparatively more convenient than peracid oxidation (1).

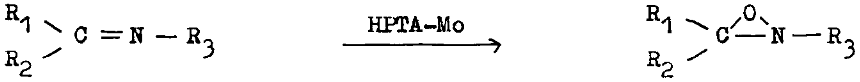
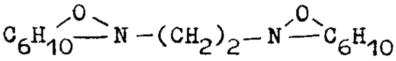


Table 1

Oxaziridines		b.p.°/mm (m.p.)	n_D^{20}	Yields %
$R_1=H;\ R_2=CH_3$	$R_3=C_6H_{11}$	40-41/0.5	1.4580	95
$R_1=R_2=CH_3$		78-79/8	1.4500	85
$R_1, R_2 = C_5H_{10}$		95-96/0.3	1.4930	90
$R_1, R_2 = C_5H_{10};\ R_3=C_6H_5$		(77-78)	---	92
$R_1=H;\ R_2=CH_3;\ R_3=C_6H_5CH_2$		95-96/1	1.5030	80
 $C_6H_{10}\overset{O}{—}N-(CH_2)_2-N\overset{O}{—}C_6H_{10}$		(105-107)	---	66

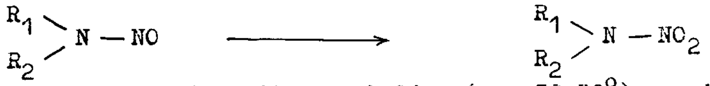
It is known that various peracids are used to obtain N-oxides of aromatic nitrogen-containing heterocycles. We have succeeded in persuading the reagent HPTA-$MoCl_5$ to react readily with various bases and give very high yields of N-oxides (see table 2). This method is superior to the peracid route, since oxidation proceeds more rapidly and N-oxide yields are higher.

Table 2

N-oxides	m.p. (b.p./mm Hg)	Yield %
Pyridine	65-67	100
2-picoline	(123-124/15)	100
3-picoline	33-35	100
2,4,6-collidine	(105/5)	95
4,4-bipyridyl (dioxide)	305-306	80
2-phenylpyridine	155-155.5	90
methyl nicotinate	95-100	90
4-acetamidopyridine	266-267	40
2,6-dimethyl-3,5-dicarbethoxypyridine	108-110	90
quinoline	61-62	100
2-methylquinoline (hydrate)	77-78	95-100
methyl quinaldinate	89-90	90
benzo(f)quinoline	128-130	95-100
acridine	168.5-169	100
phenazine (dioxide)	202-203	90
2,3,5,6-tetramethylpyrazine (dioxide)	220-222	80
papaverine	168-170	70

The method has however some limitations, thus 2,2'-bipyridyl and o-phenanthroline are not oxidized at all.

Emmons showed (2) that for the oxidation of nitrosamines to nitramines a strong oxidizer is required such as trifluoroperacetic acid. We have established that in the prolonged oxidation of nitrosamines with reagent HPTA-$MoCl_5$ nitramine yields reach 80 per cent.



$$R_1R_2N-NO \longrightarrow R_1R_2N-NO_2$$

Thus from nitrosomorpholine nitromorpholine (m.p.52-53°) was isolated and nitrosodimethylamine and nitrosopiperidine were converted into N-nitrodimethylamine (m.p.54-55°) and N-nitropiperidine (m.p.-5-6°) respectively.

References.

1. E.Schmitz, "Dreiringe mit zwei Heteroatomen", Springer-Verlag, 1967.

2. W.Emmons, J.Am.Chem.Soc., 76, 3468 (1954).