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Oxidation of Organonitrogen Compounds by the Methyltrioxorhenium-Hydrogen Peroxide System

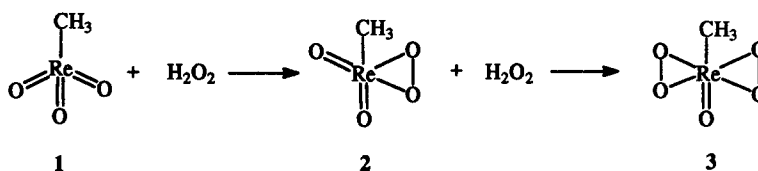
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Abstract: Methyltrioxorhenium catalyzes the reaction of hydrogen peroxide with organonitrogen compounds. The reactions are facile and high yield at room temperature or below. The observed chemistry is similar to that previously described by us using dimethyldioxirane as the oxidant.



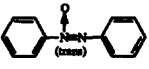
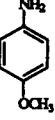
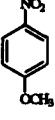
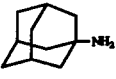
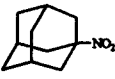
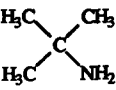
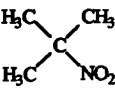
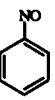
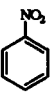
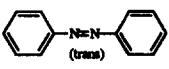
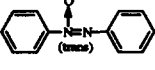
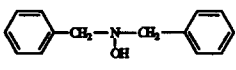
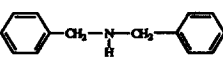
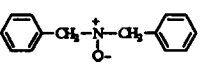


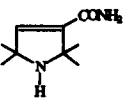
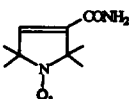
We have recently described¹ C-H insertion reactions of hydrogen peroxide catalyzed by methyltrioxorhenium **1**. The system 1/H₂O₂ had previously been reported to epoxidize unsaturated compounds², to oxidize phosphines, arsines and stibines³, arenes⁴, sulfur compounds^{5,6} and benzaldehyde.⁷ The chemistry of the 1/H₂O₂ system is reminiscent of the work of ourselves and others in dioxirane chemistry.⁸ This comparison has led us to study the reactions of the 1/H₂O₂ system with a variety of organic nitrogen compounds (Table 1). Work by Herrmann⁹ and Espenson¹⁰ has shown that **1** forms two adducts with H₂O₂, **2** and **3** (Scheme 1), both of which would be expected to undergo rapid reaction with nucleophilic nitrogen.



Scheme 1

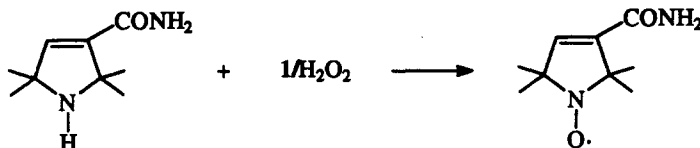
As shown in the Table the reaction proceeds smoothly and in generally high yield with the nitrogen compounds used.¹¹ The products almost exactly parallel those obtained in the corresponding dioxirane reactions.¹²⁻¹⁶ Thus both aromatic and aliphatic amines are oxidized to the corresponding nitro compounds (entries 1-4). The azoxybenzene obtained as a by product in the aniline oxidation results from oxidation of azobenzene as shown in a separate experiment (entry 6). Azobenzene is produced by reaction of aniline with nitrosobenzene which is an intermediate to nitrobenzene (entry 5).¹³ The secondary amine, dibenzylamine, is oxidized primarily to the corresponding hydroxylamine accompanied by a small amount of the nitron further oxidation product (entry 7). The tertiary amine, pyridine, is readily converted to its N-oxide (entry 8). Finally the pyrrolidine, 2,2,5,5-tetramethyl-pyrrolidine-3-carboxamide (entry 9) is rapidly converted to the nitroxide in quantitative yield¹⁷ (Scheme 2). This particular oxidation is especially significant since the synthesis of

Table 1. Oxidation of Amines with H₂O₂-Methyltrioxorhenium^a

Entry	Amines	Reaction Time (h)	Conditions Temp (°C)	Product	% Yield ^b
1		2	RT		70
					30
2		1	RT		100
3		2	60		88
4		2	RT		100
5		½	RT		100
6		3	RT		100
					80
7 ^c		¼	0		10
8 ^d		1	RT		100
9 ^e		1	0		100

a = Reactants in a molecular ratio of amine/hydrogen peroxide/MTO (12.5:312.5:1); Products were identified by comparing Gas Chromatographic properties with those of the authentic samples. b = GLC internal standard. c = Amine/hydrogen peroxide/MTO (166/33/1), MTO was added drop by drop; d = (62.5/312.5/1); e = (25/1250/1), MTO was added drop by drop.

nitroxides by standard literature methods¹⁸ is difficult with only the dioxirane method being comparable to the one described here.



Scheme 2

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11. In a typical reaction methyltrioxorhenium (0.02 g, 0.08 mmol) was added to a solution (3 mL) of H₂O₂ (25 mmol) in ethanol. This solution was then added to the amine substrate (1 mmol). The oxidation solution was prepared as described earlier¹. After stirring for the appropriate time (Table 1) water (20 mL) was added to the reaction mixture. The reaction was then extracted with CH₂Cl₂. Analyses of these solutions indicated that the reactions were very clean and contained products as shown in the Table. A

control reaction with pyridine indicated that no oxide product is formed in the absence of the catalyst in the reaction time shown.

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17. The nitroxide was identical to a sample prepared by the dioxirane route .¹⁴In particular it had the same ESR spectrum as the authentic sample.
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