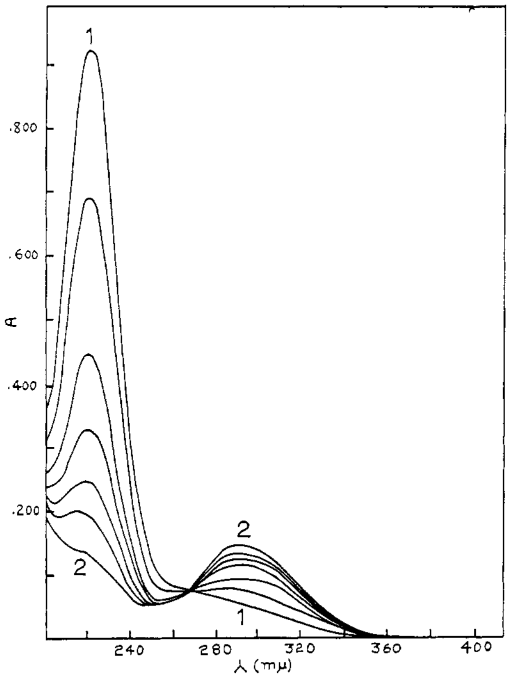

Figure 1. Change of absorption spectrum of $Ru(NH_3)_5N_2^{2+}$ during irradiation with uv light: curve 1, before irradiation; curve 2, after irradiation for 25 min; intermediate curves, approximately 4-min intervals of irradiation, beginning with curve 1. $[Ru(NH_3)_5N_2^{2+}] = 7.16 \times 10^{-4}$ *M*, in H_2O deaerated with He.

reported that the bound nitrogen in $Ru(NH_3)_5N_2^{2+}$ could be reduced by sodium borohydride,[2] but more recent work indicates this does not occur.[5]

During the course of an investigation of the chemistry of this ion in our laboratory, it was observed that the characteristic absorption peak at 221 mμ[3] of anaerobic solutions of the ion stored in quartz cells decreased significantly when kept in the light. Following this lead, we exposed a solution of $Ru(NH_3)_5N_2^{2+}$ that had been deoxygenated with He to uv light from a mercury lamp and found that the 221-mμ absorption disappeared completely and the absorption characteristic of an Ru(III) species appeared after a short period of irradiation (15 min–3 hr, depending on concentration and light intensity) (Figure 1). Since a period of 1–2 min occurred between the time the solutions were removed from the light and the recording of the spectra, a fast dark reaction is possible. This is unlikely, however, since no further change in the spectra was observed after standing in the dark for 1 hr. Solutions in which appreciable amounts of the dimer, $Ru(NH_3)_5N_2Ru(NH_3)_5^{4+}$, prepared by passing N_2 through a solution of $Ru(NH_3)_5H_2O^{2+}$ as described by Taube,[4] were present behaved similarly, with the 262-mμ absorption of the dimer disappearing. Solutions kept in the dark for this same period showed no change.

Further studies revealed that the photochemical oxidation proceeds equally well in acidic, neutral, or basic solutions. In HCl, $Ru(NH_3)_5Cl^{2+}$, identified by its absorption maximum at 330 mμ,[6] is the product, while in basic solution containing excess NH_3, $Ru(NH_3)_6^{3+}$, λ_{max} 280 mμ,[6] is formed. In neutral solutions, $Ru(NH_3)_5OH^{2+}$, absorbing at 290 mμ,[7] is formed (Figure 1). When the photolyzed solutions are treated with amalgamated Zn in dilute H_2SO_4, the Ru(III) species is reduced as indicated by the disappearance of its characteristic absorbance. By passing N_2 through the reduced solution, both $Ru(NH_3)_5N_2^{2+}$ and the dimer, $(Ru(NH_3)_5)_2N_2^{4+}$, are formed, again identified by their absorbance at 221 and 262 mμ, respectively.

The identification of the reduction product is clearly of the greatest importance. Since it is known that some Ru(II) species reduce H_2O,[8] it seemed probable that H_2 is the product. Repeated experiments under widely different conditions, however, showed only the presence of N_2 and a small amount of O_2 in the gas above the solution, as determined by mass spectrometric analysis.

As H_2 is absent, it is quite possible that the bound N_2 is reduced, since no other reducible species is present. Qualitative tests of the photolyzed solution for NH_2NH_2[9] and NH_2OH[10] were negative. In order to determine if NH_3 is produced, work is underway to synthesize and photolyze $Ru(NH_3)_5N_2^{2+}$ containing N^{15}. If the N^{15} appears in the NH_3 after photolysis then reduction of the bound N_2 will be confirmed.

The $Ru(NH_3)_5N_2Cl_2$ and $Ru(NH_3)_5N_2(BF_4)_2$ used in this work were prepared from $Ru(NH_3)_6Cl_3$ (Matthey Bishop and Co.) and NaN_3 using the procedure of Allen, *et al.*[2] The gas analysis was performed using an EAI quadrupole mass spectrometer, Model 200, and a Perkin-Elmer Hitachi RMU-GE mass spectrometer. Solutions were irradiated with a 125-W Hanovia low-pressure mercury lamp, or a 500-W Hanovia high-pressure mercury arc, depending on concentration.

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The Metal Ion Catalyzed Peroxide Oxidation of Organic Substrates. A Selective Synthesis of Imides

Sir:

The metal ion catalyzed decomposition of organic hydroperoxides and peroxyacids has been long known.[1,2] Recently there have been several reports on the oxidation of primary amines to oximes,[3] tertiary amines to amine oxides,[4–7] sulfides to sulfoxides,[8,9] and

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Table I. Peracetic Acid–Mn(acac)$_3$ Oxidation of Amides and Lactams

Starting Material	Product	% yield[a]
2-Pyrrolidone	Succinimide	90
N-Methyl-2-pyrrolidone	N-Methylsuccinimide	55
2-Piperidone	Glutarimide	72
3-Carbethoxy-2-piperidone	3-Carbethoxyglutarimide	70
N-Formylpiperidine	N-Formyl-2-piperidone	Low
ε-Caprolactam	Adipimide	40
Ethylacetamide	Diacetimide	59

[a] All yields reported are those actually obtained by isolation and purification, either by distillation or recrystallization. Glpc analysis in most cases indicated complete conversion to product.

Table II. Peroxide–Mn(acac)$_3$ Oxidation of other Substrates

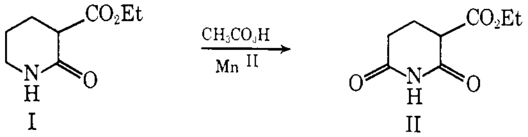
Starting material	Peroxide	Reaction time, hr	Product	Yield,[a] %
Diphenylmethane	CH_3CO_3H	16	Benzophenone	48
Cyclohexanol	*t*-BuOOH[b]	168	Cyclohexanone	16
Acetoin	*t*-BuOOH	360	Acetic anhydride	High
Adipoin	*t*-BuOOH	360	Adipic acid	41
Dimethyl sulfide	CH_3CO_3H	1	Dimethyl sulfone	100
Dimethyl sulfide	*t*-BuOOH	1	Dimethyl sulfoxide	90
Dimethyl sulfoxide	CH_3CO_3H	1	Dimethyl sulfone	100
Benzylmethyl sulfide	CH_3CO_3H	1	Benzylmethyl sulfoxide + Benzylmethyl sulfone	76 10

[a] All yields reported are those actually obtained by isolation and purification. [b] All *t*-butyl hydroperoxide reactions run at ambient temperatures.

sulfoxides to sulfones[8,9] with peroxides in the presence of catalytic amounts of transition metal ions. The autoxidation of amides to imides with air and transition metal ions has been reported, although the yields are quite low.[10–13] The oxidation of amides to imides with equimolar amounts of ruthenium tetroxide[14] or persulfate[15] is also known.

We now wish to report that amides are selectively oxidized to imides in good yield by hydroperoxides or peroxy acids in the presence of trace amounts of transition metal ions such as Co(II), Mn(II), or Mn(III). For example, using either *t*-butyl hydroperoxide or peracetic acid, ε-caprolactam was oxidized in greater than 40% yield to adipimide, a compound previously prepared in only poor yield.[16–19] The oxidation of other amides gave quite good yields of the corresponding imides as shown in Table I. The high degree of selectivity of this reaction is exemplified by the transformation of 3-carbethoxy-2-piperidone (I) to the corresponding imide (II), the only oxidation product isolated.

In a typical reaction procedure a solution of manganic acetylacetonate[20] (50 mg) and 2-piperidone (9.9 g, 0.1 mol) in ethyl acetate (50 ml) was cooled to −10°. Peracetic acid (24 g, 0.2 mol, 25% solution in ethyl acetate[21]) was added dropwise, maintaining a temperature of −10°. After the addition of peracetic acid was completed the reaction mixture was allowed to stir until a peroxide test was negative[22] (usually overnight) then filtered to remove spent catalyst. Solvent was removed under reduced pressure. Recrystallization from 2-propanol gave a white, crystalline product identical with an authentic sample of glutarimide (ir, nmr, mixture melting point).



I II

The procedure outlined for the oxidation of 2-piperidone can also be of use synthetically to oxidize aromatic hydrocarbons, alcohols, ketones, sulfides, and sulfoxides (see Table II). The scope of this novel, mild oxidation procedure and some observations regarding its mechanism will be reported in full elsewhere.

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