

tetraphenylporphyrin iron(III) (TPPFeCl) or chloro-tetraphenylporphyrin manganese(III) (TPPMnCl).

In a typical experiment, TPPMnCl (0.015 mmol) was added to a solution of **1a** (0.076 mmol) in benzene (10 ml), and the solution was refluxed for 14 h. Oxaziridines **1a-d** were rearranged smoothly to the corresponding amides **2a-d** in good yields. Similar results were obtained with the reactions under nitrogen. The control experiment without metalloporphyrins showed no thermal formation of amides **2**. As shown in Table II, TPPMnCl was a much better catalyst than TPPFeCl and the reactions with **1a-d** gave **2** in satisfactory yields. Although such conditions were less effective than the more common oxaziridines **1e-g** owing to their thermo-instability, the change of the reaction solvent from benzene to CH₃CN (i.e., the use of TPPMnCl/CH₃CN system) could shorten the reaction time and improve the yields of these amides (Table III). The rearrangements are also catalyzed efficiently

Table II. Metalloporphyrin-Promoted Rearrangement of **1** in Benzene^{a)}

Compd	Yield of 2 (%) ^{b)}	
	TPPFeCl	TPPMnCl
1a	95(89)	99
1b	90	90
1c	85	99
1d	82	88

a) Reactions were performed under reflux. Molar ratio of [1]:[metalloporphyrin] = 5:1. b) Determined by HPLC. c) Isolated yield.

Table III. TPPMnCl-Promoted Rearrangement of **1** in Acetonitrile

Compd	Molar ratio [1]:[TPPMnCl]	Condition		Yield of 2 (%) ^{a)}
		Temp(°C)	Time	
1a	10 : 1	Reflux	4	99
1b	10 : 1	Reflux	4	90
1c	10 : 1	Reflux	4	95
1d	10 : 1	Reflux	4	92
1e	5 : 1	50	18	85 ^{b)}
1f	5 : 1	50	18	90
1g	5 : 1	40	10	76 ^{b)}

a) Isolated yields. b) p-Nitrobenzaldehyde was also obtained as by-product.

by other porphyrins with high-valent metal ions but seems to be influenced by the basicity of the axial ligand of the catalyst. For example, the reaction of **1a** with pyridine-tetraphenylporphyrin iron(III) in CH₃CN gave amide **2a** (90%) with a trace of p-nitrobenzaldehyde. However, in the same reaction with pyridine-tetraphenylporphyrin iron(II),⁴⁾ the yield of **2a** decreased (24%) and the main product was p-nitrobenzaldehyde (61%). The formation of p-nitrobenzaldehyde can be explained by the pyridine-catalyzed eliminative ring cleavage of the oxaziridine.⁵⁾ Consequently, TPPMnCl/CH₃CN is the most useful catalytic system for the oxaziridine-amide rearrangement of 2-alkyloxaziridines. In the reaction of **1d** (Table III), the proton on the C-3 position shifted in preference to the migration of the isopropyl group on the same carbon to the adjacent nitrogen. This, combined with the aforementioned results, indicates that the rearrangement proceeds by an ionic mechanism involving heterolytic cleavage of the N-O bond after the coordination of the high-valent metal ions to the oxygen atom of oxaziridines and eliminates the possibility of a radical mechanism.^{1b)}

We next applied the present oxaziridine-amide rearrangement to a peptide bond formation. Oxaziridine **3**^{2a)} (1.8 mmol) was treated with TPPMnCl (0.15 mmol) in CH₃CN (50 ml) at 50 °C for 12 h. After chromatography an aspartame precursor, **4**, was isolated in 82% yield without any decrease in the optical purity.⁶⁾ The present method is superior to

REFERENCES AND NOTES

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