

Letter

Olefin Epoxidation by Manganese(III)-Porphyrin Complexes:
Effect of Pyridine on Stereoselectivity

ALEXANDER W. VAN DER MADE and ROELAND J. M. NOLTE*

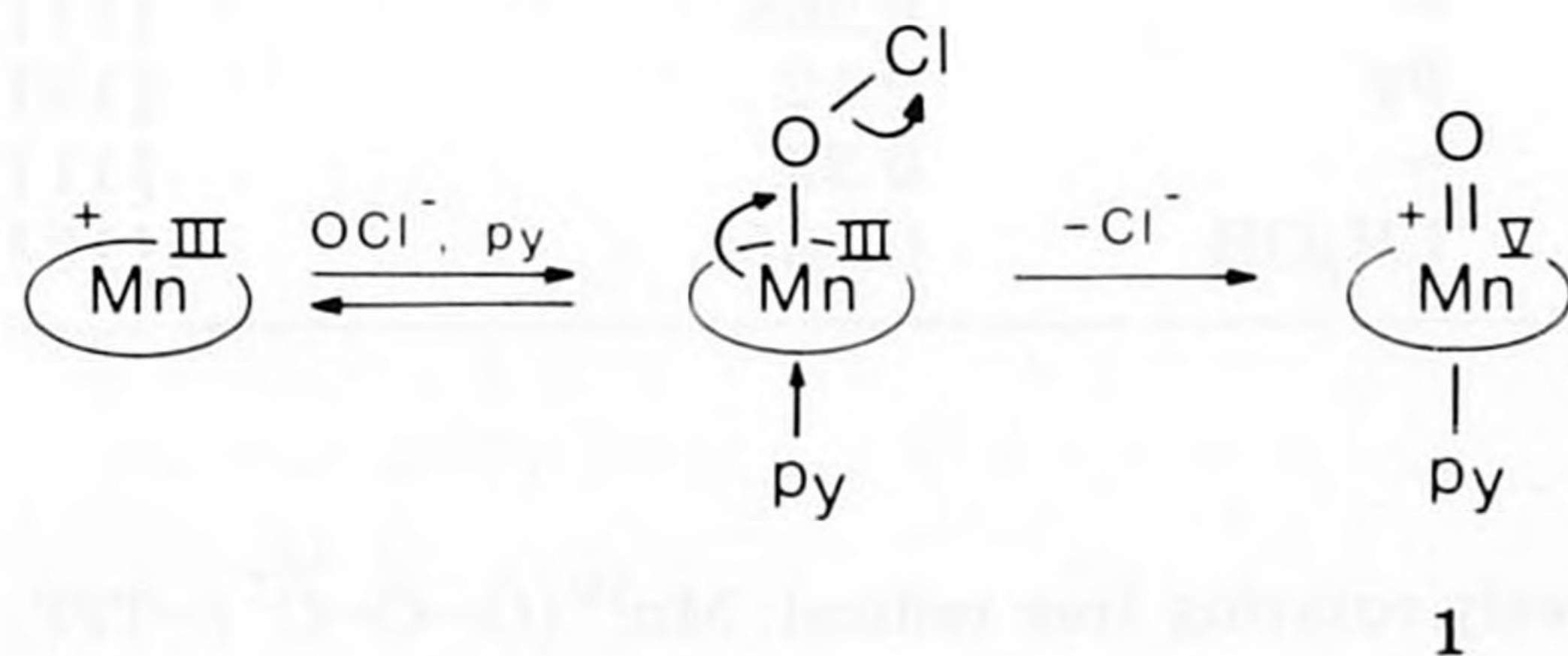
Laboratory of Organic Chemistry, University at Utrecht, Croesestraat 79, 3522 AD Utrecht (The Netherlands)

(Received April 24, 1984; accepted May 16, 1984)

Metalloporphyrin complexes are currently receiving much attention because of their ability to oxidize hydrocarbons under mild conditions [1 - 3]. Of special interest and of potential practical value is a recently developed system that consists of (tetraphenylporphinato)manganese(III) acetate ($\text{Mn}^{\text{III}}\text{-TPP}$) as catalyst, sodium hypochlorite as oxidizing agent and pyridine as co-catalyst [4, 5]. This system epoxidizes non-activated olefins with high efficiency and high selectivity. Pyridine increases both the activity and the stereoselectivity of the catalyst. For example, in the epoxidation of styrene, addition of 20 equiv of pyridine per $\text{Mn}^{\text{III}}\text{-TPP}$ reduces the reaction time by a factor of 10, while the amount of *cis*-epoxide from *cis*-stilbene increases from 35 to $\approx 100\%$ [4].

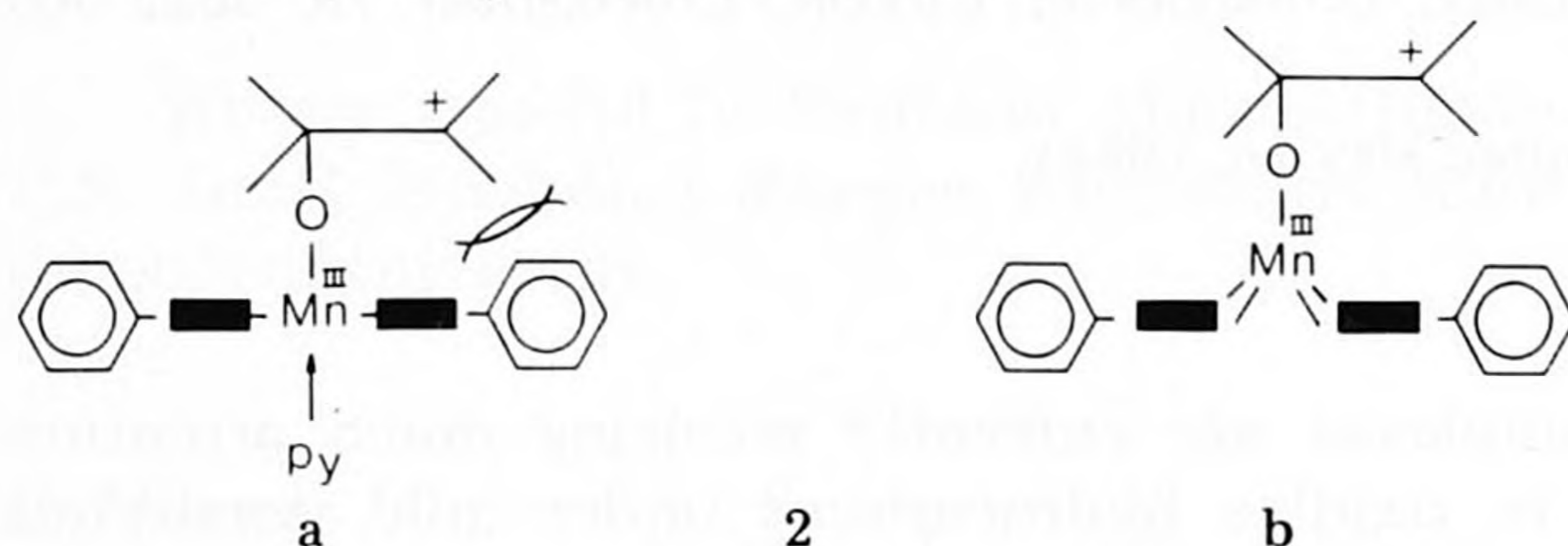
The activity-increasing effect of pyridine has been rationalized in terms of its electron donating property, which facilitates the formation of the catalytically active species (*vide infra*) [5, 6]. However, the effect of pyridine on the stereoselectivity of the reaction is not yet understood. In this communication we give an interpretation.

There is ample evidence [7, 8] that the active species in the epoxidation of olefins by $\text{Mn}^{\text{III}}\text{-TPP}$ and NaOCl is a formal oxomanganese(V)-porphyrin, $\text{Mn}^{\text{V}}(\text{=O})\text{-TPP}$ (1). This species is formed in the rate-determining step, in which a chloride ion is eliminated. The elimination of this nucleophilic particle is facilitated by the electron-donating pyridine [6].



*Author to whom correspondence should be addressed.

Species 1 (with or without coordinated pyridine) may add to the double bond of an olefin in a concerted or stepwise process [9]. The latter process is the most likely, because of the loss of stereochemistry that is observed when no pyridine is present [4]. In the intermediate that is formed, carbocation (or carbon radical*) 2, rotation may occur around the carbon-carbon bond of the substrate molecule. Steric interactions with the porphyrin ring may prevent this rotation**. These interactions will depend on the position of the manganese atom, *i.e.* in the plane of the porphyrin ligand (2a) or outside this plane (2b). Thus, in situation 2a stereochemistry can more effectively be maintained than in 2b.



In Table 1 we have collected from the literature X-ray data of manganese-porphyrin complexes that are relevant to our problem. No oxomanganese(V)-porphyrin complex has been structurally characterized. However, the complex nitrido[tetrakis(*p*-methoxyphenyl)porphinato]manganese(V), $\text{NMn}^{\text{V}}\text{-TpMPP}$, is known. In this complex the manganese atom is 0.388 Å out of the porphyrin plane, which is an impressively large displacement. Also, in the complexes $\text{N}_3\text{Mn}^{\text{III}}\text{-TPP}$ and $\text{ClMn}^{\text{III}}\text{-TPP}$ the displacement of the manganese atom is large, *i.e.* 0.23 and 0.265 Å, respectively. However, when in these complexes an axial ligand such as pyridine or methanol is present, the displacement is considerably reduced. These data are in line with

TABLE 1

Out-of-plane displacement of the manganese atom in the direction of ligand L^1 in some manganese-porphyrin complexes, $\text{L}^1\text{L}^2\text{Mn-TPP}$

Complex	L^1	L^2	Displacement (Å)	Ref.
$\text{NMn}^{\text{V}}\text{-TpMPP}$	N	—	0.388	[10]
$\text{ClMn}^{\text{III}}\text{-TPP}$	Cl	—	0.265	[11]
$\text{Cl(Py)Mn}^{\text{III}}\text{-TPP}$	Cl	Py	0.12	[12]
$\text{N}_3\text{Mn}^{\text{III}}\text{-TPP}$	N_3	—	0.23	[11]
$\text{N}_3(\text{CH}_3\text{OH})\text{Mn}^{\text{III}}\text{-TPP}$	N_3	CH_3OH	0.085	[13]

*The intermediate may also be a freely-rotating free radical: $\text{Mn}^{\text{IV}}(\text{O}-\overset{\vee}{\text{C}}-\overset{\vee}{\text{C}}^{\bullet})\text{-TPP}$; compare ref. 7.

**Groves has recently observed that substituents at the *ortho* position of the phenyl rings of $\text{Mn}^{\text{III}}\text{-TPP}$ increase the stereoselectivity of *cis*-stilbene epoxidation; see ref. 7.

our interpretation. Thus, pyridine is likely to increase the steric interactions in the addition intermediate **2** and consequently, the stereoselectivity of the reaction.

Acknowledgement

We thank Prof. W. Drenth for valuable discussions.

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