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A NEW CATALYTIC ROUTE FOR THE EPOXIDATION OF STYRENE WITH SODIUM HYPOCHLORITE ACTIVATED BY TRANSITION METAL COMPLEXES

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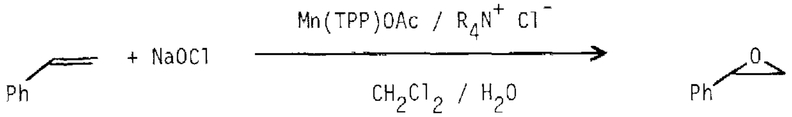
Summary : Preliminary results on the transition metal catalyzed epoxidation of styrene and cyclohexene with sodium hypochlorite solution and phase-transfer reagent are described.

The recent report of a mild oxidation of benzyl alcohol to benzaldehyde[1] prompts us to present here our own results on the epoxidation of styrene with sodium hypochlorite catalyzed by transition metal complexes. To our knowledge this new route is presumably the first one using a catalytic activation of sodium hypochlorite. Non-catalytic epoxidations have been obtained with sodium hypochlorite and unsaturated ketones[2] or polycyclic aromatic hydrocarbons[3].

In this communication the epoxidation of styrene is performed under mild conditions by treating an organic solution of the starting material with an aqueous sodium hypochlorite solution in the presence of a phase-transfer reagent and an organometallic complex.



The results (see table 1) have been obtained according to the following procedure : to 0.025 mmol of catalyst and 0.05 mmol of benzyldimethyltetradecylammonium chloride were added 10 m of dichloromethane and 1 mmol of olefin ; finally 5 mL of 0.35 M aqueous sodium hypochlorite solution (pH = 12) were added and the mixture stirred at room temperature.

Styrene is readily oxidized in the presence of the tetraphenylporphine or Schiff bases complexes, whereas only traces of oxidation are detectable without catalyst. It is surprising that $VO(Acac)_2$ (an efficient catalyst for epoxidation with alkyl hydroperoxides) has no catalyti activity in this reaction.

The similar yield of styrene oxide obtained with Mn(TPP)OAc under air or nitrogen suggests that the oxygen atom of the epoxide probably arises from the hypochlorite rather than from the molecular oxygen. Preliminary results with cyclohexene indicate a conversion of 70 % and a yield in cyclohexene oxide of 15 % after 3 hours reaction with Mn(TPP)OAc as catalyst in the same conditions as with styrene. No traces of cyclohexanone were observed in this reaction.

Table 1. Oxidation of styrene with sodium hypochlorite catalyzed by transition metal complexes.

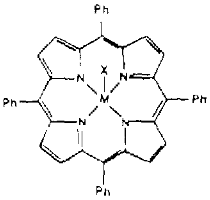
Complexes	Reaction time (hours)		
	1	2	3
Mn(TPP)OAc	68^{a} (28)^{b}	75 (34)	80 (36)^{c}
Fe(TPP)Cl	18 (2)	28 (2)	33 (2)
Co(TPP)Br	42 (6)	53 (6)	53 (6)
Schiff bases complexes^{d}	-	-	17 - 38 (0-8)

[a] *Conversion of styrene in % into various oxidation products.*

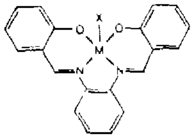
[b] *The yield of epoxide with respect to the starting material is indicated in parentheses (%).*

[c] *For the same reaction run under an inert atmosphere (nitrogen) the conversion in 76 % and the epoxide yield 40 % after 3 hours.*

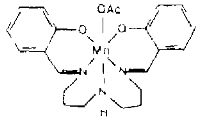
[d] *Complexes used : Mn(Saldpr)OAc, Mn(Saloph)Br, Mn(Saloph)OAc, Co(Saloph)O_2 (abbreviations according to Basolo et al. 4).*



M(TPP)X



M(saloph)X



Mn(saldpr)OAc

Further work is in progress to apply this epoxidation route to other substrates.

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