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Nickel-Catalyzed Epoxidation of Olefins with NaOCl

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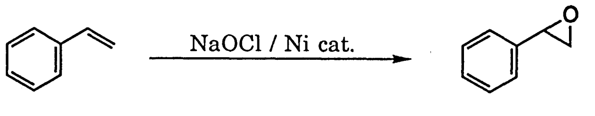
Synopsis. Nickel complexes of bidentate heterocyclic amines such as 2,2′-bipyridine and 1,10-phenanthroline have been found to be active catalysts for the epoxidation of olefins with hypochlorite as terminal oxidant. Nickel complex of 1-methylimidazole which is monodentate ligand also indicated epoxidation ability.

The development of inexpensive systems for the direct epoxidation of olefins is one of the most important theme both industrial and academic field of synthetic chemistry,[1] because epoxides are important intermediates of variety of useful products. And the design of convenient catalytic systems using simple metal complexes with inexpensive oxygen donors such as H_2O_2, *t*-BuOOH and NaOCl as terminal oxidant is current interest.[2] Epoxidation of olefins was extensively investigated in relation to the enzymatic oxygenation for the last decade with metal complex catalysts.[3] In these studies, manganese, iron, and chromium complexes of porphyrins and Schiff bases were chosen as catalysts. Recently, nickel complexes such as Ni(salen)[4] and Ni(cyclam) have been reported to act as catalysts for the epoxidation of olefins with NaOCl[5,6] and PhIO[7,8] as the terminal oxidants.[9] Here we report our results on the epoxidation of olefins catalyzed by nickel complexes of bidentate heterocyclic amine ligands such as 2,2′-bipyridine and 1,10-phenanthroline with NaOCl.



Results and Discussion

The results of the epoxidation of styrene by some nickel complexes of heterocyclic amines with NaOCl were summarized in Table 1. The epoxidation of styrene were performed typically by stirring the mixture of styrene, aqueous solution of nickel catalyst and NaOCl at room temperature. Styrene oxide was mainly obtained, and a considerable amount of benzoic acid was also produced. Among the bidentate ligands examined, 2,2′-bipyridine gave the best result on the selectivity of styrene oxide. $Ni(bpy)Cl_2$ and $Ni(bpy)_2Cl_2$ showed almost the same results (Run 3). Use of organic solvents such as CH_2Cl_2 and benzene in the epoxidation of styrene decreased the selectivity of epoxide (Run 2). Monodentate ligands such as 1-methylimidazole also indicated epoxidation ability but lowered the yield of the epoxide (Run 6).

Unlike the nickel complex catalyzed epoxidation reaction reported so far, the nickel complex described here is used as aqueous solution. Fine black precipitates which act as catalyst were appeared in a few minutes by the addition of NaOCl to the aqueous nickel complex solution. So the quaternary ammonium salts were not effective in this system as the phase-transfer catalysts.[5,6]

Table 2 showed the results of the epoxidation of styrene with various amount of $Ni(bpy)_2Cl_2$ catalyst. The best yield of styrene oxide was obtained when 2 mol% of $Ni(bpy)_2Cl_2$ was used (Run 3). The lower amount of catalyst decreased the selectivity of epoxide (Runs 4—7). On the other hand, the use of higher amount of catalyst did not increase the yield of epoxide (Runs 1, 2), and the conversion of styrene were lowered. When $Ni(bpy)_2Cl_2$ and NaOCl were mixed without styrene, NaOCl decomposed with evolution of gas. These results indicated that considerable amounts of NaOCl decomposed without the oxygen transfer to styrene, when large amount of nickel complex existed.

Epoxidations of other olefins were also investigated, and the results were summarized in Table 3. CH_2Cl_2

Table 1. Nickel Complexes-Catalyzed Epoxidation of Styrene with NaOCl[a)]

Run	$Ni(L)_nCl_2$	Conv./%[b)]	Yield/% Styrene[b)] oxide	Yield/% Benzoic[c)] acid
1	$Ni(bpy)_2Cl_2$	99	74	15
2	$Ni(bpy)_2Cl_2/CH_2Cl_2$	97	33	9
3	$Ni(bpy)Cl_2$	98	69	15
4	$Ni(dm\text{-}bpy)_2Cl_2$	99	54	30
5	$Ni(phen)_2Cl_2$	98	36	37
6	$Ni(Me\text{-}im)_4Cl_2$	85	19	27

a) 1.0 M NaOCl (12.5 mmol) was added to the mixture of styrene (5.0 mmol) and 0.050 M aq solution of catalyst (0.10 mmol), and the resulted mixture was stirred vigorously at room temperature for 5 h. b) Determined by GC. Yield based on styrene used. c) Isolated yield.

Table 2. $Ni(bpy)_2Cl_2$-Catalyzed Epoxidation of Styrene with NaOCl[a)]

Run	Cat./mol%	Conv./%[b)]	Turnover[c)]	Yield/% Styrene[b)] oxide	Yield/% Benzoic[d)] acid
1	10	89	9	49(55)	24(27)
2	5	95	19	68(72)	12(12)
3	2	99	50	74	15
4	1	95	95	61(64)	19(20)
5	0.5	72	144	44(61)	13(18)
6	0.2	60	300	18(30)	11(19)
7	0.1	59	590	12(20)	23(39)

a) 0.050 M $Ni(bpy)_2Cl_2$, 2.5 equiv 1.0 M NaOCl, for 5 h, at room temperature. b) Determined by GC. The numbers in parentheses are the yield based on consumed styrene. c) Turnover=consumed styrene/nickel catalyst. d) Isolated yield.

Table 3. $Ni(bpy)_2Cl_2$-Catalyzed Epoxidation of Olefins with NaOCl[a]

Run	Olefin	NaOCl/equiv	Solvent	Time/h	Conv.[b]/%	Yield/%	
						Epoxide[b]	Benzoic acid[c]
1	Styrene	2.5	—	5	99	74	15
2	α-Methylstyrene	5	—	6	100	53	15[d]
3	*trans*-β-Methylstyrene	3.5	—	2	100	28[e]	15
4	*cis*-β-Methylstyrene	4	—	4	100	25[f]	19
5	*trans*-Stilbene	10	CH_2Cl_2	6	100	34[c,e]	21
6	*cis*-Stilbene	2.5	CH_2Cl_2	5	100	31[c,e]	19
7	Cyclohexene	6	CH_2Cl_2	3	91	10	—
8	Norbornene	5	CH_2Cl_2	3	100	14[g]	—

a) 2 mol% 0.050 M $Ni(bpy)_2Cl_2$, 1.0 M NaOCl, at room temperature. b) Determined by GC. c) Isolated yeild. d) Acetophenone 12%. e) *trans*-Epoxide. f) 8% *cis*- And 17% *trans*-epoxide. g) *exo*-Epoxide.

was used as organic solvent in the epoxidation of *trans*-stilbene and norbornene which were solid at room temperature. The epoxidation of olefins were proceeded smoothly under the same reaction conditions with styrene oxide. But the yields of the epoxides were lower than the case of styrene. In the epoxidation of α-methylstyrene, epoxide was mainly obtained in 53% yield with acetophenone and benzoic acid in 12% and 15% yields respectively. The epoxide obtained by the oxidation of *trans*-β-methylstyrene was *trans*-epoxide only. On the other hand, both *trans*- and *cis*-epoxides were obtained in the epoxidation of *cis*-β-methylstyrene in 17% and 8% yields respectively. The epoxide obtained in the epoxidation of *trans*- and *cis*-stilbene were *trans*-stilbene oxide. These results show that this epoxidation is proceeded by radical process. Contrary to the case of styrene, in the epoxidation of cyclohexene and *cis*-stilbene, use of CH_2Cl_2 as organic solvent gave better selectivities of epoxides than the reaction without organic solvent.

Conclusion

The bidentate heterocyclic amines such as 2,2′-bipyridine and 1,10-phenanthroline are good ligands for nickel-catalyzed olefin epoxidation with NaOCl. Bipyridines were more readily available than porphyrin and Schiff base ligands, so the use of catalyst having bipyridine ligand must provide synthetically useful method for the epoxidation of olefins. Since the selectivity of epoxides by the system described above were not satisfactory, we are studying to improve the selectivity of epoxides.

Experimental

cis-β-Methylstyrene was prepared by the hydrogenation of 1-phenylpropyne.[10] Epoxides other than styrene oxide, cyclohexene oxide, and α-methylstyrene oxide used as GC standards were prepared by epoxidation of the corresponding alkenes with *m*-chloroperbenzoic acid under standard conditions.[11] The other olefins, epoxides, and amine ligands were commercially available, and purified by crystallization or distillation before use. NaOCl was obtained as aqueous solution (1.9—1.5 M) and titrated before use (1 M=1 mol dm^{-3}). The NiL_nCl_2 catalysts were prepared by dissolving $NiCl_2\cdot 6H_2O$ and *n* equivalents of the amine ligand in distilled water as 0.050 M solution. All the catalysts prepared were stand at room temperature for at least 1 day and used as aqueous solution. Analytical TLC and PTLC were performed with Merck $60F_{254}$ and $60PF_{254}$ respectively. Analyses of oxidation products were performed on a Hitachi 163 gas chromatograph attached with Shimadzu CR-5A CHROMATOPAC as integrator. ^{1}H NMR spectra were recorded at 60 MHz on a JEOL PMX-60Si spectrometer with tetramethylsilane as internal standard.

Styrene Oxidation. In a typical experiment, 1.0 M NaOCl (12.5 mL, 12.5 mmol) was added to the mixture of styrene (0.52 g, 5.0 mmol) and 0.050 M aqueous nickel catalyst (2.0 mL, 0.10 mmol), and the resulted mixture was stirred vigorously at room temperature. A fine black precipitate formed in a few minutes upon addition of NaOCl. After 5 h stirring, the mixture was passed through a short Celite column to remove black precipitate. The filtrate was extracted with CH_2Cl_2 (10 mL×2). The yield of styrene oxide was determined by GC analysis of the CH_2Cl_2 extract. Benzoic acid was isolated from the acidified aqueous layer by CH_2Cl_2 extraction. The oxidations of styrene in Tables 1 and 2 were performed in a same manner with appropriate amount of nickel catalyst.

Oxidations and analyses of *trans*-β-methylstyrene and *cis*-β-methylstyrene were performed in a same manner with styrene oxidation.

Oxidation of α-Methylstyrene. The oxidation was performed in a same manner with styrene oxidation under the conditions described in Table 3. The CH_2Cl_2 extract of the reaction mixture were concentrated, and then distilled by Kugelrohr under reduced pressure (80 °C, 10 mmHg, 1 mmHg=133.322 Pa). The yields of α-methylstyrene oxide and acetophenone were determined by the comparison of the ^{1}H NMR integration of the distillate with that of dibenzyl ether added as an internal standard. The yields of α-methylstyrene oxide and acetophenone were 53% and 12% respectively. Benzoic acid was isolated from the acidified aqueous layer by CH_2Cl_2 extraction in 15% yield.

Oxidation of *trans*-Stilbene. NaOCl (1.0 M, 20 mL, 20 mmol) was added to the mixture of *trans*-stilbene (0.36 g, 2.0 mmol) in CH_2Cl_2 (10 mL) and aqueous $Ni(bpy)_2Cl_2$ (0.050 M, 0.80 mL, 0.040 mmol). The resulted mixture was stirred vigorously at room temperature. The disappearance of *trans*-stilbene was monitored by TLC. After the complete conversion of *trans*-stilbene, the mixture was passed through a short Celite column and the filtrate was extracted twice with CH_2Cl_2. The CH_2Cl_2 extract was dried over anhydrous Na_2SO_4 and the solvent was removed out by evaporation. The residue obtained was separated on silica-gel PTLC with CH_2Cl_2 : hexane=1 : 1 as eluent. *trans*-Stilbene oxide (R_f=0.6) was obtained in 34% yield. Benzoic acid was isolated by the CH_2Cl_2 extraction of the acidified aqueous layer in 21% yield. No *cis*-stilbene oxide was detected in the reaction mixture by TLC and ^{1}H NMR.

cis-Stilbene was oxidized and analyzed in a same manner with *trans*-isomer. Cyclohexene and norbornene were oxidized in a same manner with *trans*-stilbene under the conditions described in Table 3, and the yields of epoxides were determined by GC.

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4) Abbreviations used: salen, *N,N'*-ethylenebis(salicylideneamine); cyclam, 1,4,8,11-tetraazacyclotetradecane; bpy, 2,2'-bipyridine; dm-bpy, 4,4'-dimethyl-2,2'-bipyridine; phen, 1,10-phenanthroline; Me-im, 1-methylimidazole.

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