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EPOXIDATION OF ALKENES WITH IODOSYLBENZENE CATALYZED BY Cr (III) SCHIFF BASES

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Chromium (III) Schiff base complexes particularly those containing salen or binaphenyl ligands are effective catalyst for the epoxidation of alkenes often utilized terminal oxidants like t-BuOOH acting via a high valant Cr(V) Oxo species. Epoxides are versatile compounds that form building blocks of many pharmaceuticals and fine chemicals. Therefore, the design and development of new chiral catalyst for enantio selective epoxidation is of current significance.

Epoxides are important synthetic intermediates for the synthesis of oxygen-containing natural and synthetic compounds. Access to a variety of epoxides has largely been successful due to the remarkable catalytic activity of transition metal complexes, which have a unique ability to bring the alkene substrate and the oxygen source within the coordination sphere of the metal leaving to a facial transfer of oxygen atom to the carbon-carbon double bond. These are highly useful intermediates for the manufacture of a range of commercial products. Their selective synthesis is a subject of considerable academic and industrial interest. Olefin epoxidation is one of the main routes, which leads to the production of epoxides on both at laboratory and industrial scale. In the mid-1980s Kochi and cowerkers reported that Cr(salen) complexes were capable of catalyzing the epoxidation of unfunctionalized alkenes using PhIO as the stoichiometric oxidant. The catalyst was used at 20mol% with respect to (wrt) PhIO and 1mol % w.r.t. alkene. Good yields were obtained for many alkenes and from the outset it was noted that addition of oxygen donor compounds (ligends) such as pyridine N-oxide (Pyo) and triphenyl phosphine oxide (Ph_3PO) increased reaction rates. The effect of donor ligands on the related metal (porphyrin) epoxidizing system is well known. Different transition metal complexes of metalloporphyrins, schiff bases, macrocycles etc. have been employed as catalyst for oxygen transfer reactions. The metals include Fe (III), Mn (III), Ti (IV), Mo (V), Mo (VI), Cr (III), Ru (VI), Ru (III) etc. Metal (salen)-mediated epoxidation continues to attract a great deal of attention and research continues into both mechanistic details and practical improvements. Chromium (salen) complexes have been shown to be capable to mediating a variety of other reactions, as well as the asymmetric epoxidation of alkene.

EXPERIMENTAL

Reagents

The starting alkenes viz. cyclohexene and norbornene. The hydrocarbons were checked by gas chromatography to ensure that no oxidation product was left in the substrate.

Solvents

Purified benzene, acetonitrile, acetone, methanol, ether, methyl cyanide and m-xylene, were used as solvent in various reactions. Dichloromethane used as solvent was obtained commercially. It was purified by washing with 5% sodium carbonate solution, followed by water. Then it was dried over anhydrous calcium chloride and finally fractioned. The fraction of boiling range 40-410C was collected and used.

Product Analysis

The epoxidation reactions and the products formed thereby were analysed by gas chromatography using Nucon-Amil gas chromatograph XE-60 as G.C.Column.

EPOXIDATION WITH Cr (III) SCHIFF BASES AS CATALYST

Epoxidation of cyclohexene

Epoxidation of cyclohexene using [Cr (HMBPREN) (H2O)2] CI, (1mg) as catalyst was carried out by taking cyclohexene (1.25m mol), iodosylbenzene (0.7 m mol) in dichloromethane (5ml). The contents were stirred for half hour at 350C with the help of a teflon coated magnetic needle. The product analysed by G.C. at 1200C using X. E.- 60 as the analytical column.

Effect of Solvent

The epoxidation of alkenes was extended to the effect of solvents. Different solvents like benzene, acetone, dichloromethane, acetonitrile were used separately under otherwise similar reaction condition as maintained for a typical procedure of olefin epoxidation.

Effect of catalyst concentration

The effect of catalyst concentration on the epoxidation of cyclohexene was studied. Different concentration of the catalyst [Cr (HMBPREN) (H2O)2\]CI varying from 0.005, 0.010, 0.020, 0.030, 0.040m mol were taken with (1.25 m mol) of cyclohexene and (0.7m mol) of iodosylbenzene, in 5ml of dichloromethane. The contents were stirred for one hour and products analysed by gas chromatography.

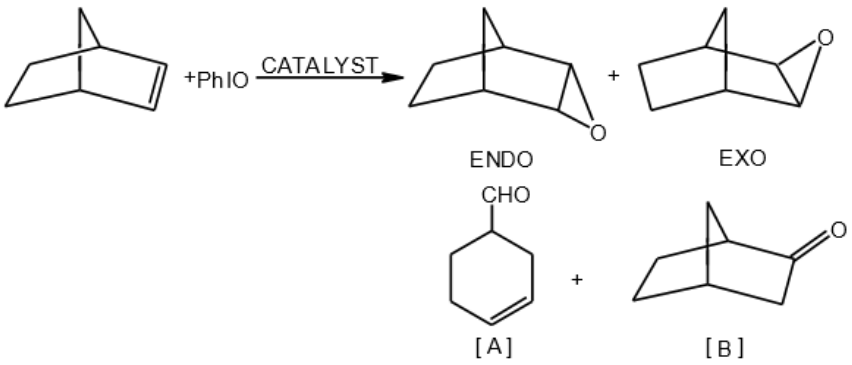
Epoxidation of Norbornene

Epoxidation of norbornene was carried out by taking 1.25m mol of norbornene and (0.7m mol) of iodosylbenzene in 5ml of dichloromethane, 1 mg of [Cr (HMBPREN) (H2O)2] CI catalyst was added, the rest of the procedure was similar to that used for cyclohexene epoxidation.

Competitive epoxidation

The competitive epoxidation of various cyclo olefins viz. cyclohexene, cycloheptene and norbornene was studied by taking (1.25m mol) of cyclohexene, (1.25m mol) of other cyclo olefin, with (0.002m mol) of calalyst and (1.0m mol) iodosylbenzene in (5ml) of dichloromethane in a three necked round bottom flask. The contents were stirred at 300C for one hour. On completion of the reaction the contents were filtered and product analysed by G.C.

Many researchers e.g. Bruice et al and Traylor et al etc. too have suggested that the formation of two types of epoxide (endo and exo) shows that rotation of the double bond takes place. It can be suggested that it is due to asymmetric insertion of oxygen, where two C-O bonds are formed simultaneously but at different rate. These observations rule out the involvement of oxo-metallacyle, concerted and ion pair intermediate in the epoxidation process. Involvement of such intermediates would produce only one type of epoxide, which is quite contrary to the observed facts. The remaining possibilities are the carbocation or free radical intermediates. Both addition of electrophiles or radicals to norbornene and the formation of norbornene metal complex occur exclusively on the exo-side as do peracid epoxidation and electrocyclic addition. On the basis of aforesaid discussion a following mechanism is being suggested.



(Table-1) Epoxidation of cyclohexene catalyzed by Cr (III) Schiff base complexes

S.NO.	CATALYST	PRODUCT (m mol)*		
		EXPOXIDE	CYCLOHEX-ENOL	CYCLOHEXE-NONE
1.	$[Cr(SALEN)(H_2O)_2]Cl$	0.059	0.063	0.024
2.	$[Cr(HMBEN)(H_2O)_2]Cl$	0.068	0.034	0.038
3.	$[Cr(HPBEN)(H_2O)_2]Cl$	0.052	0.033	0.036
4.	$[Cr(HPHBEN)(H_2O)_2]Cl$	0.050	0.031	0.030
5.	$[Cr(BHBEN)(H_2O)_2]Cl$	0.075	0.026	0.021
6.	$[Cr(CHBEN)(H_2O)_2]Cl$	0.045	0.032	0.028
7.	$[Cr(HNBEN)(H_2O)_2]Cl$	0.046	0.022	0.021

*Yields are based on amount of Phl generated.

(Table - 2) Effect of solvent on the epoxidation of cyclohexene catalyzed by [Cr (HMBPREN)(H_2O)$_2$Cl]

*Yields are based on amount of PhI generated.

S.NO.	ADDITIVES	PRODUCTS* (m mol)		
		EPOXIDE	CYCLOHEXENOL	CYCLOHEXENONE
1.	Pyridine	0.026	0.06	0.026
2.	Imidazole	0.023	0.03	0.011
3.	CTABr	0.019	0.08	0.022
4.	Triton X-100	0.036	0.09	0.051
5.	SLS	0.041	0.07	0.021

(Table - 3) Effect of additives on oxidation of cyclohexene catalyzed by [Cr (HMBPREN)(H_2O)$_2$Cl]

*Yields are based on amount of PhI generated.

S.NO.	SOLVENT	PRODUCTS* (m mol)		
		EPOXIDE	CYCLOHEXENOL	CYCLOHEXENONE
1.	Acetone	0.03	0.028	0.032
2.	Acetonitrile	0.02	0.013	0.052
3.	Dichlormethane	0.09	0.045	0.058
4.	Benzene	0.04	0.023	0.046
5.	m-Xylene	0.01	0.008	0.023

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