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EPOXIDATION OF OLEFINS WITH HYDROGEN PEROXIDE USING AN ISOCYANATE AS CO-REACTANT

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A new epoxidation method has been found in which hydrogen peroxide is utilized under essencially neutral conditions. The procedure involves the initial reaction of an isocyanate with hydrogen peroxide to produce an active complex, which has been used to epoxidize olefinic double bond.

It is well known an isocyanate(RNCO) reacts with a nucleophilic reagent(HB) to give an adduct(RNHCOB) (1,2). It is possible, then, that hydrogen peroxide may attack an isocyanate to form a peroxycarbamic acid ($RNHCO_3H$) which would cause an epoxidation if an olefin is included in the reaction system.

Reaction between phenyl isocyanate and hydrogen peroxide in the presence of olefin at room temperature gave 1,3-diphenylurea, epoxide and carbon dioxide. Table 1 summarizes the yields of epoxide and 1,3-diphenylurea observed in the experiments carried out with added cyclohexene using

different molar ratio of phenyl isocyanate and hydrogen peroxide at 20°C.

Table 1

Epoxidation of Cyclohexene with Phenyl Isocyanate and Hydrogen Peroxide

Mole Ratio C_6H_5NCO to H_2O_2	Time (hr)	Yield of epoxide (%)(a)	Yield of 1,3-diphenylurea (%)(b)
1 : 1	24	33	94
1.6 : 1	24	54	92
2 : 1	24	68	95
4 : 1	24	69	98

(a), (b) Based on hydrogen peroxide used

The yield of epoxide was 68% when the molar ratio of phenyl isocyanate and hydrogen peroxide was 2:1,this value was as nearly twice as that of 1:1 ratio, and the yield was nearly the same when phenyl isocyanate was used in excess. These results suggested that the present epoxidation proceeded on the stoichiometry shown in Equation 1.

$$2RNCO + H_2O_2 + \geq C{=}C\leq \longrightarrow \geq C\overset{O}{-}C\leq + (RNH)_2CO + CO_2 \quad (1)$$

The results obtained with phenyl isocyanate and with p-chlorophenyl isocyanate which were used to epoxidize some olefins at 20°C in various solvents using two moles of isocyanate per mole of hydrogen peroxide are summarized in Tables 1 and 2.

The yield of epoxide was increased when solvent was non polar such as n-pentane or benzene. p-Chlorophenyl isocyanate instead of phenyl isocyanate gave somewhat better yield probably due to the electron withdrawing effect of chlorine atom.

Table 2

Epoxidation of Olefins with Phenyl Isocyanate and Hydrogen Peroxide in Various Solvents at 20°C

Olefin	Solvent	Yield of Epoxide(%)[c]
cyclohexene	DMF	trace
	THF	15
	dioxane	23
	ether	49
	chloroform	55
	benzene	68
	n-pentane	77
styrene	ether	23
	chloroform	40
	benzene	40
2-hexene	ether	37
	chloroform	39

(c) Based on hydrogen peroxide used

Table 3

Epoxidation of Olefins with p-Chlorophenyl Isocyanate and Hydrogen Peroxide in Ether or Benzene at 20°C

Olefin	Solvent	Yield of Epoxide(%)[d]
cyclohexene	ether	58
	benzene	75
styrene	ether	25
	benzene	42

(d) Based on hydrogen peroxide used

From these results, this new oxidation procedure may be regarded as being useful in the synthesis of epoxides. The present method is very simple and can be done under mild condition without no by-products due to the oxirane-ring opening by acids or water.

The reaction mixture of two moles of phenyl isocyanate and one mole of hydrogen peroxide showed absorption maximum at 314mμ($\log\varepsilon$=4.24) and this absorption may be due to phenyl isocyanate-hydrogen peroxide complex similar to the one previously reported about the mixture of aryl isocyanate and peracetic acid(3). The spectrum showed the complete conversion of isocyanate to the complex and it was observed that the absorption was vanished by the addition of olefin, and at the same time the formation of epoxide and 1,3-diphenylurea was found.

These facts suggested that active species of olefin epoxidation may not the peroxycarbamic acid but this isocyanate-hydrogen peroxide complex. Since this reaction follows Equation 1, this complex can be thought to be formed with two moles of isocyanate and one mole of hydrogen peroxide.

The following reaction path may account for the results obtained;

$$2RNCO + H_2O_2 \longrightarrow \text{complex} \qquad \text{complex} + \succ C{=}C\prec \longrightarrow \succ C\!-\!C\prec + (RNH)_2CO + CO_2$$

Further work on the mechamism and optimum synthetic conditions of this reaction is in progress.

References

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