Addition of Polyethyleneglycols to Asymmetrical Epoxides

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SUMMARY

The reaction of some aromatic and aliphatic asymmetrical epoxides with polyetheyleneglycols was investigated in the presence of $HClO_4$. The products of the addition were examined by ^{13}C NMR. Some of the products were further converted into novel epoxides and tried for chemical behavior. Phenyl substituted-aromatic-asymmetrical epoxides just gave single addition products by following an S_n2 like mechanism whilst the aliphatic epoxy derivatives formed both the isomers of the addition products.

INTRODUCTION

Epoxides as monomers were known to react with alcohols in the presence of acids(1a–b). The initial step of formation of a tertiary oxonium ion was considered as a rate determining step. However, the alcohols and particularly polyethyleneglycols are strongly able to form hydronium ions decreasing the activity of an intermediate step(1b).

In our previous studies we have already searched for the adducts of the alcohols with epichlorhydrine and with some of the alkyl an alkyloxy oxiranes. We reported the structures of isomers and also partly discussed the reaction mechanism in a qualitative way(2a–d).

Including the results of the present study, we generally found that the asymmetrically substituted oxiranes such as 1,2-epoxyalkanes gave 1-carbon substituted adducts together with 2-substituted products due to effect of hyperconjugation of alkyl groups (I.b.). Halomethylene and also alkyloxy oxiranes on the other hand led to more 1-adducts due to steric and mesomeric effects(I.c–e).

Steric effects play an important role as the reaction of styreneoxide with ethyleneglycol yielding 99% of 1-phenyl-2-(β-hydroxy)ethoxy-1-ethanol

(I.a.) was demonstrated (Fig.I). $HClO_4$ as a catalyst can protonate the glycoles as well as epoxides in nonsolvent media. The less nucleophilicity of perchlorate anion has affects the intermediates in the bond breaking step.
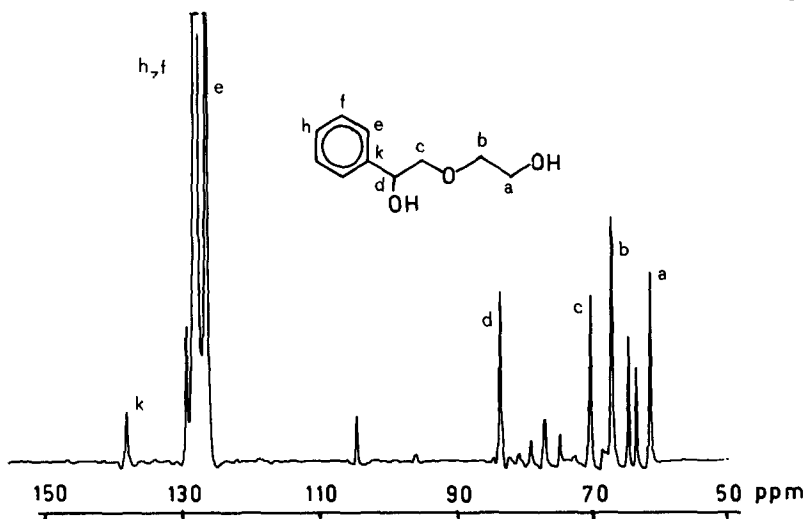

Figure-1. 15 MHz ^{13}C NMR spectra of 1-phenyl-2-(β-hydroxy)ethoxy-1-ethanol in CDCl$_3$. TMS was the internal reference. The CHCl$_3$ extract of row product was distilled at 160-170°C/13 torr.The peaks at 63 ppm indicates only unreacted styreneoxide of small amount.

RESULTS AND DISCUSSION

In earlier studies we have prepared some asymmetrical glycoles as intermediates (2c-f), However,we have obtained the mixtures of isomers (2a) in this paper we wish to present the results of the reaction of some epoxides with various substituents and polyetyhleneglycols.

The oxonium ion with a nortropene like intermediate structure (3) could give either an intermolecular reaction or react with another monomer from both sides of the epoxide ring particularly in the presence of aliphatic R,R'- groupings. In the case of aromatic R'- substituents the β- carbon preferably attacked by the nucleophile in the presence of any Lewis acid. Pasika has already reported that the condensation of the styreneoxide gave mostly the "head to tail" form of oligomers (4). Therefore the reaction is S$_n$2 type with an intermediate step of inversion of the configuration (I.a.). In the case of aliphatic substituents dissociation of epoxides is more likely and therefore the isomeric mixtures were formed involving S$_n$1 type reaction (I.a - e,II,III.).
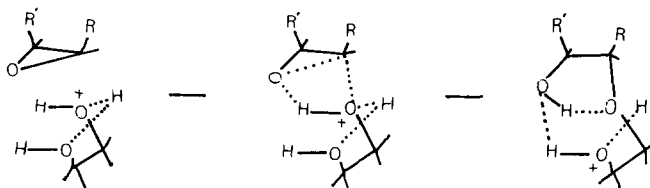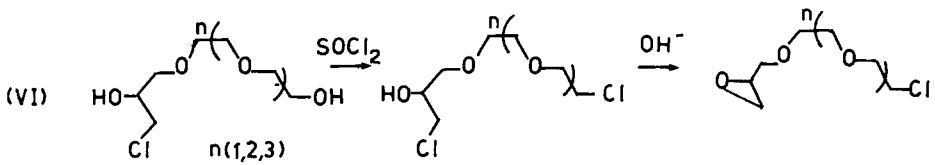
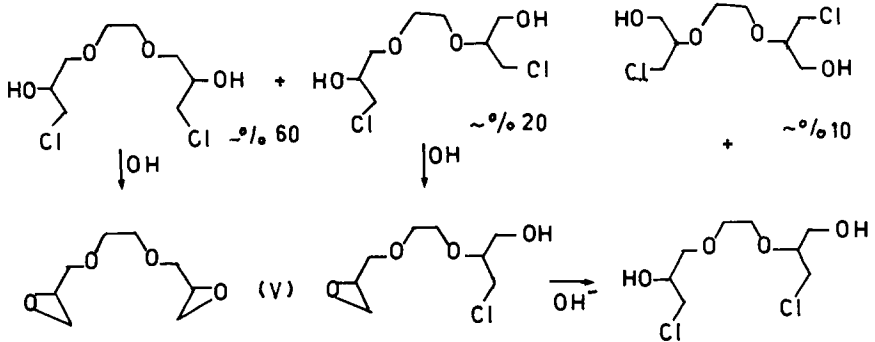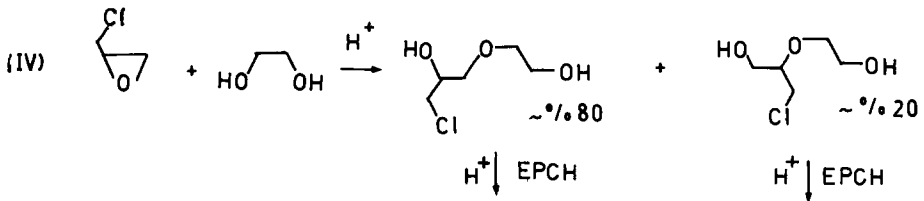|								
I.a.	(R':	C_6H_5	R:	H)	99%			
I.b.	(R':	C_2H_5	R:	H)	50%	(R':H	R: C_2H_5)	50%
I.c.	(R':	CH_2Cl	R:	H)	80%	(R':H	R:CH_2Cl)	20%
I.d.	(R':	$ClC_2H_4OCH_2$	)		90%	(R :H	)	
I.e.	(R':	$C_6H_{11}OCH_2$	)		95%	(R :H	)	

The addition of epichlorohydrine to β-chloro ethanol yields the product of 1,6-dichloro-4-oxa-2-hexanol. The reaction of this compound with NaOH gives 1,2-epoxy-4-oxa-chlorohexane in ether solutions. However, the long chain chlorohydrines with an -OH end group were epoxidized in rather mild conditions such as carbonates as bases (III.) Such an epoxide formation was found to be quite interesting. We were able to separate the complex mixtures of addition products as indicated in equation VI-V. We therefore obtained a typical diepoxide of 1,2,9,10-diepoxy-4,7-dioxadecane as it is characterized in Fig.II. This compound was quite stable but the condensation with glycoles in the presence with $HClO_4$ was failed.

On the other hand some of the "polyoxaepichlorohydrines" were tried for the chlorination in order to form the derivatives, equation-VI. The reaction of such derivatives with bases usually gave the olefines and no cyclic ether type of compounds.

EXPERIMENTAL

The addition of epoxides were carried in an explosion proof fume cupboard. In a 1,0 lt round bottom flask 1,0 mol glycol was mixed with a catalytic amount of $HClO_4$ and stirred for one hour. To this stirred solution 1,5 mol of epoxide was added dropwise with great caution. The reaction mixture was stirred overnight then treated with 1,0g $NaHCO_3$. Row mixture was washed with water and dried over Na_2CO_3 and then distilled poly (epoxy-chlorhydrines) were then obtained from the 50% - 20% solutions of polyoxachlorohydrines in ether or dioxane with an equimolar amount of

(II) + R (OH, HOC₂H₄O)

$R \ (OH, HOC_2H_4O)$

(III)

$R \left[Br, Cl, OC_2H_4OH, O(C_2H_4)_2OH, O(C_2H_4)_3OH, OH \right]$

(IV)

$\sim \% \, 80$ $\sim \% \, 20$

$H^+ \mid EPCH$ $H^+ \mid EPCH$

$\sim \% \, 60$ $\sim \% \, 20$ $\sim \% \, 10$

$\mid OH$ $\mid OH$

(V) $\overrightarrow{OH^-}$

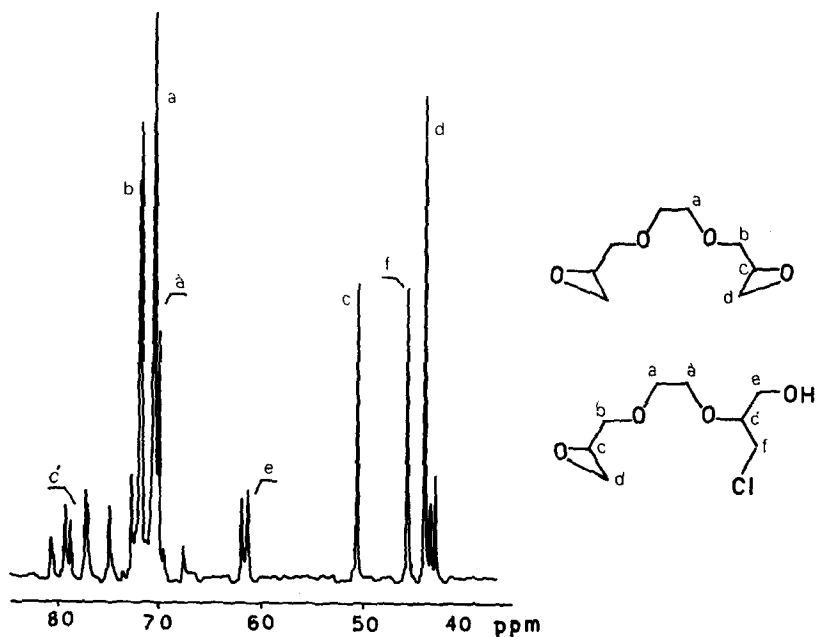(VI) $\xrightarrow{SOCl_2}$ $\xrightarrow{OH^-}$

$n(1,2,3)$
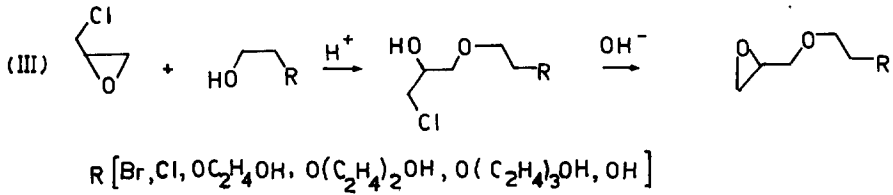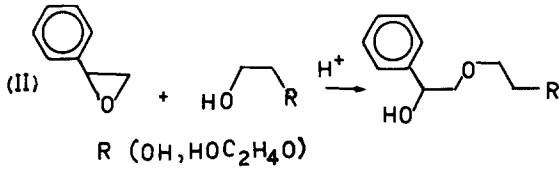
Figure-II. 15 MHz ^{13}C NMR spectra of 1,2,9,10-diepoxy-4,7-dioxadecane and
1,2-epoxy-4,7-dioxa-8-chloromethyl-9-nonanol in CDCl$_3$(a
product mixture). TMS was an internal reference. The sample
was obtained by distillation at 120-150°C /0,5 torr.

sodium carbonate. Separation of the reaction products were tried on a 5%
OVI coulumn by G.C. with a temperature programing of 5°C /min.
    ^{13}C NMR analyses were conducted on a JEOL spectrometer, model FX60C,
and operating in noise decoupling mode with a long puls interval time (5).
The proton decoupled off resonance spectra was used to identify the primary
and secondary carbons. On the other hand in order to search for the mecha-
nistic route of the reactions we particularly analysed the row reaction
mixtures by quantitative ^{13}C NMR spectra in NOE suppressed (modulated pulse
decoupling) mode. However, due to the short relaxation times of the large
molecules rather dilute solutions were tried in CDCl$_3$ with several number
of scans.

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