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Addition of Alcoholes to Asymmetric Epoxides

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SUMMARY

Formation of some asymmetric glycoles by the addition of some alcoholes or glycoles to the asymmetric epoxides in the presence of $HClO_4$ were investigated by ^{13}C NMR and the results were simply discussed. It was cleared that the formation of the adducts were led by the electronegativity of the side groups as well as steric nature of the nucleophile involved in the reaction is mostly due to the behavior of the oxonium ions formed as intermediates in the reactions.

INTRODUCTION

Addition polymerisation is at the present still contraversial subject despite the fact that the large number of papers published in this field. In our studies we sythesised some chiral macrocyclic ethers starting from asymmetric derivatives of glycoles(1). In our earlier study we have already obtained 9-chloro-3,6-dioxanonane-1,8-diol from diethyleneglycole and epichlorhydrine in the presence of $HClO_4$ without a solvent to form some chiral polyoxalactones(2). We also tried the role of H_2SO_4 in such a reaction(3).

Propagation of epoxides in the cationic polymerisation is usually considered as proceeding via a tertiary oxonium , e.g., for the polymerisation of 1,2-epoxyalkane where acids initiate the reaction.

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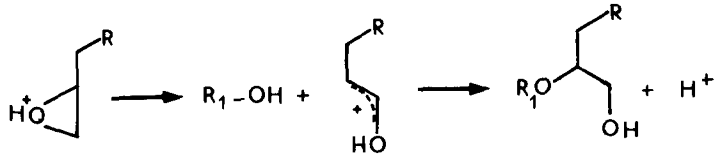
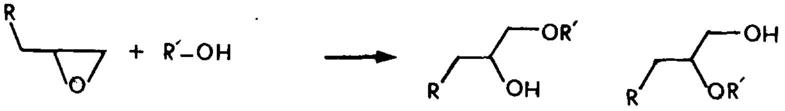
However following step of bond dissociation have been mostly reported that the ring opening is determined by the secondary carbonium ion like S_N1 reactions.



In our studies we observed that the less hindered primary carbon was attacked in certain degree depending on both of the structure of alcohole and epoxide (Table-I).

Table-1. The addition products of alcoholes to glycoles.



R	R'	yield %	yield %
Cl	C_2H_4OH	75	25
Cl	$C_2H_4OC_2H_4OH$	85	15
Cl	$C_2H_4OC_2H_4OC_2H_4OH$	97	3
Cl	$s-C_6H_{11}$	97	3
$s-C_6H_{11}O$	$C_2H_4OC_2H_4CI$	95	5
$s-C_6H_{11}O$	$C_2H_4OC_2H_4OH$	97	3
$i-C_4H_9O$	C_2H_4OH	70	30
$i-C_4H_9O$	$C_2H_4OC_2H_4OH$	70	30
CH_3	C_2H_4OH	50	50
CH_3	$C_2H_4OC_2H_4OC_2H_4OH$	86	14

RESULTS AND DISCUSSIONS

In our studies we reacted the epoxides with equimolar amounts of alcoholes in the presence of catalytic amounts of perchloric acid during satisfactory period of time depending on the reactants. The results,as they are compiled in table-I,indicated that the formation of derivatives in acidic media strongly influenced from side groupings. Particularly electron withdrawing power of the substituent increases the formation of primer adduct as well as the bulky alkoxides. As epichlorhydrine give rise to formation of 97 % of 1-cyclohexyloxy-3-chlor-2-propanol with cyclo hexanol (Figure-1) exhibiting the role of hinderence of the alcohol involved,although the fact that inductive effects fairly supports the carbonium ion mechanism.

Our results, however, led us to the conclusion that the rate of reactions mostly determine the structure of product due to the fact that the intermediates formed play important roles.

Reactions were known involved via the oxonium ions in the presence of acids which are expected to form the adducts by breaking the weakest bond (6). Therefore more electronegative

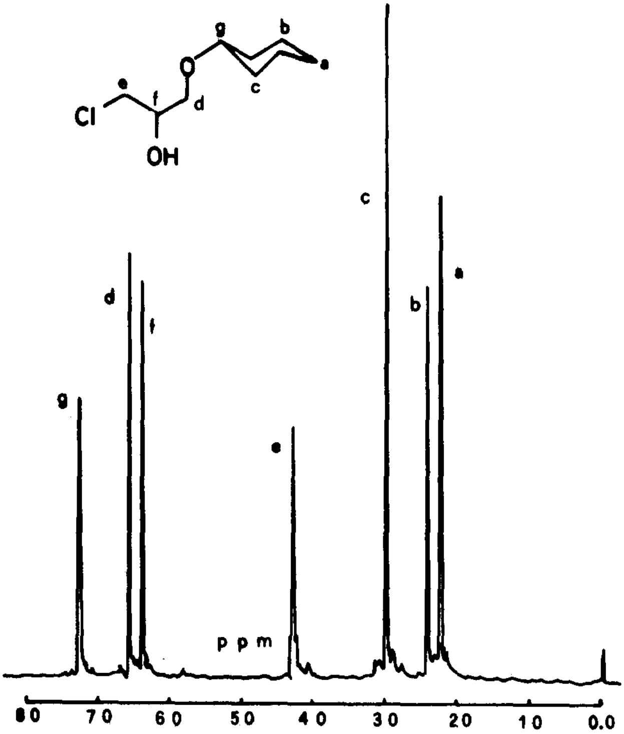
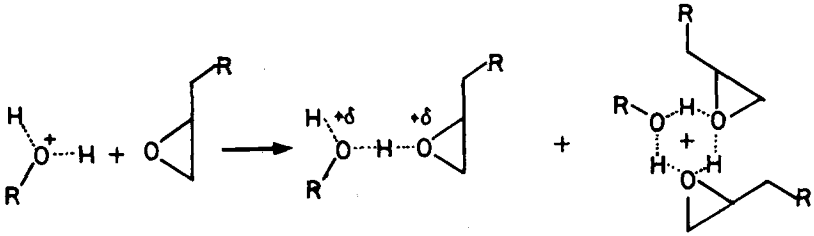


Figure-1.2o MHz ^{13}C spectrum of 1-cyclhexyloxy-3-chlor-1-propanol.

substituent give less stable stable oxonium ion formed.Accordingly 1,2-epoxybutane is more reactive than 1,2-epoxy-3-chlorpropane which gave less stable oxonium ion of high entropy to break any bond almost regardless whatever the substituent is as soon as it was attacked.

It could also be discussed that such a mechanism is also influenced by formation of oxoniums of both sides.Therefore initial steps could be discribed in a better way that the less stable oxonium ions of more entropy give rise formation of epoxide agregation becouse of the higher polarity of the oxonium complex in order to delocalize the positive charge.



Consequently it is therefore a nucleophilic attack of epoxide to the protoneted alcohol of more stability of positive charge gave seconder adducts in certain amounts despite the fact that they could have behaved as bulky alcoholes (Figure-IIa,b,c). It is obviously explained that the 1,2-epoxy-3-chlorpropane proceeds rather slowly as it is controlled by the electron donecity of the substituent (Table-1).

EXPERIMENTAL

Equimolar amounts of reactants were reacted in the presence of catalytic amounts of $HClO_4$ (70 % Fluka).Ratios of products were determined after they had been distilled at reduced pressure. ^{13}C spectra were run under NOE supressed conditions to determine the ratios,however,overall results were still claimed that they are in 85-90 % of corrections.Solutions were prepared in $CDCl_3$. Epichlorhydrine derivatives were also converted into their Acetyl derivatives to run the ^{1}H spectra and the results were found almost in accordance with the ^{13}C analyses.It is also important to note that dimerisations were observed in above

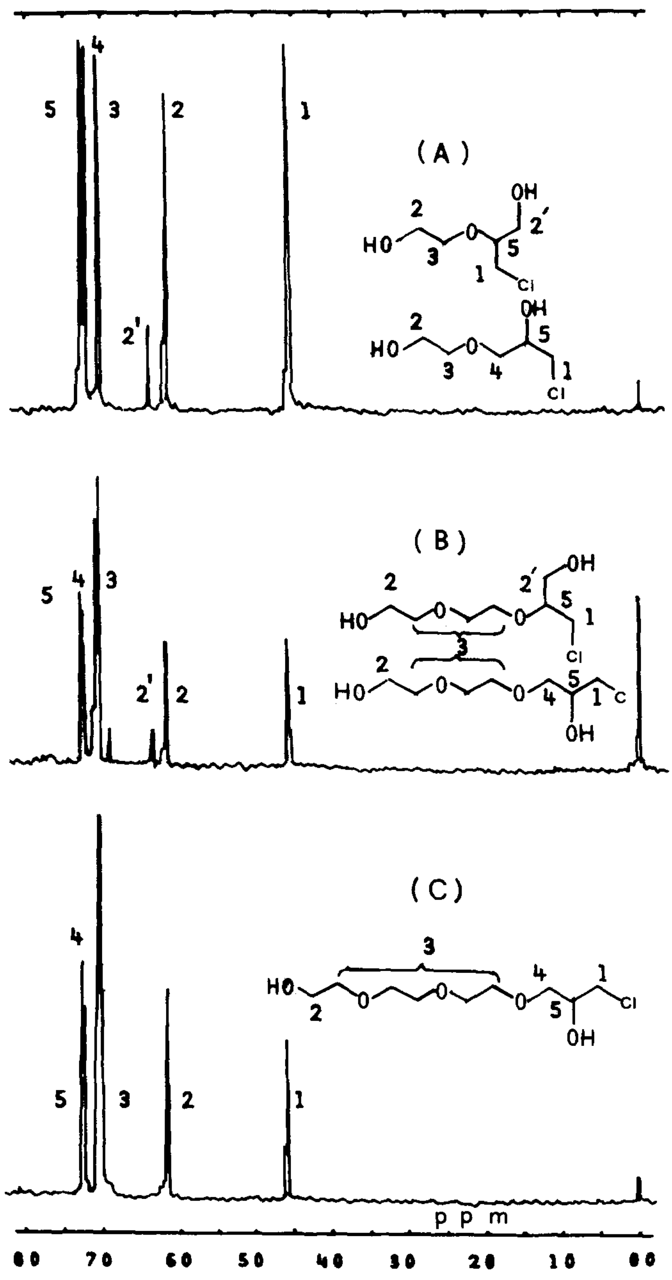


Figure-II. ^{13}C spectrum of A.6-chloro-3-oxahexane-1,5-diol,
B.9-chloro-3,6-dioxanonane-1,8-diol,
C.12-chloro-3,6,9-trioxadodecane-1,11-diol.

conditions up to 30 % depending on the nature of alcohol. We therefore first distilled the the reaction mixture to isolate the mono adducts.

ACKNOWLEDGEMENT

^{13}C spectra were at Research Institut of Organic Chemistry of ANKARA University by CFT-20 Model of VARİAN-AG spectrometer operating at 20 MHz frequency, therefore greatly acknowledged.

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