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J.M.S.—PURE APPL. CHEM., A30(1), pp. 35–49 (1993)

# REACTIVE IONIC OLIGOMERS. II. OLIGOMERS OF AMMONIUM QUATERNARY SALTS OBTAINED FROM THE REACTION OF DIETHYLAMINE WITH EPICHLOROHYDRINE

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## ABSTRACT

The reactions of diethylamine (DEA) and diisopropylamine with epichlorohydrine (ECH) used in excess to prepare reactive ionic oligomers which contain ammonium quaternary salt groups were studied. The ionic oligomers which contain 2,3-epoxypropyl and 2-hydroxy-3-chloropropyl as reactive groups were only prepared in the case of DEA. Because the reaction between DEA and ECH was found to lead to the formation of an azetidinium salt as an intermediary product, the reaction between ECH and (*N*,*N*-diethyl-2-hydroxyazetidinium) chloride (Q) was also investigated to discover if this reaction involves a rearrangement of Q. It is also reported how the reactive group content and molecular weight of the ionic oligomers are influenced by such reaction conditions as the DEA/ECH ratio, solvent, temperature, and time.

## INTRODUCTION

The reactions of synthetic and natural polymers offer an attractive way to get materials with wished for properties. For instance, the grafting of ammonium quaternary salt groups on cellulose materials improves the dyeability and the accessibility of water-soluble finishing reagents, and allows for the production of fabrics with ion-exchange properties [1, 2]. Ammonium quaternary salts with 2,3-

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epoxypropyl groups in the molecule are particularly interesting due to their high reactivity toward many polymeric materials including the celluloses.

Trialkyl-2,3-epoxypropylammonium salts can be prepared by the reaction between tertiary amines and epichlorohydrine (ECH) for a few cases only. For example, the reaction of trimethylamine with ECH leads to (trimethylglycidyl ammonium) chloride [3] or its (trimethyl-3-hydroxy-1-propenyl ammonium) chloride isomer [4], depending on the synthesis conditions. Also, the reaction between triethyl amine and ECH leads mainly to [2-hydroxytrimethylene-1,3,-bis-(triethylammonium)] chloride [5] instead of (triethylglycidyl ammonium) chloride, as expected.

To get oligomers with quaternary nitrogen atoms and glycidyl or chlorohydrine reactive groups, the reaction between dialkylamines and ECH should be studied thoroughly. The possibility of obtaining several compounds as the result of the direct interaction between ECH and dimethylamine (DMA) was demonstrated in a previous paper [6]. The present paper reports on the reaction of diethylamine (DEA) and diisopropylamine (Di-PA) with ECH (used in excess). Compounds with ammonium quaternary salt and reactive groups like 2,3-epoxypropyl and 3-chloro-2-hydroxypropyl were obtained for DEA only.

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## EXPERIMENTAL

### Materials

Diethylamine was previously distilled. ECH was boiled for 8 h on KOH. The fraction boiling at 116–117°C was used. Anhydrous ethanol (EtOH anh.), acetone of reagent degree, and anhydrous diethyl ether were used as received. [2-Hydroxytrimethylene-1,3-bis(triethylammonium)] chloride (Bis Q), used as a standard compound for GPC, was synthesized as previously reported [6]. (Triethylglycidylammonium) iodide [TEGAI], used as a standard compound, was synthesized via quaternization of diethylglycidylamine (DEGA) with ethyl iodide in acetone at room temperature.

Elemental analysis of TEGAI ($C_9H_{20}NOI$). Calculated: C, 37.89; H, 7.02; N, 4.91; I, 44.56%. Found: C, 37.53; H, 7.25; N, 4.58; I, 44.46%. $^1$H-NMR(DMSO): 1.2 and 3.5 ppm for ethyl groups and 2.8 and 3–4 ppm for glycidyl groups.

(*N*,*N*-Diethyl-3-hydroxyazetidinium) chloride (Q) was prepared via reaction of DEA with ECH (ECH/DEA molar ratio = 1/1 at 50°C, for 120 min). The azetidinium salt Q was separated by filtration and purified by recrystallization from acetonitrile.

Elemental analysis of Q ($C_7H_{16}NOCl$). Calculated: C, 50.76; H, 9.67; N, 8.46; $Cl_i$, 21.45; $Cl_c$, 0%. Found: C, 50.45; H, 9.52; N, 8.12; $Cl_i$, 21.27; $Cl_c$, 0%. $^1$H-NMR(DMSO): 1.25 and 3.55 ppm for ethyl groups, 3.8–4.8 ppm for ring groups, and 6.7–6.9 ppm for the hydroxyl group.

### Methods

The reaction of DEA with ECH was performed similarly with that of DMA with ECH [6], with the difference that DEA was added at 26–30°C within 2 hours.

Diethyl ether was used as a nonsolvent for the separation of the ionic reaction products from the reaction medium. The separated products were vacuum dried on $P_2O_5$.

The reaction of Di-PA with ECH was carried out at 50°C for 30 h by using an amine/ECH molar ratio of 1/2. The reaction product was separated as crystals by filtration from diethyl ether and purified by recrystallization from acetonitrile.

The reaction of azetidinium salt Q with ECH was carried out by using a Q/ECH molar ratio of 1/5. The ionic compounds were separated from the reaction mixture with diethyl ether.

All ionic reaction products were characterized by using elemental analysis, epoxy group content, and IR and $^1$H-NMR spectral methods. The epoxide coefficient (EC), defined as the epoxide group equivalents per 100 g sample, was determined by HBr addition carried out in glacial acetic acid [7]. IR spectra were recorded on a Perkin-Elmer Model 577 spectrophotometer. $^1$H-NMR spectra were recorded at 60 MHz using DMSO-$d_6$ as solvent. GPC analyses were performed in the following conditions: a 615 Sephadex column (270 × 6 mm) and a Pierce CH chromatoflowdetector equipped with a 2925 UV monitor and 254 nm filter.

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## RESULTS AND DISCUSSION

The reaction between DEA and ECH was primarily studied by measuring the ionic chlorine content ($Cl_i$) and the HBr consumption of the reaction mixture as functions of the reaction time. The data for a DEA/ECH molar ratio of 1/2 and a reaction temperature of 50°C are given in Fig. 1. It is observed that the change of the two parameters ($Cl_i$ content increasing and the HBr consumption decreasing) is rapid at the beginning of reaction. Subsequently, the reaction of DEA with ECH was carried out under various conditions: with and without solvent, at two temperatures, and for different time periods. Analytical data for the isolated ionic products

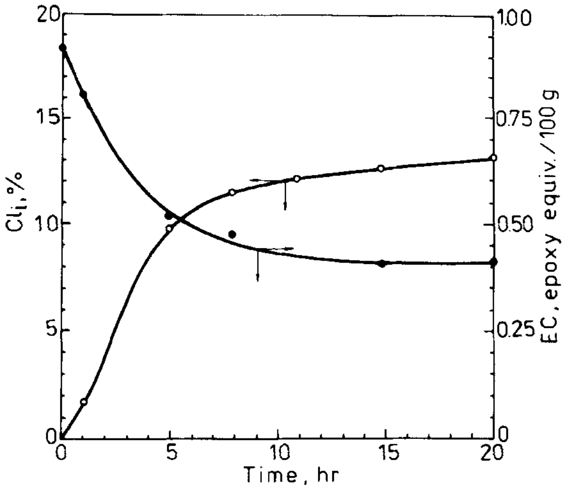

FIG. 1. Dependence of $Cl_i$ (○) and EC (●) on the reaction time. Reaction conditions: DEA/ECH molar ratio = 1/2; 50°C.

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are given in Table 1 and Figs. 2 and 3. For the same solvent and temperature, $Cl_i$ content decreases while $Cl_c$ and EC contents increase with the reaction time. This means that the product which appears immediately after the reactants come in contact is an ionic product without epoxy groups and $Cl_c$. Such a product should be the result of the following two successive reactions: an initial reaction due to the nucleophilic attack of the amine on the epoxy ring which leads to 1-diethylamino-3-chloropropanol-2 [8–10] (Scheme 1) and the isomerization of aminochlorohydrine (1) to DEGA·Ch or azetidinium salt Q according to Scheme 2.

The analytical data for the ionic product isolated from the reaction mixture after the first hour are the following: C, 50.35; H, 9.73; N, 8.15; $Cl_i$, 21.46; $Cl_c$, 0; EC, 0%; and they correspond rather well to the compound Q discussed in the Experimental Section. In addition, the IR spectrum (Fig. 4, Spectrum 3) shows an absorption band at 1090 $cm^{-1}$ which can be assigned to a secondary alcohol group; there is no one band characteristic of epoxy groups. The conclusion that the ionic product which appears at the beginning of reaction is the azetidinium salt Q is also supported by its $^1$H-NMR spectrum (Fig. 5B). A product of such as this has already been reported for the reaction between DEA and ECH carried out at 50°C but for a 1/1 molar ratio [12]. Moreover, it was observed that the formation of *N*-alkyl-2-azetidinols by cyclization of the addition products of ECH and hindered primary amines is optimum at a temperature of 50°C [13].

Our observation that the content of compound Q decreases while the epoxy

TABLE 1. Analytical Data for the Ionic Products Obtained by the Reaction of DEA with ECH at a DEA/DCH Molar Ratio of 1/2

| | Reaction conditions | | | Analytical data[a] | | | |
|---|---|---|---|---|---|---|---|
| Sample | Solvent | Temperature, °C | Time, h | $Cl_i$, % | $Cl_t$, % | $Cl_c$, % | EC, epoxy equivalent/100 g |
| $M_1$ | EtOH | 30 | 4 | 18.25 | 20.29 | 2.04 | – |
| $M_2$ | EtOH | 30 | 21 | 17.21 | 20.04 | 2.83 | 0.073 |
| $M_3$ | EtOH | 30 | 47 | 16.35 | 20.48 | 4.13 | – |
| $M_4$ | EtOH | 50 | 5 | 18.54 | 21.45 | 2.91 | 0.085 |
| $M_5$ | EtOH | 50 | 10 | 17.92 | 22.97 | 5.02 | – |
| $M_6$ | EtOH | 50 | 20 | 16.31 | – | – | – |
| $M_7$ | EtOH | 50 | 25 | 15.01 | 23.86 | 8.85 | 0.168 |
| $M_8$ | – | 50 | 5 | 15.32 | 22.20 | 6.88 | – |
| $M_9$ | – | 50 | 10 | 14.82 | 23.62 | 8.80 | 0.144 |
| $M_{10}$ | – | 50 | 20 | 13.85 | 23.92 | 10.07 | 0.205 |
| $M_{11}$ | – | 50 | 25 | 13.61 | 23.93 | 10.32 | – |
| $M_{12}$ | – | 50 | 30 | 13.32 | 24.12 | 10.80 | 0.210 |
| $RIO_1$[b] | – | – | – | 13.76 | 27.52 | 13.76 | 0.387 |

[a] $Cl_i$ = ionic chlorine; $Cl_t$ = total chlorine; $Cl_c$ = covalent chlorine; $Cl_c = Cl_t - Cl_i$; EC = epoxide coefficient.

[b] Calculated values for $C_{10}H_{21}O_2NCl_2$.

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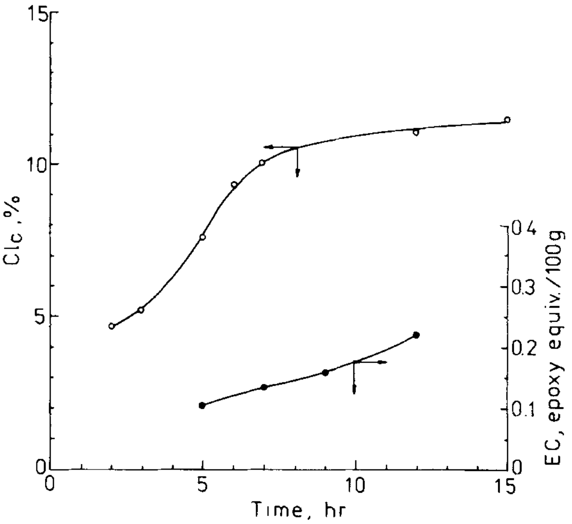


FIG. 2. Dependence of $Cl_c$ (○) and EC (●) on the reaction time. Reactions conditions: DEA/ECH molar ratio = 1/4; 50°C.

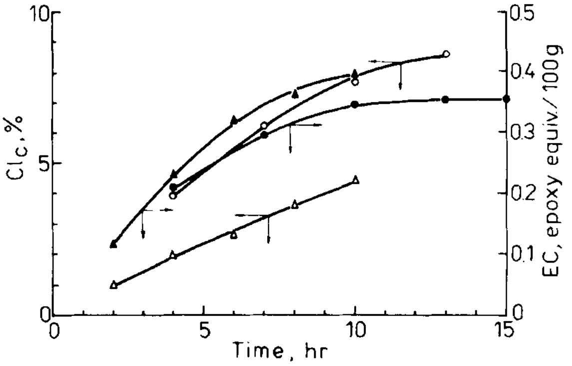
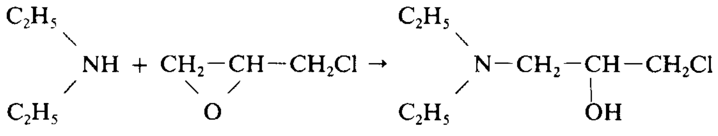


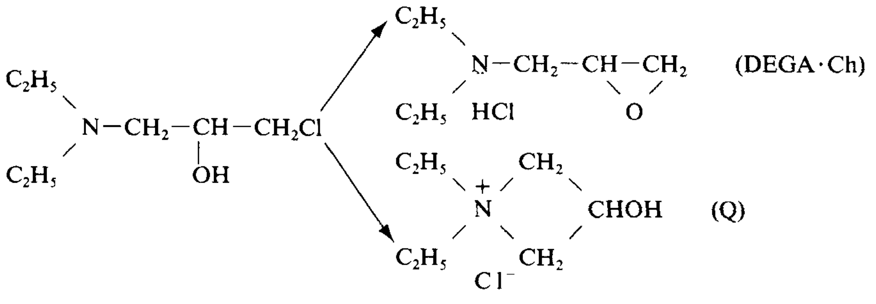
FIG. 3. Dependence of $Cl_c$ (○,△) and EC (●,▲) on the reaction time. Reaction conditions: 50°C; DEA/ECH molar ratio = 1/6 (○,●) and 1/15 (△,▲).



$$\begin{matrix} C_2H_5 \\ \diagdown \\ \; NH \\ \diagup \\ C_2H_5 \end{matrix} + \underset{\diagdown\, O\, \diagup}{CH_2-CH}-CH_2Cl \rightarrow \begin{matrix} C_2H_5 \\ \diagdown \\ \; N \\ \diagup \\ C_2H_5 \end{matrix}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2Cl$$

(1)

SCHEME 1.



SCHEME 2.

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group and $Cl_c$ contents increase with reaction time leads to the assumption that the compound Q reacts with ECH (used in excess) and generates ionic products which contain reactive groups. By using TEGAI as a reference compound, it was found that the IR spectra of the reactive products of DEA and ECH at reaction times much longer than 1 hour show absorption bands which are characteristic for the following groups and bonds: epoxy rings (880, 920, and 1260 $cm^{-1}$), C—Cl bonds (690 $cm^{-1}$), and alcohol secondary groups (1100 $cm^{-1}$).

To establish a reaction mechanism for the formation of the final ionic products, the reaction between Q and ECH at a Q/ECH molar ratio of 1/5 was carried out at 50, 60, and 80°C, and the reactive ionic products corresponding to different reaction times were characterized by their EC (Fig. 6), $Cl_i$, and $Cl_c$ (Table 2).

It is observed that the temperature affects both the reaction process and the structure of the products. The EC increases continuously with the reaction time if the temperature is 50 or 60°C and shows a maximum when the temperature is 80°C. Nevertheless, it can be concluded for the first reaction stage (namely, when EC is growing) that products with the same EC value have the same chemical structure because they have approximately equal values for $Cl_i$ and $Cl_c$. This means that the temperature does not affect the reaction mechanism in the first stage. It is of interest to compare the analytical characteristics of the ionic products obtained at 50°C at this stage by reacting ECH with Q (Table 2, Fig. 6) and DEA (Fig. 3) respectively. The values of EC and $Cl_c$ for the products obtained from Q are somewhat lower than those for the products from DEA at the same reaction time and an amine/ECH molar ratio of 1/6. As a direct reaction between the azetidinium salt and ECH is less probable, we suppose (1) an endothermal transposition of Q in (diethylglycidylamine) hydrochloride (DEGA·Ch) which should react directly with ECH to give the reactive ionic products $RIO_1$ and $RIO_2$ (Scheme 3) and (2) a transformation of DEGA·Ch into a tertiary amine by the reaction with ECH and the simultaneous formation of 1,3-dichloropropanol-2. Support for such assumptions is the transformation of Q into DEGA which was observed by $^1H$-NMR spectra when Q was heated in DMSO at 110°C. An ammonium bisquaternary salt (Bis Q, Experimental Section) results from the reaction of triethylamine with ECH. Also, it is possible to consider that an ammonium bisquaternary salt ($RIO_3$, Scheme 3) results from the reaction of DEGA with ECH.

The formation of products having epoxy groups and $Cl_c$ is one argument for the fact that the reacting species is mainly DEGA·Ch instead of DEGA at a DEA/

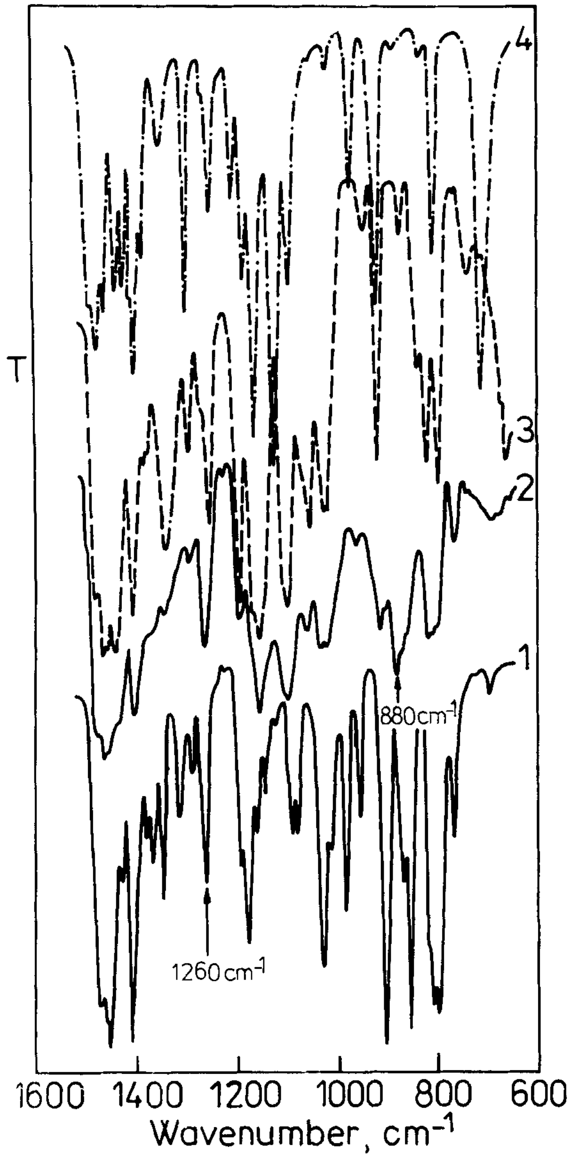

FIG. 4. IR spectra of the products: (1) (triethylglycidyl ammonium) iodide; (2) RIO $M_{19}$ sample (Table 3); (3) (*N,N*-diethyl-2-hydroxy azetidinium) chloride; (4) the product of the reaction of Di-PA with ECH.

ECH molar ratio < 1/4. At DEA/ECH molar ratios higher than 1/6, the reaction between DEGA with ECH probably prevails because the products obtained in these conditions have lower $Cl_c$ values and higher EC values than those from a 1/1 ratio of the $RIO_2$ oligomer molecule.

The general formula of the reactive ionic oligomers resulting from the reaction between DEA and ECH at high ECH/amine molar ratios would be as follows:

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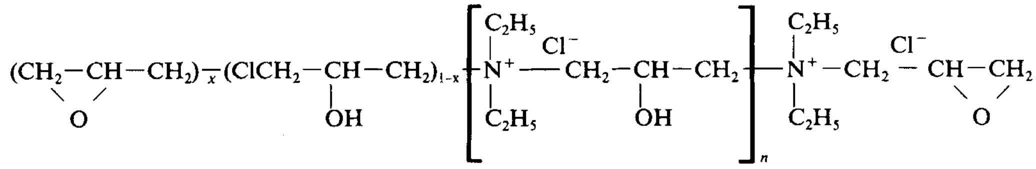

$$(\underset{\diagdown\ O\ \diagup}{CH_2-CH}-CH_2)_{\overline{x}}(ClCH_2-\underset{OH}{CH}-CH_2)_{1-x}\left[\overset{C_2H_5}{\underset{C_2H_5}{N^+}}\overset{Cl^-}{-}CH_2-\underset{OH}{CH}-CH_2\right]_n\overset{C_2H_5}{\underset{C_2H_5}{N^+}}\overset{Cl^-}{-}CH_2-\underset{\diagdown\ O\ \diagup}{CH-CH_2}$$

RIO

A secondary reaction which results in a decrease of EC and $Cl_i$ and an increase of $Cl_c$ with reaction time when the temperature is higher than 60°C (Fig. 6, Table 2) is perhaps the oligomerization of ECH due to the secondary hydroxyl groups of the product $RIO_2$ in Scheme 3. The resulting oligomer $RIO_4$ is given in Scheme 4.

Determination of the structural parameters $n$ and $x$ from the analytical data ($Cl_i$, $Cl_c$, EC) by a method previously used [6] is not possible here because some azetidinium salt Q (or DEGA·Ch) is present in the ionic reaction product RIO.

The conclusions based on the $^1$H-NMR spectra are only approximate because the ionic products are mixtures of components which are difficult to separate. Nevertheless, these spectra are useful for identifying the components and establishing an average composition of the products. As an example, the $^1$H-NMR spectrum of product $M_{15}$ together with the spectrum of compound Q are shown in Fig. 5. The signal assignment for the second spectrum is taken from the literature [12]. Comparison of the two spectra shows the presence of salt Q. This conclusion is supported by both the signal of the OH group and the signals characteristic of the protons of the azetidinium ring. The percentage of salt Q can easily be determined by taking into account the relative intensity of the hydroxyl group signal because its

TABLE 2. Analytical Data for the Reactive Ionic Products Obtained by Reacting Azetidinium Salt Q with ECH at a Q/ECH Molar Ratio of 1/5

| Sample | Temperature, °C | Time, h | Analytical data | | |
|---|---|---|---|---|---|
| | | | $Cl_i$, % | $Cl_t$, % | $Cl_c$, % |
| $Q_1$ | 50 | 2 | 19.90 | 21.97 | 2.07 |
| $Q_2$ | 50 | 4 | 17.40 | 22.88 | 5.48 |
| $Q_3$ | 50 | 6 | 15.76 | 23.58 | 7.82 |
| $Q_4$ | 50 | 8 | 15.23 | 23.43 | 8.20 |
| $Q_5$ | 50 | 10 | 14.54 | 23.89 | 9.35 |
| $Q_6$ | 50 | 12 | 13.73 | 24.83 | 11.10 |
| $Q_7$ | 60 | 1 | 17.59 | 22.54 | 4.95 |
| $Q_8$ | 60 | 2 | 14.81 | 23.38 | 8.57 |
| $Q_9$ | 60 | 3 | 13.57 | 23.85 | 10.28 |
| $Q_{10}$ | 60 | 4 | 12.90 | 24.16 | 11.26 |
| $Q_{11}$ | 60 | 5 | 12.30 | 24.56 | 12.26 |
| $Q_{14}$ | 80 | 1 | 11.77 | 25.41 | 13.64 |
| $Q_{15}$ | 80 | 2 | 11.53 | 25.94 | 14.41 |
| $Q_{16}$ | 80 | 3 | 11.27 | 26.53 | 15.26 |
| $Q_{17}$ | 80 | 4, 5 | 10.67 | 26.77 | 16.10 |
| $Q_{18}$ | 80 | 6 | 10.58 | 27.03 | 17.45 |

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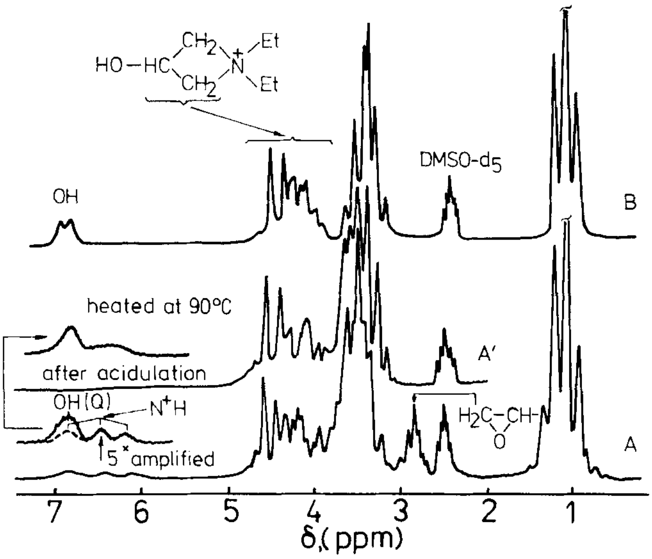

FIG. 5. $^1$H-NMR spectra of azetidinium salt Q (B) and of the product $M_{15}$; (A) the spectrum of a solution in DMSO-$d_6$; (A′) the spectrum of the same solution after acidification with $CF_3COOH$.

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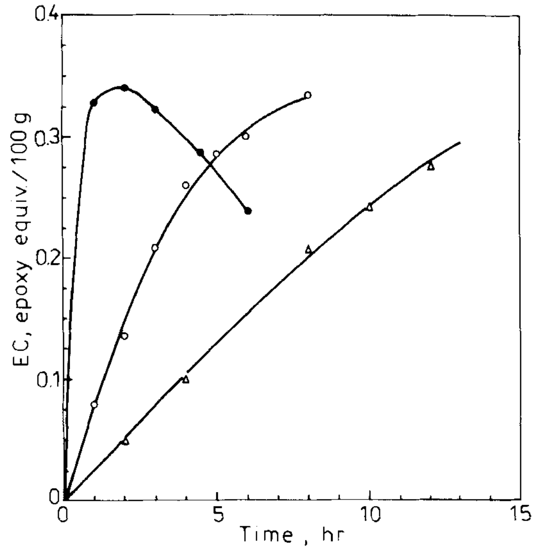

FIG. 6. Dependence of EC on the reaction time of Q with ECH at the molar ratio Q/ ECH = 1/5; (△) 50°C; (○) 60°C; (●) 80°C.

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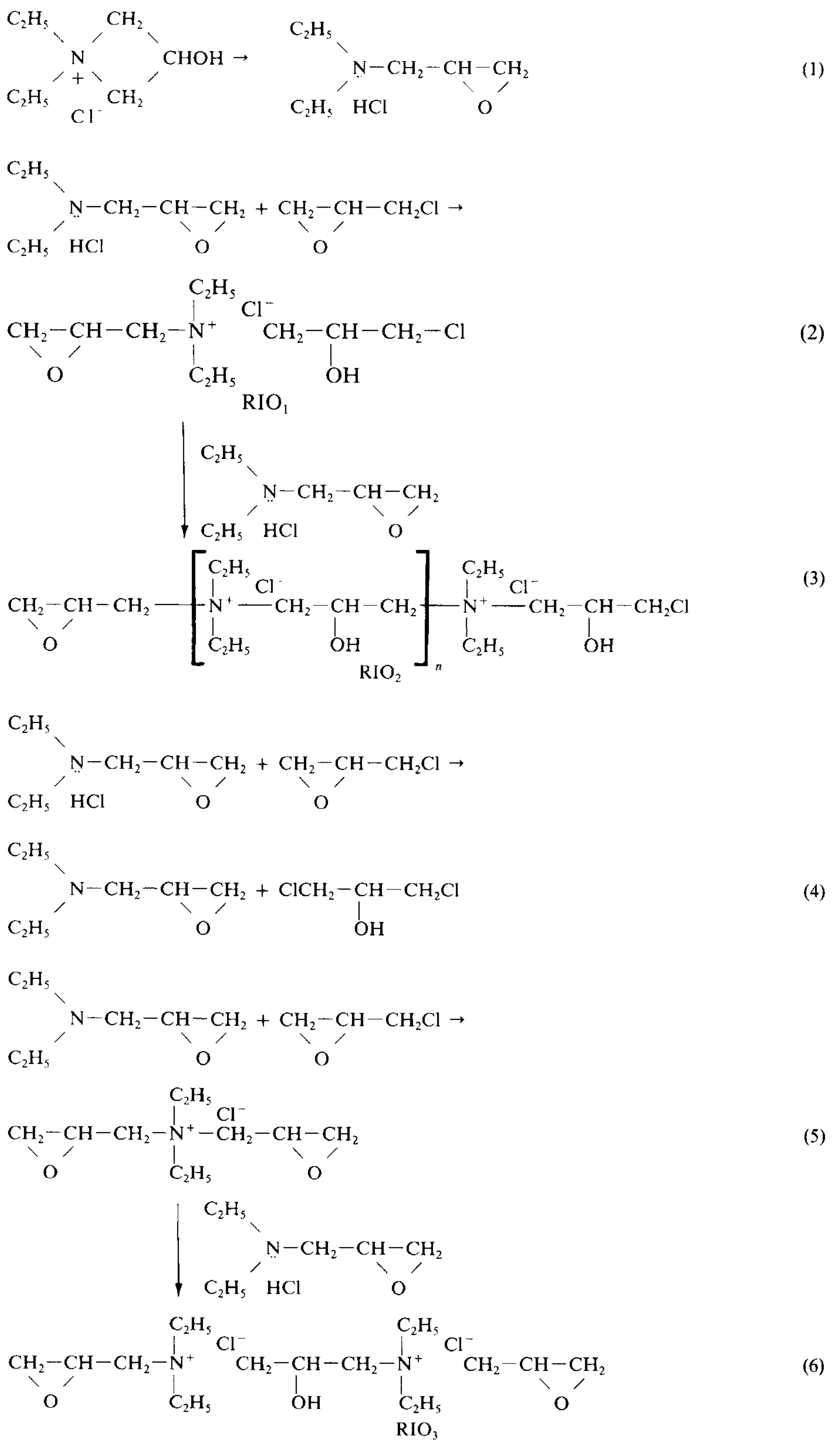

SCHEME 3.

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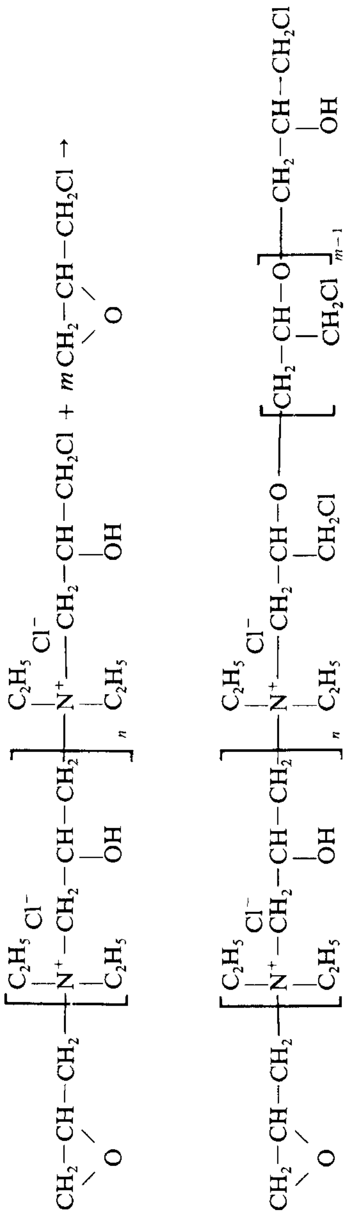

RIO$_4$

SCHEME 4.

proton does not exchange in normal conditions with other labile protons of the main product. Unfortunately, this signal is overlapped by other broad signals for almost all the reaction products. These broad signals were assigned to $^+$NH groups due to their behavior upon heating. A possible reaction compound with the $^+$NH group would be DEGA·Ch. The ratio between compounds Q and DEGA·Ch can be estimated, but with quite low accuracy due to the mentioned overlapping. The data obtained in such a way are given in Table 3.

It can also be noticed from Table 3 that after an initial increase in the amount of Q, a continuous diminution follows as the reaction develops. The same remark concerning DEGA·Ch product is also valid.

In addition, the $^1$H-NMR spectra allow the epoxy groups content to be determined by using the signal at 2.7–3.0 ppm which, as observed from Spectrum A (Fig. 5), disappears at acidulation. The epoxy groups can only be assigned to the compound RIO, which is the main component.

The experimental data obtained by GPC on the molecular weight distribution of the ionic oligomers issued from the reaction of DEA with ECH at 50°C for a DEA/ECH molar ratio of 1/15 at different reaction times are given in Table 4. The average molecular weight is at a minimum after about 8 h reaction time, followed by a slower increase. The minimum value of the average molecular weight corresponds to an *n* value of 0.93.

In order to emphasize the influence of the amine substituent sizes on the reaction products, the reaction between Di-PA with ECH was also carried out (see the Experimental Section). The ionic reaction product was found to contain only $Cl_i$ (18.29%) without epoxy groups. It was expected there would be an azetidinium

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TABLE 3. Data on the Composition of the Ionic Oligomers Calculated from $^1$H-NMR Spectral Analysis

| | Reaction conditions[a] | | | Composition[b] | | |
|---|---|---|---|---|---|---|
| Sample | Reactants | Molar ratio | Time, h | RIO | Q | DEGA·Ch |
| $M_{13}$ | DEA/ECH | 1/15 | 2 | 1 | 1.3 | – |
| $M_{14}$ | DEA/ECH | 1/15 | 4 | 1 | 3.0 | 1.5 |
| $M_{15}$ | DEA/ECH | 1/15 | 6 | 1 | 2.0 | 2.0 |
| $M_{16}$ | DEA/ECH | 1/15 | 8 | 1 | 0.3 | 0.3 |
| $M_{17}$ | DEA/ECH | 1/15 | 10 | 1 | 0.3 | 0.1 |
| $M_{18}$ | DEA/ECH | 1/6 | 7 | 1 | 0.3 | – |
| $M_{19}$ | DEA/ECH | 1/6 | 10 | 1 | 0.25 | – |
| $M_{20}$ | DEA/ECH | 1/6 | 13 | 1 | 0.7 | 0.7 |
| $Q_2$ | Q/ECH | 1/5 | 4 | 1 | 1.8 | 1.8 |
| $Q_3$ | Q/ECH | 1/5 | 6 | 1 | 0.8 | 1.6 |
| $Q_4$ | Q/ECH | 1/5 | 8 | 1 | 0.25 | 0.75 |

[a] Reaction temperature 50°C.

[b] RIO = reactive ionic oligomers; Q = (*N*,*N*-diethyl-2-hydroxy azetidinium) chloride; DEGA·Ch = (*N*,*N*-diethylglycidylamine) hydrochloride.

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TABLE 4. Influence of the Reaction Time on the Molecular Weight to the Oligomers Obtained from the Reaction of DEA with ECH at a DEA/ECH Molar Ratio of 1/15 at 50°C[a]

| | | $M_1$ | | $M_2$ | | $M_3$ | | $M_4$ | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Time, h | $M_w$[b] | $\omega$, %[c] | $M_w$ | $\omega$, % | $M_w$ | $\omega$, % | $M_w$ | $\omega$, % | $\overline{M}_w = \Sigma\omega_i M_{wi}$[d] |
| 2 | 5 | 353.5 | 0.381 | 410.2 | 0.143 | 532 | 0.327 | 894 | 0.142 | 492.3 |
| 3 | 8 | 343.6 | 0.65 | 468.7 | 0.250 | 756 | 0.095 | – | – | 412.3 |
| 4 | 12 | 370 | 0.576 | 403.7 | 0.134 | 479 | 0.189 | 743 | 0.100 | 432.04 |
| 5 | 16 | 398.6 | 0.69 | 523 | 0.173 | 816.6 | 0.137 | – | – | 477.4 |

[a] GPC with water as solvent.

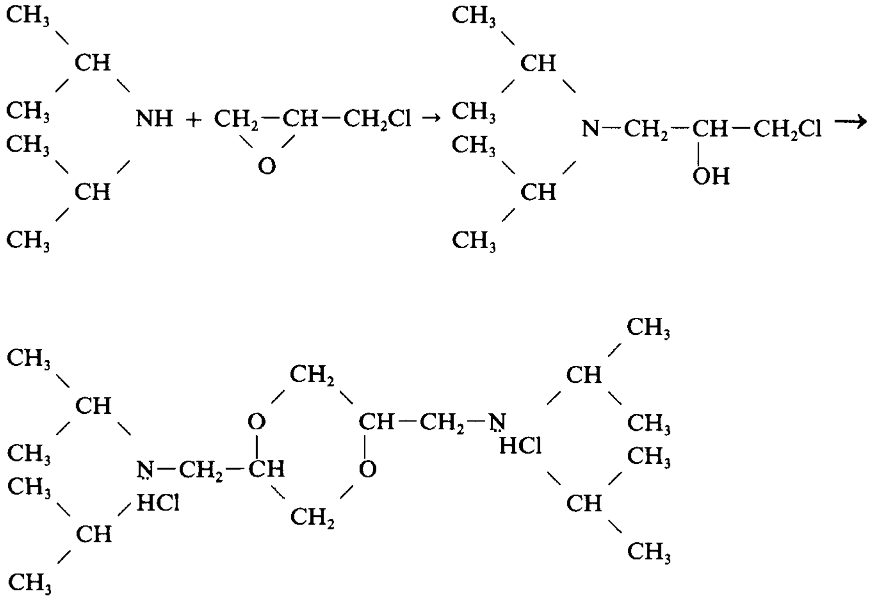
[b] Molecular weight of the $i$ fraction.

[c] Weight fraction.

[d] Average molecular weight of the oligomer.

salt structure similar to compound Q. The elemental analyses were calculated for $C_9H_{20}NOCl$: C, 55.81; H, 10.33; $Cl_i$, 18.25; N, 7.23%. Found: C, 55.54; H, 10.32; $Cl_i$, 18.29; $Cl_c$, 0; N, 6.82%.

The corresponding IR spectrum (Fig. 4, Spectrum 4) shows the following. The adsorption bands which are characteristic of the epoxy groups are absent. There is a band at 920 $cm^{-1}$ which can be assigned to the symmetrical deformation of an ether ring and another one at 1090 $cm^{-1}$ which can arise from the asymmetrical deformation of a dioxanic ring. Absorption bands for the isopropyl group are observed at 1110 and 1390 $cm^{-1}$. Taking into account the above data, we suppose a disubstituted dioxanic structure which can appear according to Scheme 5.



SCHEME 5.

The formation of disubstituted dioxanic rings by the reaction of cyclic secondary amines (morfoline, piperidine) with ECH at an equivalent molar ratio has been noted [9]. A similar structure for the reaction product of diethanolamine and ECH has also been pointed out [14].

## Dependence of the Oligomer Structure on the Reaction Conditions

### Influence of the Temperature

The influence of reaction temperature on the output of products which contain epoxy and chlorohydrine groups is demonstrated when the reaction of DEA with ECH is carried out in EtOH anh. and a DEA/ECH molar ratio of 1/2 (Table 1). The transformation of azetidinium salt Q into reactive products is very slow at 30°C, and the appearance of ionic products possessing $Cl_c$ and the epoxy group is noteworthy after 25 h at 50°C (sample $M_7$).

### Influence of the Solvent

By comparing the analytical characteristics of the ionic products listed in Table 1, it is observed that the values of EC and $Cl_c$ are higher when the reaction is carried out without solvent (experiments $M_8$-$M_{12}$) than when a solvent like EtOH anh. is used (experiments $M_4$-$M_7$).

### Influence of the DEA/ECH Molar Ratio

The value of the DEA/ECH molar ratio influences both the transformation of the azetidinium salt into reactive ionic oligomers and the structures of these oligomers.

DEA/ECH molar ratios of 1/2 (experiments $M_8$-$M_{12}$, Table 1) and 1/4 (Fig. 2) result in ionic products with a $Cl_c$ of 10–11% and a maximum EC of 0.21 epoxy equivalent/100 g, respectively. These data show essential differences compared to those calculated for the $RIO_1$ structure (Table 1). The lower values for $Cl_c$ and EC suggest the presence of products with a structure closer to $RIO_2$ (at $n = 1$; analysis calculated for $C_{17}H_{37}N_2O_3Cl_3$; $Cl_i$, 16.76; $Cl_c$, 8.38; EC, 0.236%). The lower values of $Cl_i$ and EC and the higher value for $Cl_c$ compared to $RIO_2$ proves the presence of oligomers with a higher $Cl_c$ content and a lower epoxy groups content ($RIO_4$-type structures). The reaction products obtained at DEA/ECH molar ratios of 1/6 and 1/15 (Fig. 3) are characterized by much lower $Cl_c$ values and much higher EC values compared to $RIO_2$. These features are for oligomers with $RIO_3$ as the predominant structure (at $n = 1$; analysis calculated for $C_{17}H_{36}N_2O_3Cl_2$: $Cl_i$, 18.34; $Cl_c$, 0; EC, 0.516%) with a $RIO_2$ oligomer mixture. The GPC results for the products obtained at a DEA/ECH molar ratio of 1/15 (Table 4) support the assertion that these have a degree of oligomerization of $\sim 1$.

## CONCLUSIONS

Ionic oligomers with reactive groups can be obtained by the reaction of DEA with ECH.

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Reactive ionic oligomers with a low oligomerization degree ($n \simeq 1$) result when the reaction is carried out at 50°C, without solvent, and by using DEA/ECH molar ratios higher than 1/6. At a DEA/ECH molar ratio of 1/15, after a reaction time of 8 h, an ionic oligomer with predominant 2,3-epoxypropyl groups, an oligomerization degree of $\simeq 1$, and a Q/RIO molar ratio of $\simeq 0.3/1$ results.

The reaction of diisopropylamine, a steric hindered secondary amine, with ECH leads to a disubstituted dioxanic cycle without reactive groups.

## REFERENCES

[1] W. R. Goynes and R. R. Benerito, *J. Appl. Polym. Sci., 36,* 1255 (1988).
[2] I. Simkovic, A. Ebrigerova, and M. Antal, *Ibid., 23,* 1955 (1987).
[3] J. D. McClure, *J. Org. Chem., 35,* 2059 (1970).
[4] D. M. Burness, *Ibid., 29,* 1862 (1964).
[5] J. B. McKelvey, R. R. Benerito, and T. L. Ward, *Ind. Eng. Chem., Prod. Res. Dev., 6,* 115 (1967).
[6] S. Drăgan, V. Bărboiu, L. Ghimici, and Gh. Stoica, *J. Macromol. Sci.—Chem., A28,* 283 (1991).
[7] R. R. Jay, *Anal. Chem., 36,* 667 (1964).
[8] Houben-Weil, *Methoden der Organischen Chemie,* Vol. XI/1, 1957, p. 323.
[9] D. L. Heywood and B. Phillips, *J. Am. Chem. Soc., 80,* 1257 (1958).
[10] C. M. Bruneau and J. Lesec, *Bull. Soc. Chim. Fr.,* p. 3275 (1968).
[11] I. Dobas and J. Eichler, *Chem. Prum. 24/49,* 463 (1974).
[12] J. H. Ross, D. Baker, and A. T. Coscia, *J. Org. Chem., 29,* 824 (1964).
[13] V. R. Gaertner, *J. Org. Chem., 32,* 2972 (1967).
[14] J. B. McKelvey, B. G. Webre, and R. R. Benerito, *J. Org. Chem., 25,* 1424 (1960).

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