Technical

Analysis of Cationic and Amphoteric Surfactants: IV. Structural Analysis of the Amphoteric Surfactants Obtained by the Reaction of 1-(2-Hydroxyethyl)-2-alkyl-2-imidazoline with Ethyl Acrylate

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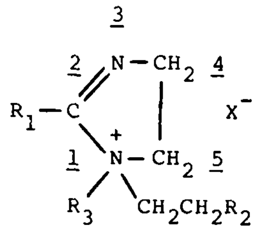
ABSTRACT

Structural analysis of amphoteric surfactants obtained by the reaction of 1-(2-hydroxyethyl)-2-alkyl-2-imidazoline (HEAI) with ethyl acrylate or β-propiolactone has been investigated. These amphoteric surfactants were hydrolyzed under aqueous alkaline media, followed by acid hydrolysis to afford fatty acids and diamine derivatives. By the analysis of the resulting fatty acids, it has been found that ethyl acrylate adds to the carbon atom alpha to an imidazoline ring in the absence of solvent. On the other hand, the resulting diamine derivatives were identified by the isolation and their syntheses, and were quantitatively analyzed by gas chromatography. Based upon the results of their analyses, it has been demonstrated that the reaction products can be divided into three types. In addition, on reaction of HEAI with β-propiolactone, it was found that quaternization at the nitrogen atom of 3-position occurred selectively.

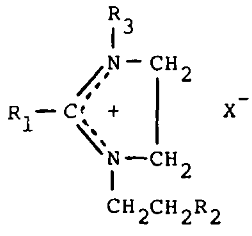
INTRODUCTION

Imidazolinium surfactants have long been believed to have a structure indicated by the formula I, which is presented in the first report of the syntheses of these surfactants by Mannheimer (1). Subsequent studies (2) on these surfactants presented a different structure such as II; however, no clear proof could be made. Recently, Trivedi et al. (3) demonstrated by means of ^1H- and ^{13}C-NMR spectrometry that the main product obtained by the reaction of 1-methyl-2-benzyl-2-imidazoline with methyl bromide or dimethyl sulfate had a symmetrical structure such as **II**.

In the previous paper (4), the authors analyzed the structure of the polyamines obtained by hydrolysis of imidazolinium cationics, and found that quaternization selectively occurred at the 3-nitrogen of an imidazoline ring to afford **II**.



(I)



(II)

$R_1 = C_7H_{15} - C_{17}H_{35}$
$R_2 = OH, OCH_2CH_2COO^-, NHCOR$ etc.
$R_3 = CH_2COO^-, CH_2CH_2COO^-, CH_3, CH_2CH_3$ etc.

On the other hand, it is well known that imidazoline derivatives are labile under aqueous alkaline conditions to give amides such as **III** and **IV** by ring-opening reaction (Scheme 1) (5,6). In the presence of water, especially under alkaline conditions, imidazolinium derivatives such as **II** are not formed, and the reaction of amide, **III** or **IV**, with various quaternization agents occurs. It is, therefore, easily estimated that these reaction products become a complex mixture. Some investigators (2) attempted to analyze these products; however, there were many problems to be studied. The authors tried to identify the structure of these products by analyzing fatty acids and polyamines formed by hydrolysis of these products, since it seems difficult to analyze these products directly.

This paper deals with structural analysis of the products obtained by the reaction of 1-(2-hydroxyethyl)-2-alkyl-2-imidazoline (HEAI) with ethyl acrylate, and also deals with the reaction of HEAI with β-propiolactone.

MATERIALS AND METHODS

Apparatus

^1H- and ^{13}C-nuclear magnetic resonance (NMR) spectra were obtained with JEOL PS-100 and PFT-100 NMR spectrometers (^1H, 100 MHz; ^{13}C, 25 MHz). The other apparatus were similar to those previously described (4).

Hydrolysis Procedures

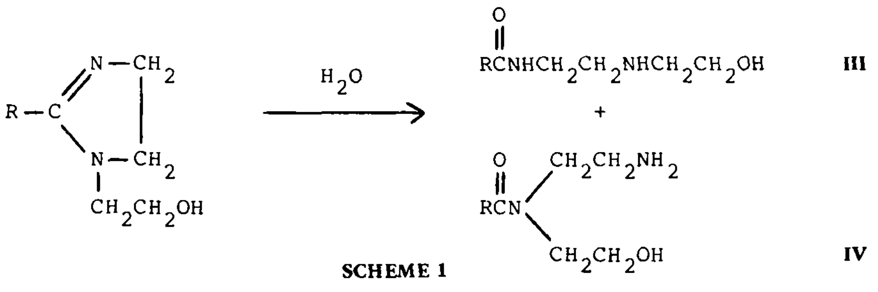
Procedures are similar to those previously described (4).

Analysis of Fatty Acid

Procedures for extraction of fatty acid and for methyl esterification are similar to those previously described (4). Determination of homolog distribution of fatty acid was carried out under the same gas chromatographic conditions as described in the previous paper (4). Analysis of dibasic acid was performed under the conditions indicated in Table I A.

Analysis of Diamine Derivatives

Aqueous layer extracted with ether as described above was concentrated to dryness under reduced pressure, and the residue was extracted with methanol. The extract was concentrated, and the residue was dissolved in ethanol. The solution was saturated with gaseous hydrogen chloride and refluxed for 2 hr. The cooled solution was concentrated to dryness under reduced pressure, and acetic anhydride and pyridine (3 mL each) were added to the residue. The resulting solution was magnetically stirred overnight at room



SCHEME 1

TABLE I

Operating Conditions for Gas Chromatography

	A	B
Instrument	Shimadzu 4CM-PF	Shimadzu 4CM-PF
Column	3% JXR-Silicone on Gas Chrom Q, 60-80 mesh, 2 m X 3 mm i. d., glass	3% OV-17 on Gas chrom Q 80-100 mesh, 1.5 m X 3 mm i. d., glass
Oven Temp.	150-280°C, 10°C/min	230°C
Injection Temp.	280°C	280°C
Detector Temp.	280°C	280°C
Detector	FID (H_2 0.6 Kg/cm^2, Air 1.0 Kg/cm^2)	FID (H_2 0.6 Kg/cm^2, Air 1.0 Kg/cm^2)
Carrier gas	He 40 ml/min	He 40 ml/min

temperature, and then concentrated under reduced pressure. The residue was dissolved in ethanol, neutralized with ammonium carbonate and filtered. The filtrate was concentrated under reduced pressure and analyzed by GC under the conditions shown in Table I B.

Isolation of Dibasic Acid XI

HEAI (R = $C_{11}H_{23}$) was allowed to react with two equivalent mol of ethyl acrylate at 60-65 C for 4 hr, and the product was treated as described above to give fatty acid methyl esters. These esters contained 88.7% of dibasic acid dimethyl ester by GC analysis. This diester was isolated by column chromatography on silica gel (eluent, benzene). Isolated diester was hydrolyzed with 1 N ethanolic potassium hydroxide to afford colorless crystals of dibasic acid **XI**, which was recrystallized from *n*-hexane repeatedly.

XI. Melting point, 58.0-58.5 C; found; C, 66.04%; H, 10.32%; O, 23.61%; calcd. for $C_{15}H_{28}O_4$, C, 66.14%; H, 10.36%; O, 23.49%; IR (neat, cm^{-1}) 1710; ^{1}H-NMR (ppm; solvent, $CDCl_3$) 0.85 (3H, t; CH_3), 1.25 (18H, br. s; $-CH_2-$), 1.9 (2H, m; $\underline{CH}_2CH_2COOH$), 2.4 (2H, t, J = 6 Hz; $\underline{CH}_2COOH$), 2.15-2.55 (1H, m; $\underline{CH}COOH$), 10.5 (2H, br. s; $\overline{COOH}$).

Dimethyl ester of **XI**. IR (neat, cm^{-1}) 1740, 1200, 1160; ^{1}H-NMR (ppm; solvent, $CDCl_3$) 0.85 (3H, t; CH_3), 1.25 (18H, br. s; $-CH_2-$), 1.9 (2H, m; $\underline{CH}_2CH_2COOCH_3$), 2.3 (2H, t, J = 6 Hz; $\underline{CH}_2COOCH_3$), 2.15-2.55 (1H, m; $\underline{CH}COOCH_3$), 3.55 (6H, s; $COOCH_3$); ^{13}C-NMR (ppm; solvent, $CDCl_3$) 14.1 (q), 22.7 (t), 27.3 (t), 29.6 (t), 31.9 (t), 32.0 (t), 32.4 (t), 44.8 (d), 51.5 (q), 173.4 (s), 176.1 (s).; MS m/e (rel. int.) 128 (100), 160 (97), 100 (57), 184 (40), 152 (35), 87 (26), 74 (21), 148 (19), 269 (18, M-31), 83 (18).

Lactonization of Dibasic Acid XI

A mixture of dibasic acid **XI** (1.36 g, 5 mmol), pyridine (0.8 mL, 10 mmol), lead tetraacetate (2.4 g, 5 mmol) and benzene (10 mL) was stirred under nitrogen. On warming, a vigorous reaction with gas evolution began when the bath temperature reached ca. 50 C. When the reaction subsided (2-3 min), the bath temperature was raised and the mixture was maintained at gentle reflux for ca. 1.5 hr. During the course of the reaction a white precipitate, lead acetate, formed. The mixture was cooled, decanted from the lead acetate, and the lead acetate was washed with a small amount of bezene. The combined solution was washed with 10-mL portions of water, 10% sodium carbonate and 2 N hydrochloric acid, and then dried over sodium sulfate. Removal of benzene gave 0.62 g (55% yield) of lactone **XIII**, which was purified by preparative TLC on silica gel to afford 0.52 g of colorless crystals.

Melting point, 27.5-28.0 C; IR (neat, cm^{-1}) 1770; ^{1}H-NMR (ppm; solvent, $CDCl_3$) 0.88 (3H, t; CH_3), 1.36 (16H, br. s; $-CH_2-$), 1.70 (2H, m; $-\underline{CH}_2CH<$), 2.43 (4H, m; $\underline{CH}_2\underline{CH}_2CO-$), 4.9 (1H, m; CH); ^{13}C-NMR (ppm; solvent, $CDCl_3$) 14.1 (q), 22.8 (t), 25.4 (t), 28.1 (t), 28.8 (t), 29.7 (t), 32.0 (t), 35.7 (t), 80.9 (d), 177.0 (s).; MS m/e 226 (M^+; found 226.1962, calcd. for $C_{14}H_{26}O_2$ 226.1962).

Reduction of Lactone XIII

In a 50-mL flask equipped with a reflux condenser, were placed lactone **XIII** (160 mg) and 10 mL of anhydrous ether, and 150 mg of lithium aluminum hydride was added to the solution. The reaction mixture was refluxed for 1 hr, and then cooled. Ethyl acetate was added carefully to the solution, and 2 N sulfuric acid was added to dissolve aluminum oxide. The resulting solution was extracted twice with 50 mL of ether. Ethereal layer was combined, washed with water, dried over sodium sulfate and evaporated under reduced pressure to give 150 mg of diol **XIV** (94% yield), which was recrystallized from *n*-hexane to afford 130 mg of colorless crystals.

Melting point, 55 C; found; C, 72.74%; H, 13.15%; calcd. for $C_{14}H_{30}O_2$, C, 72.99%; H, 13.13%; IR (KBr, cm^{-1}) 3250, 1130, 1110, 1075, 1040; ^{1}H-NMR (ppm; solvent, $CDCl_3$) 0.87 (3H, t; CH_3), 1.24-1.55 (22H, br. s; $-CH_2-$), 2.23 (2H, s; OH), 3.60 (3H, m; $\underline{CH}OH$ and $\underline{CH}_2OH$).

Synthesis of Diamine VI

A solution of 1-(2-hydroxyethyl)-2-methyl-2-imidazoline (10 g) in 50 mL of water was stirred at room temperature overnight. On evaporation of water under reduced pressure, 11.3 g of pale yellow crystals of N-acetyl-N′-hydroxyethylethylenediamine was obtained.

A mixture of the above diamine (500 mg, 3.42 mmol), ethyl acrylate (390 mg, 3.90 mmol) and methanol (0.5 mL) was stirred at room temperature for 5 hr, and then concentrated under reduced pressure. Acetic anhydride and pyridine (1 mL each) was added to the residue, and the resulting solution was stirred at room temperature overnight. After removal of acetic anhydride and pyridine under reduced pressure, preparative TLC of the residue on silica gel gave 780 mg of diacetyl monoethyl ester of **VI** (79.2% yield).

IR (neat, cm^{-1}) 3350, 1730, 1650, 1530, 1240, 1190, 1040; ^{1}H-NMR (ppm; solvent, $CDCl_3$) 1.24 (3H, t, J = 7 Hz; $COOCH_2\underline{CH}_3$), 1.95 (3H, s; Ac), 2.01 (3H, s; Ac), 2.39 (2H, t, J = 7 Hz; $\underline{CH}_2COO$), 2.47 (2H, t, J = 7 Hz; NCH_2), 2.67 (4H, t, J = 7 Hz; NCH_2), 3.23 (2H, dt, J = 5, 7 Hz; $AcNH\underline{CH}_2$), 4.00 (2H, m; $\underline{CH}_2OAc$), 4.07 (2H, q, J = 7 Hz; $COOCH_2$), 6.70 (1H, br. s; $AcN\underline{H}$); MS m/e 288 (M^+; found 288.1710, calcd. for $C_{13}H_{24}N_2O_5$ 288.1685).

Synthesis of Diamine VII

Acetic anhydride (2.45 mg, 24 mmol) was dropped during 15 min to the magnetically stirred solution of N-hydroxyethylethylenediamine (1 g, 9.6 mmol) in 10 mL of methanol, and the solution was allowed to stand for 3 hr at room temperature. Evaporation of methanol and acetic acid under reduced pressure afforded 1.8 g of N,N′-diacetyl-N-hydroxyethylethylenediamine.

Sodium (0.12 g, 5.3 mmol) was added with heating to the above diamine (1 g, 5.3 mmol), and then ethyl acrylate (0.53 g, 5.3 mmol) was added to the reaction mixture, which was kept at 70 C for 5 hr with magnetic stirring. After cooling, a small amount of ethanol was added to the mixture to decompose excess sodium, and then 20 mL of chloroform was added. The solution was filtered, and the filtrate was concentrated. Preparative TLC of the residue on silica gel afforded 0.95 g of diacetyl monoethyl ester of **VII** (62.2% yield).

IR (neat, cm^{-1}) 3300, 1730, 1630, 1250, 1190, 1040; ^{1}H-NMR (ppm; solvent, $CDCl_3$) 1.28 (3H, t, J = 7 Hz; $COOCH_2\underline{CH}_3$), 1.96 (3H, d, J = 2 Hz; Ac), 2.08 (3H, d, J = 2 Hz; Ac), 2.53 (2H, t, J = 7 Hz; CH_2COO), 3.30-3.80 (10H; NCH_2 and OCH_2), 4.11 (2H, q, J = 7 Hz; $COO\underline{CH}_2$-CH_3), 7.10 (1H, br. s; NH); MS m/e 288 (M^+; found 288.1663, calcd. for $C_{13}H_{24}N_2O_5$ 288.1684).

Synthesis of Diamine VIII

Ethyl acrylate (0.53 g, 5.3 mmol) was added to the magnetically stirred solution of N-hydroxyethylethylenediamine (0.5 g, 4.8 mmol) in 0.5 mL of methanol with cooling in an ice bath. After stirring for an additional 3 hr at room temperature, the mixture was concentrated under reduced pressure, and acetic anhydride and pyridine (1 mL each) was added. After standing overnight at room temperature, the mixture was concentrated under reduced pressure. Preparative TLC of the residue on silica gel afforded 1.06 g of triacetyl monoethyl ester of **VIII** (67% yield).

IR (neat, cm^{-1}) 3450, 1730, 1630, 1240, 1190, 1040; ^{1}H-NMR (ppm; solvent, $CDCl_3$) 1.23 (3H, t, J = 7 Hz; $COOCH_2\underline{CH}_3$), 1.90-2.20 (9H, br. s; Ac), 2.56 (2H, t, J = 7 Hz; CH_2COO), 3.33-3.68 (8H; NCH_2), 4.05 (2H, m; $\underline{CH}_2OAc$), 4.10 (2H, q, J = 7 Hz; $COOCH_2$); MS m/e 330 (M^+; found 330.1773, calcd. for $C_{15}H_{26}N_2O_6$ 330.1789).

Synthesis of Diamine IX

Benzyl chloride (259 mg, 2.05 mmol) was added to the solution of N-acetyl-N′-hydroxyethylethylenediamine (300 mg, 3.05 mmol) in 3 mL of ethanol, and the resulting solution was stirred at room temperature overnight. After evaporation of ethanol, the residue was purified by preparative TLC on silica gel to give 180 mg of N-acetyl-N′-benzyl-N′-hydroxyethylethylenediamine (0.66 mmol, 32.2% yield).

This compound was dissolved in 15 mL of 6 N hydrochloric acid, and the solution was refluxed for 4 hr. After concentration, the residue was dissolved in 3 mL of methanol, and passed through Dowex 1X4 (OH^-) column with methanol. Eluate was concentrated to 0.5 mL volume, and then ethyl acrylate (160 mg, 1.6 mmol) was added with magnetic stirring. After standing overnight, the solution was concentrated under reduced pressure, and then the residue dissolved in 3 mL of methanol was hydrogenated in the presence of 50 mg of 10% Pd/C at room temperature and atmospheric pressure overnight to remove the benzyl group. After removal of Pd/C by filtration, the filtrate was concentrated. The residue was dissolved in ethanol saturated with gaseous hydrogen chloride, and refluxed for 1.5 hr. After removal of ethanol, acetic anhydride and pyridine (1 mL each) was added to the residue, and the mixture was left overnight at room temperature. After concentration under reduced pressure, the residue was dissolved in ethanol, and neutralized with ammonium carbonate. Insoluble matter was filtered off, and the filtrate was concentrated under reduced pressure. Preparative TLC of the residue on silica gel gave 60 mg of diacetyl diethyl ester of **IX** (23.5% yield).

IR (neat, cm^{-1}) 3450, 1730, 1640, 1230, 1180, 1040; ^{1}H-NMR (ppm; solvent, $CDCl_3$) 1.20 (6H, t, J = 7 Hz; $COOCH_2\underline{CH}_3$), 2.02 (3H, s; Ac), 2.12 (3H, s; Ac), 2.30-2.80 (10H; NCH_2 and CH_2COO), 3.15-3.75 (4H; $AcN\underline{CH}_2$), 3.90-4.30 (6H; $COOCH_2$ and $\underline{CH}_2OAc$); MS m/e 388 (M^+; found 388.2196, calcd. for $C_{18}H_{32}N_2O_7$ 388.2208).

Synthesis of Diamine X

Sodium (19 mg, 0.82 mmol) was added with heating to 200 mg of N-acetyl ethyl ester of **VII** (0.82 mmol), and then ethyl acrylate (90 mg, 0.9 mmol) was added. The mixture was stirred for an additional 4 hr at 90 C. A small amount of ethanol was added to the cooled mixture to decompose excess sodium. The mixture was dissolved in chloroform, filtered and concentrated under reduced pressure. Preparative TLC of the residue on silica gel gave 35 mg of diacetyl diethyl ester of **X** (12.2% yield).

IR (neat, cm^{-1}) 3350, 1730, 1640, 1540, 1290, 1190, 1040; ^{1}H-NMR (ppm; solvent, $CDCl_3$) 1.23 (6H, t, J = 7 Hz; $COOCH_2\underline{CH}_3$), 1.93 (3H, s; Ac), 2.30-2.90 (10H; NCH_2 and CH_2COO), 3.10-3.70 (6H; $NH\underline{CH}_2$ and OCH_2), 4.04 (4H, q, J = 7 Hz; $COO\underline{CH}_2CH_3$), 6.90 (1H, br. s; NH); MS m/e 346 (M^+; found 346.2084, calcd. for $C_{16}H_{30}N_2O_6$ 346.2102).

RESULTS AND DISCUSSION

Syntheses of Diamine Derivatives

On reaction of HEAI with ethyl acrylate in the absence of water, the reaction products have an imidazoline ring. However, hydrolysis of ester is carried out in order to obtain amphoteric surfactant. This subsequent hydrolysis of ester affords the ring-opening products, mono- and disubstituted amides, since imidazoline derivatives are labile under aqueous alkaline media (5,6).

The ring-opening reaction of imidazoline may occur in two directions, between the 1 and 2 or 2 and 3 positions of an imidazoline ring, and each cleavage gives amide **III** or **IV**, respectively. The ratio of **III** to **IV** varies with hydrolysis conditions such as pH, etc. Therefore, reaction of ethyl acrylate with **III** and **IV** occurs simultaneously to give a complex mixture, when HEAI is allowed to react with ethyl acrylate in the presence of water. Since direct structural analysis of these complex mixtures seemed to be difficult, the authors tried to analyze and identify the hydrolysis products of these surfactants, fatty acids and diamine derivatives.

Amphoteric surfactants synthesized under various conditions were hydrolyzed, and the corresponding fatty acids and diamine derivatives were obtained. The resulting diamine derivatives were esterified with ethanol-hydrogen chloride, acetylated and then isolated by preparative TLC on silica gel. Structural analysis of these isolated compounds suggested the presence of various diamine derivatives, which were shown in Figure 1. The diamine derivatives estimated from the reactivity of ethyl acrylate to HEAI were also indicated in Figure 1. These diamine derivatives were synthesized by the scheme shown in Figure 1, and used as the standard samples for the following studies.

Analysis of Diamine Derivatives by GC

Since diamines, V-X, are polar and nonvolatile compounds, derivatization to volatile compounds is required for GC analyses. Therefore, these compounds were acetylated after ethyl esterification in the same way as the analysis of amino acids. These diamine derivatives could be separated completely by the use of OV-17 as a GC column, as shown in Figure 2. Under these conditions, these diamine derivatives were determined with satisfactory repeatability, 3-7% of standard deviation. Incidentally, diamine X was analyzed at a column temperature higher by 20 C than usual operating conditions; however, it could not be detected from any products synthesized under various conditions.

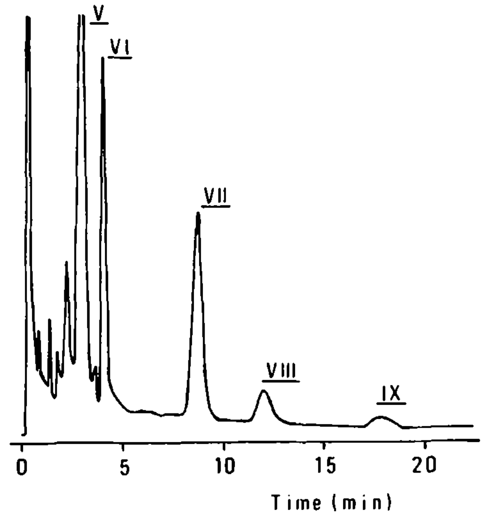


FIG. 2. Typical gas chromatogram of diamine derivatives.

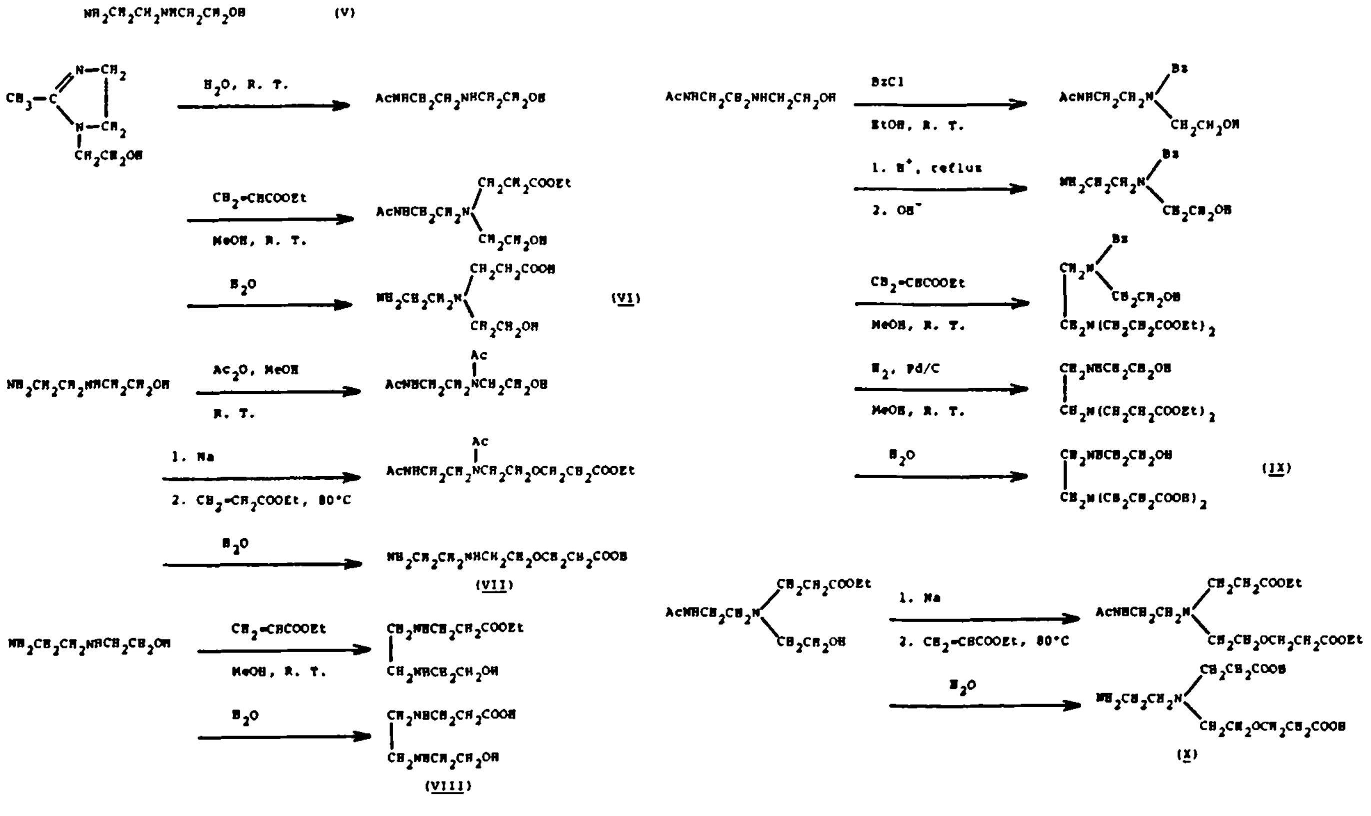
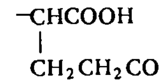


FIG. 1. Scheme for syntheses of diamine derivatives.

Structural Analyses of the Products Obtained by the Reaction of HEAI with Ethyl Acrylate in the Absence of Solvent

HEAI ($R = C_{11}H_{23}$) was allowed to react with two equivalent mol of ethyl acrylate in the absence of solvent at 60-65 C for 4 hr, and the product was hydrolyzed as described in the experimental section to give fatty acids and diamines. Figure 3 shows the gas chromatogram of the fatty acid methyl esters, and revealed two peaks, one of which is a usual reaction product, methyl laurate. The unknown compound eluted at 6.7 min in Figure 3 was isolated by column chromatography on silica gel, and then was hydrolyzed to afford colorless crystals of **XI** with a molecular formula of $C_{15}H_{28}O_4$.

^{1}H-NMR spectrum of methyl ester of **XI** revealed a singlet at 3.35 ppm assigned to two $COOCH_3$ groups, and its ^{13}C-NMR spectrum also showed the presence of two carbonyl carbons at 173.4 and 176.1 ppm. These results indicated that **XI** was a dibasic acid. Further, a signal at 44.8 ppm (d) on ^{13}C-NMR spectrum could be assigned to a methine carbon alpha to a carboxyl group. In the ^{1}H-NMR spectrum, a multiplet at 1.9 ppm (2H) coupled with a triplet at 2.3 ppm, which was assigned to a methylene group alpha to a carboxyl group. These results suggested that **XI** had a partial structure indicated below.



$$\begin{array}{l} -CHCOOH \\ \;\;| \\ \;\;CH_2CH_2COOH \end{array}$$

The above structure was also suggested by the mass spectrum of methyl ester of **XI**, in which two base peaks were observed at m/e 128 and 160. These peaks could be assigned to

$$(O \equiv CCHCH_2CH_2COOCH_3)^{+}.$$
and
$$(H_3COOCCHCH_2CH_2COOCH_3 + H)^{+}.$$

respectively. From these results, the structure of **XI** was deduced as shown in Figure 4. Further evidence was obtained as described below.

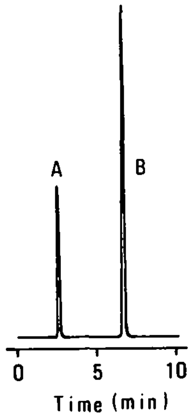


FIG. 3. Gas chromatogram of fatty acid methyl esters. (A) Methyl laurate, (B) dimethyl ester of dibasic acid XI.

On reaction of **XI** with lead tetraacetate in benzene in the presence of pyridine under reflux conditions, **XI** gave five-membered lactone, which was indicated by an absorp-

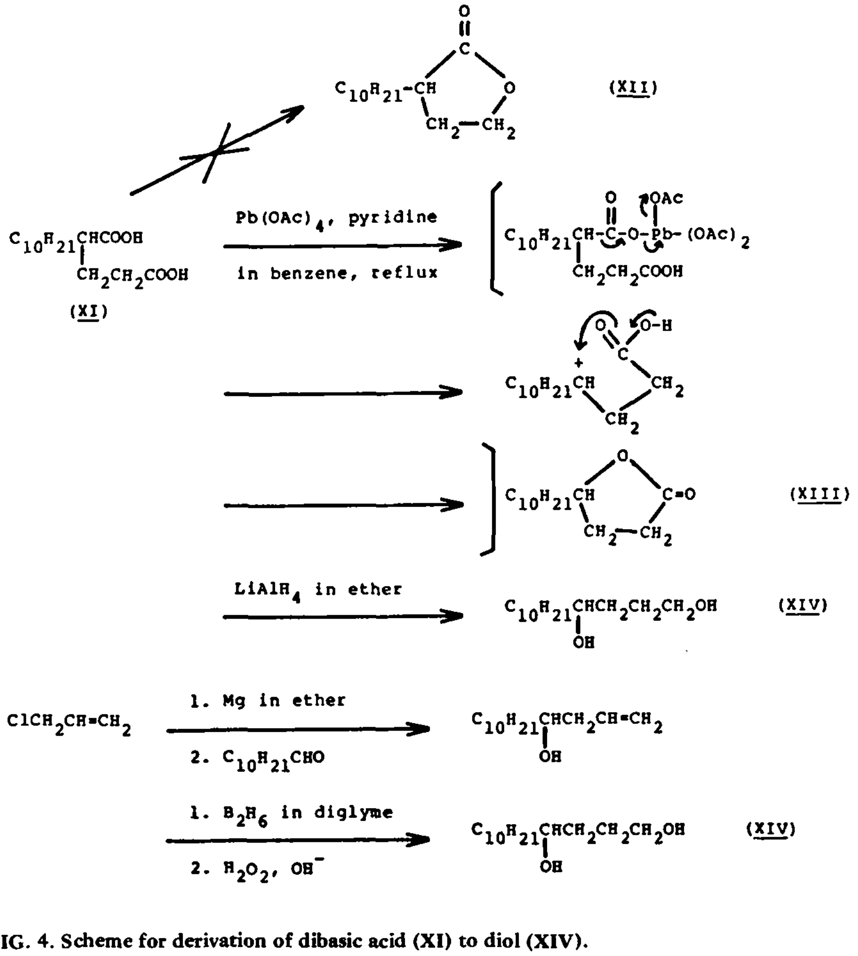


FIG. 4. Scheme for derivation of dibasic acid (XI) to diol (XIV).

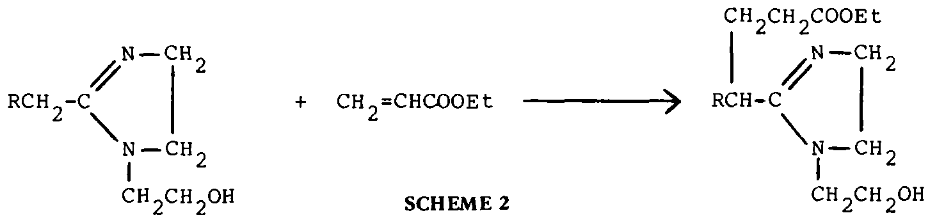
tion band at 1770 cm^{-1} on the IR spectrum. Since GC analysis of the lactone gave a single peak, it was considered that **XII** or **XIII** was selectively formed. ^{13}C-NMR spectrum of the lactone revealed three peaks at 177.0 (s), 80.9 (d) and 35.7 (t) ppm, and these peaks could be assigned to $\underline{C}=O$, $COO\underline{C}H$ and $\underline{C}H_2COO$, respectively. These results indicated that the lactone had a structure of **XIII**, which was formed selectively by the ionic mechanism as shown in Figure 4. Furthermore, reduction of **XIII** with lithium aluminum hydride in ether gave a diol **XIV**, which was identified by comparing various spectral data with the authentic compound synthesized as shown in Figure 4. As a result, the structure of a dibasic acid was established as **XI**. These facts showed that ethyl acrylate added to the carbon atom alpha to an imidazoline ring as indicated in Scheme 2. It can be estimated that this reaction proceeds by a similar mechanism to the Michael reaction, since HEAI is a strong enough base to generate a carbanion at the carbon atom alpha to an imidazoline ring.

Reaction of HEAI with Ethyl Acrylate in the Absence of Solvent

HEAI (R = $C_{11}H_{23}$) was allowed to react with ethyl acrylate in the absence of solvent, and the products were treated and analyzed as described in the experimental section. The results were shown in Table II, where **V** and **VII** were detected as the main diamines. Dibasic acid **XI** was also obtained in 60-94% yields.

On the assumption described below, reaction products and each content were estimated as shown in Table III. (a) The content of each compound is calculated based on the peak area percent in Table II. (b) Diamine **V** is all derived from unreacted HEAI. (c) The reactivity of HEAI does not change by the addition of ethyl acrylate to the carbon atom alpha to an imidazoline ring. That is, the content of α-acrylated product can be calculated based on the peak area percent of dibasic acid. (d) Since ethyl acrylate does not attack directly at the nitrogen atom of the imidazoline ring under these conditions, the diamines except **V** and **VII** are derived from the products by the reaction of ethyl acrylate with amide, **III** or **IV**.

As shown in Table III, in the case of the reaction of HEAI with ethyl acrylate in the absence of solvent, α-acrylated product is formed preferentially, and this reaction proceeds over 90% in the presence of excess of ethyl acrylate. The addition of ethyl acrylate to hydroxyethyl group was also observed in the extents of 30-40%, while the etherification did not occur in the absence of a strong base such as sodium, as shown in the synthesis of **VII**. Therefore,



SCHEME 2

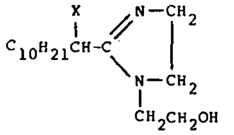
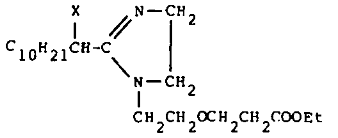
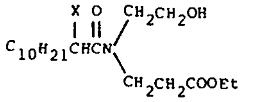
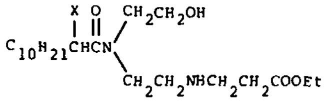
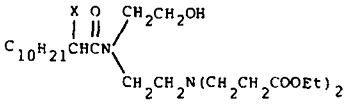
TABLE II

Results of GC Analysis of the Products Obtained by the Reaction of HEAI with Ethyl Acrylate in the Absence of Solvent

Compound		GC peak area % 1.0	2.0	3.0
		(Ethyl acrylate mol)		
CH_2NH_2 $CH_2NHCH_2CH_2OH$	(V)	49.7	61.9	62.7
CH_2NH_2 $CH_2N(CH_2CH_2OH)(CH_2CH_2COOH)$	(VI)	2.5	5.2	0.3
$CH_2NHCH_2CH_2NH_2$ $CH_2OCH_2CH_2COOH$	(VII)	41.8	22.0	33.7
$CH_2NHCH_2CH_2COOH$ $CH_2NHCH_2CH_2OH$	(VIII)	4.1	6.5	2.7
$CH_2N(CH_2CH_2COOH)_2$ $CH_2NHCH_2CH_2OH$	(IX)	1.9	4.4	0.6
$C_{10}H_{21}CHCOOH$ CH_2CH_2COOH	(XI)	60.9	88.7	93.7

TABLE III

Estimated Products from the Reaction of HEAI with Ethyl Acrylate in the Absence of Solvent

Compound		Composition %		
		1.0	2.0	3.0
		(Ethyl acrylate mol)		
	X=H	19.4	7.0	4.0
	X=CH_2CH_2COOEt (XV)	30.3	54.9	58.7
	X=H	16.3	2.5	2.1
	X=CH_2CH_2COOEt (XVI)	25.5	19.5	31.6
	X=H	1.0	0.6	0.02
	X=CH_2CH_2COOEt	1.5	4.6	0.28
	X=H	1.6	0.7	0.2
	X=CH_2CH_2COOEt	2.5	5.8	2.5
	X=H	0.7	0.5	0.04
	X=CH_2CH_2COOEt	1.2	3.9	0.56

it could be estimated that the hydroxy proton of HEAI has a somewhat higher acidity than usual for alcohols, and that the reaction was a characteristic one of the imidazoline ring.

Small amounts of **VI**, **VIII** and **IX** were also observed, as shown in Table II. These were estimated to be derived from the amides shown in Table III. Consequently, under these conditions, **XV** and **XVI** were main products, as shown in Table III.

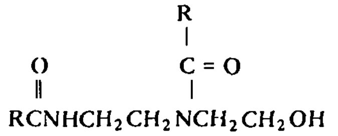
Reaction of HEAI with Ethyl Acrylate in the Presence of Water

In the case of the synthesis of imidazolinium amphoterics in the presence of water, the reaction of HEAI with ethyl acrylate can be divided into two types: (a) reaction of HEAI with ethyl acrylate in the absence of water, followed by hydrolysis of ester; and (b) reaction of HEAI with ethyl acrylate after or with hydrolysis of HEAI, followed by hydrolysis of ester.

Under these conditions, different products from those described in the preceding section could be expected. These reaction products were analyzed as shown in the experimental section and the results are shown in Table IV.

From the reaction products of condition (a), dibasic acid **XI** was detected to the extent of 60-70%, and etherified diamine **VII** was detected to the extent of 10-30% (type I). On the other hand, dibasic acid was scarcely detected under the conditions of (b); however, two types were observed. One gave **VI** as a main diamine (type II), and the other gave **VIII** and **IX** as the main diamines (type III).

On the assumption described below, reaction products and their contents were estimated as shown in Table V. (a) The content of each compound is calculated based on the peak area percent in Table IV. (b) The reactivity of HEAI does not change by the addition of ethyl acrylate to the carbon atom alpha to an imidazoline ring. (c) Under these conditions, an imidazoline ring is completely hydrolyzed to give amides. (d) Diamine **V** is all derived from amide **III**, since amide **IV** is known to isomerize to **III** under alkaline conditions. In addition, diamide **XXX** may be present (2).



$$\overset{O}{\overset{\|}{RC}}NHCH_2CH_2\underset{}{\overset{\overset{R}{|}}{\overset{C=O}{\overset{|}{N}}}}CH_2CH_2OH$$

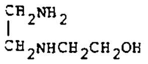
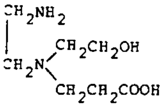
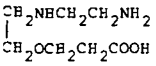
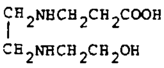
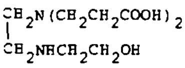
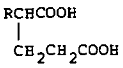
XXX

As shown in Table V, the reaction products of type I have the most complicated composition among various imidazolinium amphoterics. It is characteristic of type I that α-acrylated amides are chiefly observed, and that the etherified products such as **XX** and **XXI** are also formed. However, addition reaction to α-position and etherification only proceeded to the extent of 60-70% and 10-30%, respectively, perhaps because of the short reaction time.

In the case of type II, ethyl acrylate was allowed to react with hydrolysis products of HEAI. Hydrolysis of HEAI under alkaline conditions afforded monosubstituted amide **III**, since disubstituted amide **IV** isomerized to **III**. Therefore, in the case of type II, the reaction of **III** with ethyl acrylate preferentially occurred to afford monosubstituted

TABLE IV

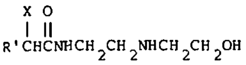
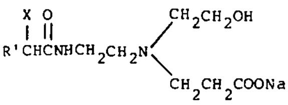
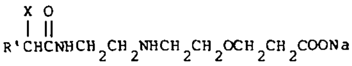
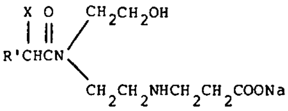
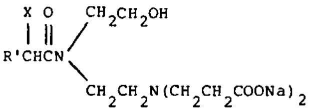
Results of GC Analysis of the Products Obtained by the Reaction of HEAI with Ethyl Acrylate or β-Propiolactone under Various Conditions

Compound		GC peak area %					
		Type-I		Type-II		Type-III*	β-propiolactone
		1.	2.*	1.	2.*		
 $\begin{array}{l}CH_2NH_2\\ \vert\\ CH_2NHCH_2CH_2OH\end{array}$	(V)	15.9	40.2	17.0	26.6	4.4	33.6
 $\begin{array}{l}CH_2NH_2\\ \vert\quad\ \ CH_2CH_2OH\\ CH_2N\\ \quad\ \ CH_2CH_2COOH\end{array}$	(VI)	53.1	21.2	79.7	63.8	7.6	2.0
 $\begin{array}{l}CH_2NHCH_2CH_2NH_2\\ \vert\\ CH_2OCH_2CH_2COOH\end{array}$	(VII)	8.8	29.8	0.1	-	-	0.4
 $\begin{array}{l}CH_2NHCH_2CH_2COOH\\ \vert\\ CH_2NHCH_2CH_2OH\end{array}$	(VIII)	10.3	6.3	0.9	5.4	47.5	63.1
 $\begin{array}{l}CH_2N(CH_2CH_2COOH)_2\\ \vert\\ CH_2NHCH_2CH_2OH\end{array}$	(IX)	11.9	2.5	2.4	4.2	40.5	0.8
 $\begin{array}{l}RCHCOOH\\ \vert\\ CH_2CH_2COOH\end{array}$	(XI)	62.4	60.1	-	-	0.8	-

* Commercial imidazolinium amphoteric surfactants.

TABLE V

Estimated Products from the Reaction of HEAI with Ethyl Acrylate under Various Conditions

Compound			Composition %				
			Type-I		Type-II		Type-III*
			1.	2.*	1.	2.*	
 $\begin{array}{l}X\ O\\ \vert\ \Vert\\ R'CHCNHCH_2CH_2NHCH_2CH_2OH\end{array}$	X=H	(III)	6.0	16.0	17.0	26.6	4.27
	$X=R_1$	(XVII)	9.9	24.2	-	-	0.03
 $\begin{array}{l}X\ O\qquad\qquad\quad CH_2CH_2OH\\ \vert\ \Vert\\ R'CHCNHCH_2CH_2N\\ \qquad\qquad\qquad\quad CH_2CH_2COONa\end{array}$	X=H	(XVIII)	20.0	8.5	79.7	63.8	7.54
	$X=R_1$	(XIX)	33.1	12.7	-	-	0.06
 $\begin{array}{l}X\ O\\ \vert\ \Vert\\ R'CHCNHCH_2CH_2NHCH_2CH_2OCH_2CH_2COONa\end{array}$	X=H	(XX)	3.3	11.9	0.1	-	-
	$X=R_1$	(XXI)	5.5	17.9	-	-	-
 $\begin{array}{l}X\ O\quad CH_2CH_2OH\\ \vert\ \Vert\\ R'CHCN\\ \qquad\quad CH_2CH_2NHCH_2CH_2COONa\end{array}$	X=H	(XXII)	3.9	2.5	0.9	5.4	49.1
	$X=R_1$	(XXIII)	6.4	3.8	-	-	0.4
 $\begin{array}{l}X\ O\quad CH_2CH_2OH\\ \vert\ \Vert\\ R'CHCN\\ \qquad\quad CH_2CH_2N(CH_2CH_2COONa)_2\end{array}$	X=H	(XXIV)	4.5	1.0	2.4	4.2	40.2
	$X=R_1$	(XXV)	7.4	1.5	-	-	0.3

$R_1=CH_2CH_2COONa$

* Commercial imidazolinium amphoteric surfactants.

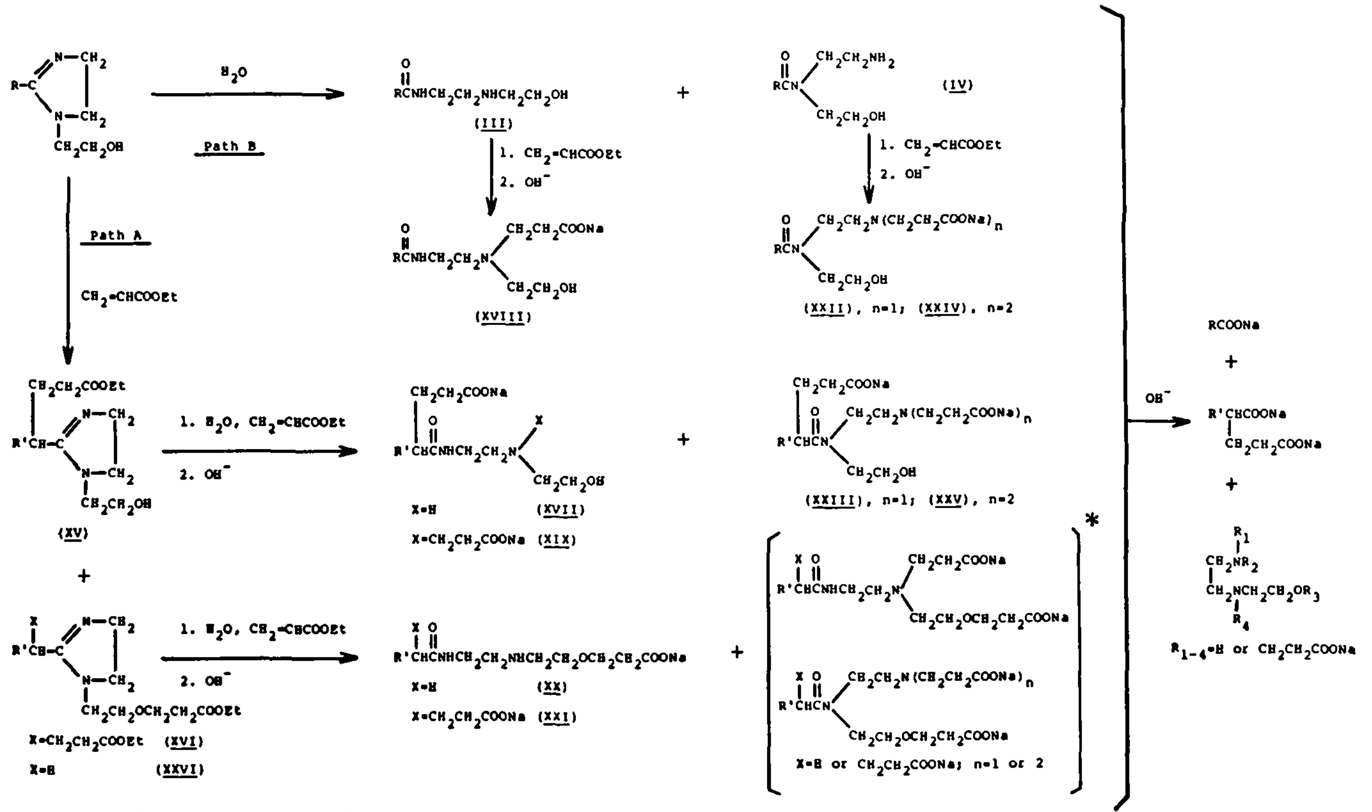


FIG. 5. Reaction pathways and products. * Not detected.

amide **XVIII** in 60-80% yields as shown in Table V. Addition to α-position and etherification with ethyl acrylate was not observed, which indicated that both reactions were characteristic of imidazoline derivatives.

Type III is a commercial product, which is characterized by the presence of disubstituted amides **XXII-XXV** over 90%. In this product, addition to α-position was observed to a slight extent, however, etherification was not. Therefore, it was estimated that type III was synthesized under the conditions where the disubstituted amide **IV** was predominantly formed.

As described above, the amphoteric surfactants synthesized under various conditions could be analyzed. However, it was found that hydrolysis of amides simultaneously occurred during the reaction, since 5-10% of fatty acid was extracted with ether from the reaction products after acidification with hydrochloric acid.

Based upon the results of structural analyses of the various reaction products, these could be divided into three types indicated below. The estimated reaction scheme is summarized in Figure 5.

Type I. Type I has the most complicated composition, and is synthesized through path A. This type is characterized by the presence of α-acrylated and etherified products such as **XX** and **XXI**.

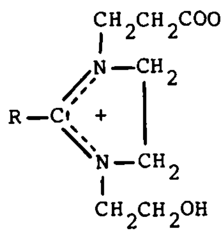
Type II. Type II is synthesized through path B, and hydrolysis of HEAI is carried out under aqueous alkaline conditions. This is characterized by the absence of α-acrylated and etherified products, and contains monosubstituted amide **XVIII** as the main product.

Type III. This type contains disubstituted amides **XXII** and **XXIV** as the main products, and also contains a small amount of α-acrylated product.

Reaction of HEAI with β-Propiolactone

Reaction of HEAI with β-propiolactone seems to be different from that of HEAI with ethyl acrylate, since β-propiolactone reacts with tertiary amine to give quaternary ammonium salt. HEAI (R = $C_{11}H_{23}$) was allowed to react with 1.1 equivalent mol of β-propiolactone at 80 C in the absence of solvent, and the products were analyzed as previously described.

As shown in Table IV, dibasic acid was not detected, and diamine **VIII** was obtained in 63.1% yield. Since an imidazoline ring is not hydrolyzed under these conditions, it can be considered that the main product is **XXVII**, indicated below. These results indicated that quaternization of an imidazoline ring selectively occurred at the nitrogen of the 3-position—the kinetically favored position in terms of the steric hindrance and the stability of product by delocalization of a positive charge (4).



XXVII

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