Hydroxyalkylation of Parabanic Acid. II. Reactions of Parabanic Acid with Oxiranes

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ABSTRACT: Reactions of parabanic acid with ethylene oxide, propylene oxide, or glycerin epichlorohydrin were studied at the initial molar ratios of reagent ranging from 1 : 1 to 1 : 8. The effects of catalyst presence and temperature on the course of reaction were analyzed. The conditions were established at which the parabanic acid ring was preserved and those at which it opened to form polymeric products. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 317–326, 2004

Key words: heteroatom-containing polymers; addition polymerization; structure

INTRODUCTION

There is virtually no information on the synthesis of monomers containing parabanic acid rings (trioxoimidazolidine rings) in their structure. An exception is the hydroxymethyl derivatives obtained in reactions of this acid with formaldehyde.[1–3] On the other hand, it is well known that polymers with trioxoimidazolidine rings have an enhanced thermal stability,[4] mechanical strength,[5,6] resistance against abrasion, elasticity, and good adhesion to metals and glass.[7,8] They can be used in manufacturing of foams, films, or fibers[9]; construction elements; electro-insulating coatings[10]; coatings and adhesives for laminates[11–14]; and coatings for metallic and ceramic surfaces.[9,10,15]

The polymers containing trioxoimidazolidine rings were not prepared from parabanic acid (PA) or its derivatives. The rings were introduced into polymer structure by closing them during polymerization of cyanoformamidyl isocyanate,[16,17] in reaction of alkyl disocyanates with bis(oxoamidesters),[18,19] or by modifying certain polymers (e.g., polyureas, with oxalic chloride).[20–22]

In literature, we have not found any data on reactions of parabanic acid with oxiranes either. One can find information on *N*-hydroxyalkylation of heterocyclic compounds of similar structure, but other than PA[23–27] (e.g., barbituric acid, uracil, dihydrouracil, hydantoin or derivatives thereof of general formula **I**)

(I) ⟶ **(II)**   (1)
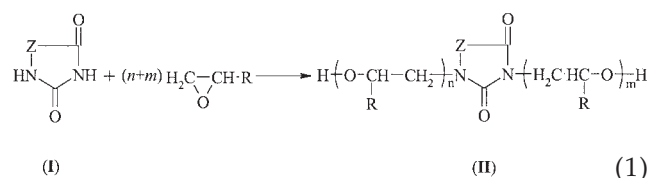
where R = H—, CH$_3$—, and
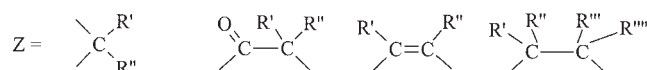
with R', R″, R‴, R″″′ representing H—, alkyl, cycloalkyl, or substituted phenyl group.

Most commonly, tetraethylammonium chloride, tertiary amines, alkali metal halides (LiCl, NaCl), or Lewis' acids (AlCl$_3$, SbCl$_5$, SnCl$_4$, FeCl$_3$, ZnCl$_2$, or BF$_3$) were used as catalysts.[25–27] To obtain compound **II,** where $n + m$ was higher than 2, a simple diol was used (i.e., with $n = m = 1$) and then supplementary oxirane molecules were added successive to its terminal hydroxyl groups. The thus obtained diols were used as semiproducts in syntheses of polyesters, polyurethanes, or glycidyl ethers. The final products were adhesives, components of coatings, laminates, etc.[25–27]

In this article, we report on the attempts to introduce trioxoimidazolidine rings into polymeric structure in a more direct way than those described in literature. We started with preparation of suitable monomers by reacting parabanic acid with some oxiranes. The oxiranes were ethylene oxide, propylene oxide, or glycerin epichlorohydrin.

EXPERIMENTAL

Reactions of parabanic acid with oxiranes

Synthesis of *N*-(2-hydroxyalkyl) hydroparabanates

In a 100-cm^3 autoclave, 11.4 g (0.1 mol) of PA prepared as described in ref. [28] was placed along with 0.4 cm^3 triethylamine, pure, Avocado, Heysham, Germany (TEA; 0.03 mol/mol PA) and 4.4 g (0.1 mol) ethylene oxide, pure, Fluka, Buchs, Switzerland (EO) or 5.8 g (0.1 mol) propylene oxide, pure, Fluka, Buchs, Switzerland (PO). The reaction mixture was mixed with a

magnetic stirrer and heated to 40°C. PA initially dissolved in oxirane to yield a homogeneous solution and then the respective hydroparabanate was precipitated. The reaction was considered completed when a small amount withdrawn from the autoclave (free of unreacted EO and traces of TEA) kept a constant weight on an analytical balance and its epoxy number was zero. The product was purified by recrystallization from isopropyl alcohol, pure p.a., POCh, Gliwice, Poland (for reactions with EO) or from butyl alcohol, pure, POCh, Gliwice, Poland (for reactions with PO).
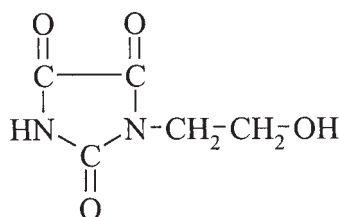
N-(2-hydroxyethyl) hydroparabanate (HEHP); yield 90%; melting point (mp) 197–198°C; EA %: Calcd.: C: 37.97; H; 3.80; N: 17.72. % Found: C: 38.35; H: 3.71; N: 17.27; MS, *m/z* = 159 [(M + 1)$^+$, 1%, 158 (M$^+$, 1%), 114 (12%), 99 (35%), 89 (25%), 86 (28%), 72 (88%), 69 (65%), 58 (80%), 45 (36%), 41 (99%); IR (KBr), [cm^{-1}]; 3500–3100 (m, —N—H and —O—H, stretch.), 2965 (w, —CH$_2$—, asym. stretch.), 2898 (w, —CH$_2$—, sym. stretch.), 1735 (s, C=O, stretch.), 1450–1432 (m, —CH$_2$—, sciss.), 1387 (m, —N—H, deform.), 1160 (m, —N—H, deform.), 1062 (m, —O—H, deform.), 985(w, —N—H, deform.); ^{1}H-NMR (d$_6$-DMSO), [δ ppm]; 3,5 (4H, s, —N—C*H$_2$*—C*H$_2$*—O—), 7–9 (2H, —OH and —NH).
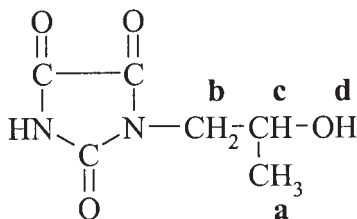
N-(2-hydroxypropyl) hydroparabanate (HPHP); yield 75%; mp: 154–155°C; EA %: Calcd.: C: 41.86; H: 4.99; N: 16.28. % Found: C: 41.47; H: 5.02; N: 16.39; IR (KBr), [cm^{-1}]; 3500–3100 (m, —N—H and —O—H, stretch.), 2948 (w, CH$_3$— and —CH$_2$—, asym. stretch.), 2875 (w, CH$_3$— and —CH$_2$—, sym. stretch.), 1752 (s, C=O, stretch.), 1446–1412 (m, —CH$_2$—, sciss.), 1386 (m, —N—H, deform.), 1130 (m, —N—H, deform.), 1116 (m, —O—H, deform.), 985 (w, —N—H, deform.); ^{1}H-NMR (d$_6$-DMSO), [δ ppm]; 1.0 (3H, d, CH$_3$—, J$_{ac}$ = 6,8 Hz), 3.35 (2H, d, —CH$_2$—, J$_{bc}$ = 5.7 Hz), 3.85 (1H, sext., —CH—, J$_{ca,cb}$ = 5.8 Hz), 3.6–5.5 (2H, —OH and —NH).

### Synthesis of *N,N'*-bis(2-hydroxyalkyl) parabanates

The synthesis of the derivatives was described in detail in ref. [29].

Reactions of parabanic acid with glycerin epichlorohydrin (ECH)

To a 100-cm^3 three-necked flask equipped with mechanical stirrer and reflux condenser, 5.7 g (0.05 mol)

PA and 9.25 g or 18.5 g ECH (glycerin epichlorohydrin, pure, Aldrich, Steinheim, Great Britain) (the molar ratios of reagents were 1 : 2 or 1 : 4, respectively) were added. The reacting mixture was heated to 110–114°C while stirring. The extent of reaction was monitored by measuring epoxy and acid numbers.

N,N'-bis(3-chloro-2-hydroxypropyl) parabanate (BCHPP); yield: 95%; EA % Calcd. C: 36.42; H: 4.01; N: 9.36. % Found: C: 36.28; H: 3.76; N: 9.11; IR (capillary film), [cm^{-1}]; 3500–3300 (w, —O—H, stretch.), 2955 (w, CH$_3$— and —CH$_2$—, asym. stretch.), 2853 (w, CH$_3$— and —CH$_2$—, sym. stretch.), 1721 (s, C=O, stretch.), 1440–1404 (s, —CH$_2$—, sciss.), 1075 (s, —O—H, deform.), 753 (s, —C—Cl, stretch.); ^{1}H-NMR (d$_6$-DMSO), [δ ppm]; 3.55 (m, 2H, —N—CH$_2$— and 1H, —CH$_2$—Cl), 3.7 (1H, d, —CH$_2$—Cl), 3.95 (1H, m, —CH—), 5.5 (1H, d, —OH); ^{13}C-NMR (d$_6$-DMSO), [ppm]; 154.1 (C$_2$), 157.5 (C$_{4.5}$), 42.1 (C$_6$), 67.2 (C$_7$), 47.1 (C$_8$).
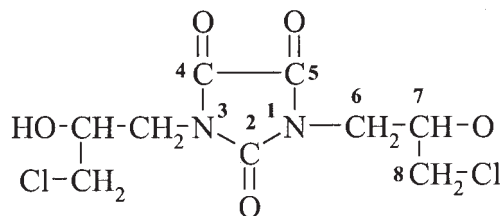
Reactions of PA with excess of oxiranes

To a 100-cm^3 autoclave, 5.7 g (0.05 mol) PA, 0–2 cm^3 of TEA (0.0–0.3 mol/mol of PA were introduced. (Some reactions were carried out without a catalyst.) Then, 0.1–0.4 mol of oxirane was added (4.4–13.2 g EO or 5.8–23.2 g PO; i.e., the amount to have the molar ratio 1 : 2, 1 : 3, 1 : 4, or 1 : 8). The reaction was carried out as described in point 1. [Most of reactions were carried out at 80°C, except of those at the molar ratio of reagents 1 : 8 that were carried out at room temperature. The solid products obtained in reactions with PO were washed with acetone and dried at reduced pressure in an oven (at ~ 40°C and 0.09 MPa = 67.5 mm Hg). The resinous products obtained with PO were freed from TEA at 80°C and 0.02 MPa = 12 mm Hg.]

Reactions of *N,N'*-bis(2-hydroxyalkyl) parabanates (BHAP) with oxiranes

In a 100-cm^3 autoclave, 0.02 mol BHEP (4.0 g) or BHPP (4.5 g) was placed along with 0.15–4.5 cm^3 TEA (0.055–0.11 mol/mol BHAP) and 0.88, 1.76, or 3.52 g of EO or 1.16, 2.32, or 4.64 g PO (i.e., the amount to have the molar ratio 1 : 1, 1 : 2, or 1 : 4). The mixture was heated at 40–50°C, while continuously stirring. BHAP gradually dissolved in oxiranes, the end of reaction was established, and the products were purified as described above.

Analytical methods

The acid number (AN) of PA and its derivatives was determined by titration with 0.1*M* potassium hydrox-

TABLE I
The Conditions of Reactions of 1 mol of Ethylene Oxide (EO) or Propylene Oxide (PO) with 1 mol of Parabanic Acid (PA) and the Properties of Products

|		Reaction conditions			Product properties		
					Acid number (mg KOH/g)		
Run	Oxirane	TEA (mol/mol PA)	Temperature (°C)	Time (h)	Calcd.	Found	mp (°C)
1	EO	0.027	35	7	355.1	350.0	197–198
2	EO	0.054	50–60	15	355.1	280	211–222
3	EO	0.081	55	8	355.1	211	218–229
4	PO	0.027	35–40	8	326.1	325.0	154–155

ide solution.[30] The epoxy number (EN) of the reaction mixtures was determined by titration with hydrochloric acid in dioxane.[31]

^{1}H-NMR spectra were recorded in d_6-DMSO solutions with hexamethyldisiloxane as internal standard on a spectrometer FT NMR 80 MHz type BS 587A (Czechoslovakia). ^{13}C-NMR spectra were recorded in d_6-DMSO solutions with tetramethyldisiloxane as internal standard on a spectrometer Brucker AMX300 (Germany). IR spectra were recorded for capillary films or KBr tablets on a Paragon 1000 FT Perkin–Elmer instrument (UK). The elemental analyses were made for carbon, hydrogen, and nitrogen on an elemental analyzer EA 1108 Carlo-Erba (Italy). The thermal analyses were performed in a ceramic pot at the following conditions: temperature range, 20–1000°C; registration time, 100 min; sample, 200 mg; amplification, DTA 1/5, DTG 1/10. The results in the form of DTA, DTG, and TG curves were recorded on a derivatograph (Paulik-Paulik-Erdey System, Hungary).

RESULTS AND DISCUSSION

### Preparation of N-(2-hydroxyalkyl) hydroparabanates and N,N'-bis (2-hydroxyalkyl) parabanates

In direct reaction of 1 mol of PA with 1 mol of EO or PO in the presence of TEA, one obtains 2-hydroxyethyl (R = H) or 2-hydroxypropyl (R = CH$_3$) hydroparabanate (III), respectively

(2)
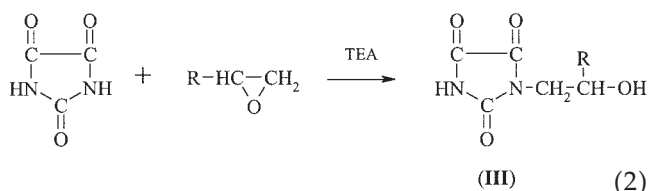
The catalytic effect of triethylamine is identical as in the reactions of PA with formaldehyde[3] and consists of creating parabanic anion that is more reactive towards the epoxy ring of oxirane than PA itself.[32] The resulting hydroparabanates are crystalline products of

well-defined melting points (Table I). In determination of AN, hydroparabanates behave as monobasic acids (similarly as PA itself), and the determined ANs are the same as calculated (Table I). The structure of hydroparabanates (III) is consistent with the results of elemental analysis as well as their IR and ^{1}H-NMR spectra (spectral data are presented in Experimental). The experiments suggest that the best conditions for preparation of hydroparabanates are at 35°C in the presence of 0.03 mol TEA per mole of PA.

In stoichiometric reactions between all imide groups of PA and oxiranes, one obtains N,N'-bis(2-hydroxyethyl)- (R = H), N,N'-bis(2-hydroxypropyl)- (R = CH$_3$), or N,N'-bis(3-chloro-2-hydroxypropyl- (R = CH$_2$Cl) parabanates (IV):

(3)
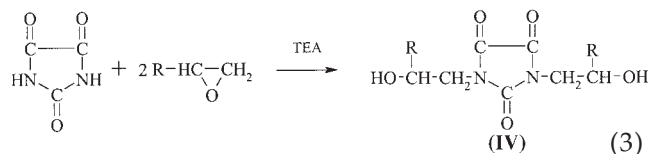
The parabanates are also crystalline substances except of the product of reaction with ECH (Table II). Their elemental composition, IR, and NMR spectra (both ^{1}H and ^{13}C) are consistent with the formula (IV).[29] The lack of a signal from protons imide in ^{1}H-NMR spectrum proves that no products of subsequent addition of oxirane to hydroparabanates are formed until an imide group remains available.

Assuming a reasonable stability of nitrogen–carbon bonds in N-(2-hydroxyalkyl) groups of parabanates dissolved in water and knowing that N,N'-bis(2-hydroxyalkyl) parabanates did not contain free imide groups, we expected zero acid numbers of these compounds because hydroxyl groups were insufficiently acidic to react with 0.1M KOH$_{aq}$. It turned out, however, that the measured acid numbers were 279, 240, and 183 mg KOH/g of BHEP, BHPP, and BCHPP, respectively (Table II). These values were consistent with those calculated assuming the parabanates to be monobasic acids. This unexpected result could be explained only in terms of decomposition of the trioxoimidazolidine ring yielding in water N-hydroxyalkyl

TABLE II
The Conditions of Reactions Between 1 mol of Parabanic Acid (PA) with 2 mol of Ethylene Oxide (EO), Propylene Oxide (PO), or Glycerin Epichlorohydrin and the Properties of Products

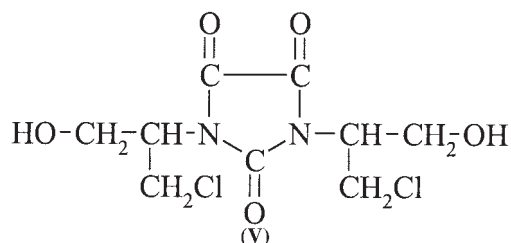| | | Reaction conditions | | | | | Product properties | | | |
| | | | | | | | | Acid number (mg KOH/g) | | |
Run	Oxirane	Solvent (g DMF/mol PA)	TEA (mol/mol PA)	Temperature (°C)	Time (h)	Appearance		Calcd.[a]	Found	mp (°C)
1	2	3	4	5	6	7		8	9	10
1	EO	1000	0.072	35–40	100	Resin		278	178	—
2	EO	1000	0.072	60	88	Resin		278	99	—
3	EO	1000	0.144	60	100	Resin		278	175	—
4	EO	1000	—	40	100	Resin		278	235	—
5	EO	—	0.030	35–40	14	White solid		278	279	80–81
6	EO	—	0.144	35–40	10	White solid		278	168	169–178
7	EO	—	0.288	35–40	7.5	White solid		278	81	180–191
8	EO	—	0.030	70	14	White solid		278	149	161–172
9	EO	—	—	40	30	White solid		278	273	81–82
10	EO	—	—	90	120	White solid		278	274	81–82
11	PO	—	0.030	35–45	16	White solid		244	240	100–101
12	PO	—	0.144	35–45	11	Resin		244	81	—
13	PO	—	0.288	35–45	8	Resin		244	54	—
14	PO	—	0.030	80	6	Resin		244	148	—
15	PO	—	0.144	80	4	Resin		244	168	—
16	PO	—	—	35–45	137	White solid		244	241	100–101
17	PO	—	—	80	11	White solid		244	238	102–103
18	ECH	—	—	110–115	3	Resin		188	183	—

[a] Calculated assuming the product of formula (IV) is formed where the ring decomposes and the respective oxaluric acid derivative is formed.

derivatives of oxaluric acid[33] that could react with KOH according to:

$$
\begin{array}{c}
\text{HO·CH·CH}_2\text{N} \overset{\displaystyle \overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}}{\underset{\underset{O}{\overset{\|}{C}}}{}} \text{N-CH}_2\text{CH·OH} + \text{KOH} \longrightarrow \text{HO·CH·CH}_2\text{NH·}\overset{O}{\overset{\|}{C}}\text{-N·}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{·OK} + \text{H}_2\text{O} \\
\hspace{3cm} \underset{\underset{R}{\overset{|}{\text{CH OH}}}}{\text{H}_2\text{C·}}
\end{array}
\tag{4}
$$
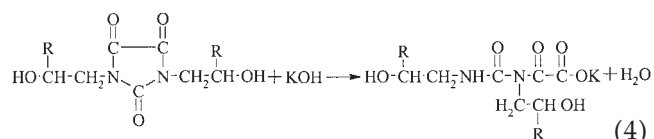
Here, a similar reaction took place as that of potassium base with unsubstituted parabanic acid (i.e., the decomposition of the acid ring). In our opinion, the latter was the main reason parabanic acid was considered in various reports as a monobasic acid.[1–3]

N,N′-bis(3-chloro-2-hydroxypropyl) parabanate (IV, R = CH₂Cl) can be obtained in a direct reaction of PA with ECH at 110–115°C without the presence of any solvent or catalyst (Table II). From IR spectrum alone, one cannot undoubtedly claim that the product has the structure (IV) with R = CH₂Cl. The same spectrum may have a product of abnormal substitution, say, compound (V):

$$
\begin{array}{c}
\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}} \\
\text{HO-CH}_2\text{-CH-N} \quad \text{N-CH-CH}_2\text{OH} \\
\underset{\text{CH}_2\text{Cl}}{} \quad \underset{O}{\overset{\|}{C}} \quad \underset{\text{CH}_2\text{Cl}}{} \\
\text{(V)}
\end{array}
$$

The decisive evidence provides ^{1}H- and ^{13}C-NMR spectra of the product. In ^{1}H-NMR spectrum, one can distinguish a doublet of chemical shift of 5.5 ppm due to hydroxyl protons. The presence of the doublet confirms structure (IV) rather than (V) because a triplet would be present otherwise. Furthermore, a multiplet at 3.95 ppm from methine protons and another multiplet at 3.7 ppm as well as a doublet at 3.55 ppm are present; the last two signals are due to methylene protons in —CH₂Cl and —N—CH₂— groups, respectively. The ratio of these signal areas was expected to be 1 : 1, but, as follows from the spectra, it was 1 : 3. This suggested that one proton in one methylene group had the same chemical shift as protons of the second methylene group. The problem is resolved by [1]H-, ^{13}C-HMQC spectrum (Fig. 1) where the signal at 3.55 ppm corresponded signals from two types of carbon atoms in ^{13}C-NMR at 42.1 and 47.1 ppm. On the other hand, the proton signal at 3.7 ppm corresponded a single carbon signal at 47.1 ppm. Furthermore, the multiplet from methine proton corresponded the carbon signal at 67.2 ppm.

Based on ^{1}H-, ^{13}C-HMBC spectrum (Fig. 2), one could correctly elucidate the proton signals at 3.55 and 3.7 ppm; the protons of 3.55 ppm signal interacted with carbon atoms resonating at 42.1, 47.1, 67.2, 154.1, and 157.5 ppm and hence were the protons of the methylene group directly linked to a nitrogen atom in the ring. The protons of the other methylene group
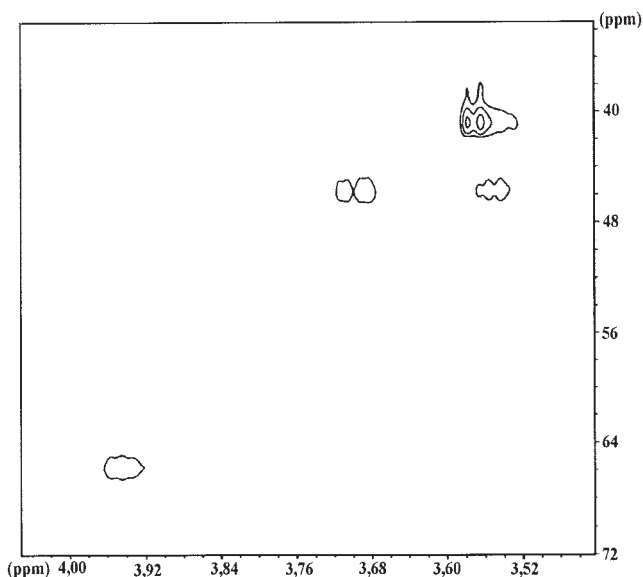
Figure 1 [1]H ^{13}C-HMQC spectrum.

interacted only with carbons resonating at 42.1 and 67.2 ppm and hence had to be ascribed to the —CH$_2$Cl group. All these findings were consistent with structure (**IV**). In the same spectra, one could also observe interactions of —OH protons with carbons of both methylene groups (42.1 and 47.1) as well as with methane carbon at 67.2 ppm.

As follows from literature data, BCHPP was prepared so far in the presence of benzyltrimethylammonium chloride catalyst from parabanic acid and a 10-fold excess of ECH. The latter had to be distilled off after the reaction.[34] In our experiments, it turned out that the stoichiometric twofold molar excess of ECH was sufficient and the presence of catalyst was unnecessary. Also sufficient was the time not exceeding 3 h. The method used by us was therefore more efficient than that described in literature.

The hydroxyalkyl hydroparabanates and parabanates can be used for preparation of acrylic or methacrylic monomers containing trioxoimidazolidine rings. Preparation of these monomers will be the subject of a forthcoming article.

Polymerization with opening trioxoimidazolidine ring

In the next step, we studied the effects of the type of solvent, amount of catalyst, and time of heating on the course of reaction of 1 mol PA with 2 mol EO or PO. In the absence of solvent, one observes a slow dissolution of PA and then precipitation of a product. This observation helped to establish the time sufficient to complete the reaction. For reactions carried out without a catalyst, heating of the reactor content to 80–90°C had no effect on the system behavior (Table II). Heating of BHEP or BHPP at this temperature even for

many hours did not affect the product as follows from unaffected acid numbers, mp values, and IR or NMR spectra.

While studying the effect of heating on formation of BHEP or BHPP in the presence of TEA, we concluded that the best temperature range was 35–40°C. Its increase beyond this value resulted in changes of the product structure (Table II, runs 2–4 and 14–15). These changes will be discussed later.

The presence of TEA catalyst considerably reduced the reaction time. It also promotes further reactions of BHEP. In the reaction of 1 mol PA with 2 mol EO at 35°C in the presence of 0.144 mol TEA, a product of rather broad melting point range, 169–178°C, quite readily decomposing was obtained (cf. Table II, run 6). Under the same conditions, a resin was obtained from PO (Table II, run 12). The systems behaved similarly at temperatures of 70–80°C in the presence 0.03 mol TEA per 1 mol PA (Table II, run 8 and 14). In the IR spectra of the products obtained from EO (Fig. 3), one observes the bands in the range 3100–3500 cm^{-1}, due to stretching vibrations in —OH and ⟨NH groups and the band due to deformational vibrations of primary hydroxyl groups (1075 cm^{-1}). Furthermore, bands are present at ~ 1660, 1533, and 1275 cm^{-1} (i.e., at the frequency corresponding to the first and second amide band in secondary amide and to stretching vibrations of C—O bond in aliphatic esters). Similar were the IR spectra of the product obtained under the same conditions from PO. The presence of these bands can be explained in terms of polymerization of the resulting parabanate by opening its trioxoimidazolidine ring. A polymer formed in this way contains both ester and amide groups. It should be pointed out that the product contains sequences (units) with unchanged trioxoimidazolidine rings as well. This conclusion follows
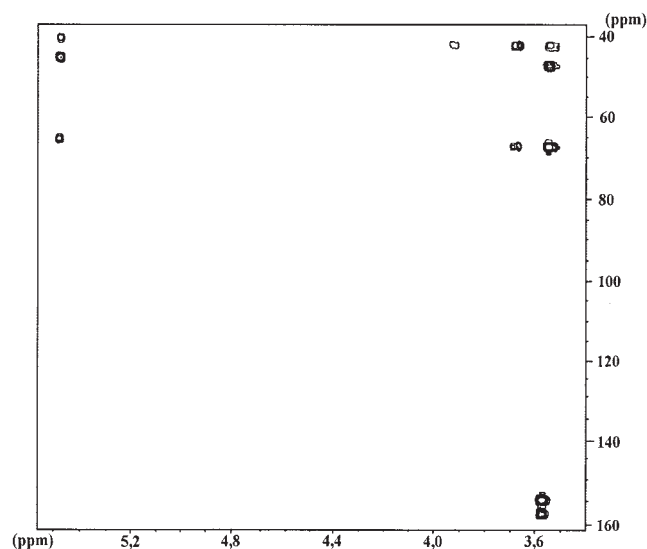

Figure 2 ^{1}H ^{13}C-HMBC spectrum of *N,N'*-bis(3-chloro-2-hydroxypropyl) parabanate.
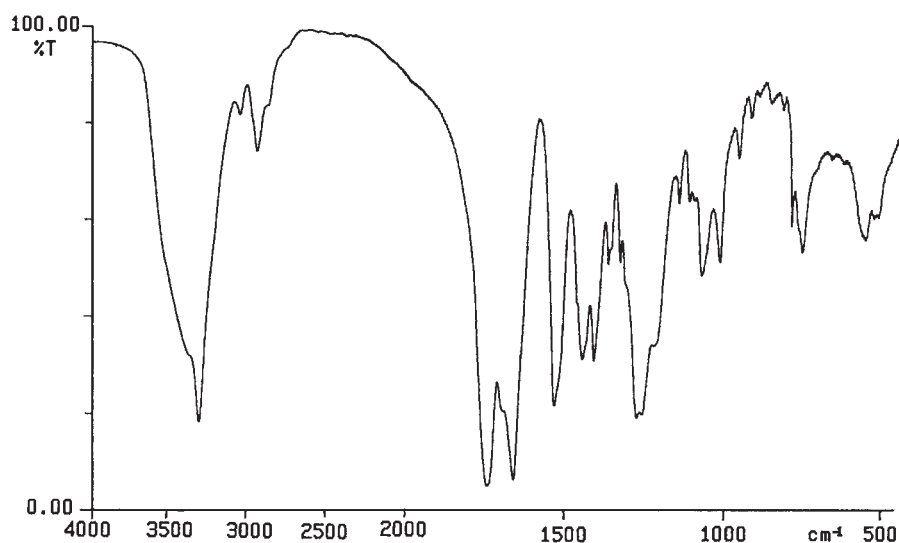
Figure 3 IR spectrum of the product of reaction between parabanic acid and ethylene oxide at the starting molar ratio 1 : 2 in the presence of catalyst (0.144 mol triethylamine/mol parabanic acid) at 35°C.

from the nonzero acid number values measured for the products.

Further evidence for these processes provide ^{1}H-NMR spectra of the products. In the spectrum of the product obtained from EO in the presence of catalyst (Fig. 4), one observes a split of methylene proton signals in the structure N—CH_2—CH_2—O. The chemical shift of one of the signals (at 3.45 ppm) stays identical as in BHEP,[29] but the second appears already at 4.1 ppm and is due to methylene protons in —CH_2—O—(CO)—.[32] There are also signals in the range 8.4–9.1 and at 4.7 ppm characteristic for the mobile protons in amide and hydroxyl groups.[35] They vanish from spectra as heavy water is added.

Similarly, in the spectrum of the polymeric product obtained in reaction of 1 mol of PA with 2 mol of PO, one observes, besides the signals from methyl, methylene, and methine protons of the shifts identical to those in BHPP spectrum, also an additional multiplet at 4.6 ppm due to methane protons in —CH—O—(CO)—.

Examinations of thermal stability of the polymers obtained by decomposition of parabanic acid ring that took place in the reaction with oxiranes revealed that the stability was comparable to that of N,N'-bis(2-hydroxyalkyl) parabanates (BHEP and BHPP). In both cases, the highest rate of thermal decomposition occurred at ~ 230°C.
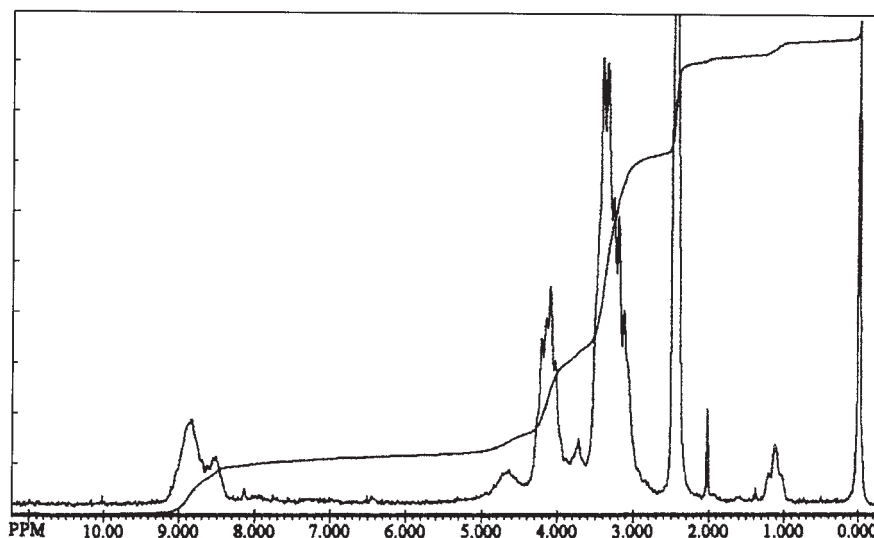

Figure 4 ^{1}H-NMR spectrum of the product of reaction between parabanic acid and ethylene oxide at the starting molar ratio 1 : 2 in the presence of catalyst (0.144 mol triethylamine/mol parabanic acid) at 35°C.

TABLE III
Reaction of Parabanic Acid (PA) with Excess of Ethylene Oxide (EO), Propylene Oxide (PO), or Glycerin Epichlorohydrin (ECH) and the Properties of Products

|			Reaction conditions				Product properties			
Run	Oxirane	Molar excess of oxirane	Solvent (g DMF/mol PA)	TEA (mol/mol PA)	Temperature (°C)	Time (h)	Appearance	Acid number (mg KOH/g) Calcd.[a]	Found	mp (°C)
1	2	3	4	5	6	7	8	9	10	11
1	EO	3	1000	0.072	60	163.5	Solid	228	113	196–198
2	EO	3	1000	0.144	60	147.5	Solid	228	58	157–168
3	EO	3	1000	—	60	177	Solid	228	50	146–148
4	EO	3	—	0.072	70	85	Solid	228	—[b]	192–202
5	EO	3	—	0.072	40	125	Solid	228	—[b]	190–201
6	EO	3	—	—	40	148	Solid	228	128	172–175
7	EO	4	—	—	70	264	Solid	193	—[b]	190–193
8	EO	4	—	0.072	40	168	Solid	193	—[b]	200–220
9	EO	4	—	0.072	70	94	Solid	193	—[b]	205–224
10	EO	8	—	0.072	25	18	Solid	120	—[b]	168–195
11	EO	2[c]	—	0.030	50	24	Solid	193	—[b]	167–180
12	EO	4[c]	—	0.030	50	35.5	Solid	148	—[b]	168–176
13	PO	3	—	—	35–40	92	Solid	195	224	104–105
14	PO	4	—	—	35–40	139	Solid	162	234	101–102
15	PO	3	—	0.144	35–40	56	Resin	195	117	—
16	PO	4	—	0.144	35–40	63	Resin	162	119	—
17	PO	8	—	0.144	35–40	140	Resin	97	83	—
18	PO	3	—	0.288	75–80	6	Resin	195	167	—
19	PO	4	—	0.288	75–80	13	Resin	162	116	—
20	PO	8	—	0.288	75–80	80	Resin	97	79	—
21	PO	1[d]	—	0.054	35–40	170	Resin	195	67	—
22	PO	2[d]	—	0.110	35–40	73	Resin	162	55	—
23	ECH	4	—	—	110–115	28.5	Resin	116	44	—

[a] Acid number calculated assuming the ring decomposes during titration (see note under Table II).
[b] Acid number not measured due to insolubility of product.
[c] N,N′-bis(2-hydroxyethyl) parabanate was used instead of PA.
[d] N,N′-bis(2-hydroxypropyl) parabanate was used instead of PA.

In reactions of 1 mol PA with 3 mol EO carried out in a solvent (DMF) and in the presence of TEA catalyst (0.072 mol) at 60°C (Table III) apart from the product of addition of oxirane, products of ring-opening polymerization (**VI**) were present. About 50 mol % of rings were found to undergo this decomposition under the reaction conditions (cf. Table III)


(VI)
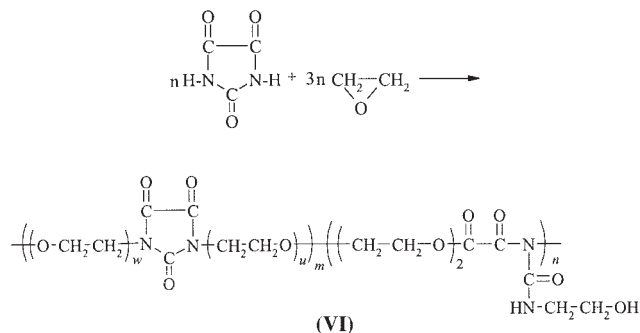
where $w + u = 3$.

In ^{1}H-NMR spectrum of the product, there are signals due to protons from methylene groups in —N—CH_2–CH_2—O— and —CH_2—O(CO)— at 3.45 and 4.1 ppm, respectively. Another wide signal due to amide protons is present in the range 8.4–9.1 ppm. In IR spectrum, one observes the first and second band due to secondary amide group (1659 and 1534 cm^{-1}) and a broad band due to stretching vibrations of —OH and 〈HN groups (3100–3500 cm^{-1}), similar to the product of polymerization of BHEP.

The reaction of 1 mol PA with 3 mol EO carried out without catalyst yields the same product (Table III, run 3). With 0.144 mol TEA (Table III, run 2), another polymeric compound is obtained with the fraction of parabanic acid rings somewhat smaller (∼ 0.2 mol per mole of product; cf. Table III, run 2). From its ^{1}H-NMR spectrum, it follows that the ratio of signals at 3.45 and 4.1 ppm is 1 : 3. This indicates that 2-hydroxyethyl group in the side chain becomes activated and a branched or eventually crosslinked polymer (**VII**) is obtained. Assuming a small content of unchanged parabanic acid rings,

TABLE IV
Elemental Analysis of the Products of Hydroxyethylation of Parabanic Acid (PA) or *N,N'*-bis(2-Hydroxyethyl)
Parabanate (BHEP) with Ethylene Oxide (EO)

No.	Starting compounds and their molar ratios	% N		% C		% H	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
1	PA : EO = 1 : 3	11.46	12.09	43.90	42.01	5.69	5.41
2	PA : EO = 1 : 4	9.65	11.9	45.52	43.6	6.21	5.88
3	BHEP : EO = 1 : 2	9.65	11.54	45.52	44.02	6.21	5.83
4	BHEP : EO = 1 : 4	7.41	11.75	47.62	43.75	6.88	5.48

the following structure can be estimated basing on ^{1}H-NMR spectra:

$$\left[\left(CH_2\!-\!CH_2\!-\!O\right)_2 \overset{\overset{O}{\parallel}}{C}\!-\!\overset{\overset{O}{\parallel}}{C}\!-\!N\right]_n$$

(VII)
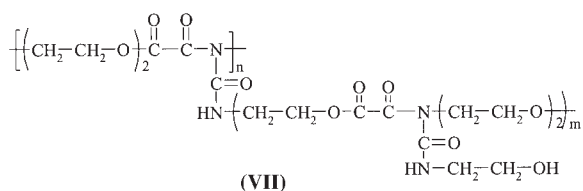
The weight analysis of the products obtained at different molar ratios of reagents in the range 1 : 3 to 1 : 8 shows that one linear constitutional unit originating from trioxoimidazolidine ring always contains three oxyethylene units. This is due to the fact that the linear polymer of structure (**VI**) precipitates from the solution and cannot react with excess EO.

The reactions between BHEP with EO at molar ratios 1 : 2 and 1 : 4 (Table III, runs 11–12) carried out in the presence of TEA proceed in the same way. This is confirmed by elemental analysis of products (Table IV).

Somewhat different are the reactions of PA with excess of PO. We have noticed that at the molar ratio of reagents 1 : 3 or 1 : 4 at 35–40°C and without TEA, the only product of reaction was BHPP (Table III, runs 13 and 14) that dropped out from the reaction mixture and did not react with PO excess. Reactions carried out in the presence of 0.144 mol of TEA per mole of PA at the same temperature of 35–40°C yielded products with most of trioxoimidazolidine rings decomposed into linear fragments. In IR spectra (Fig. 5b) of the product obtained in the presence of TEA at the molar ratio 1 : 3, one can observe both the first and the second band of secondary amide (1680, 1513 cm^{-1}), but the intensity of the second amide band is much weaker than in the spectrum of a similar product obtained at a molar ratio of 1 : 2 [Fig. 5(a, b)]. In the product with yet higher excess of PO (molar ratio 1 : 4), the intensity of the band in question is smaller than for the product obtained with 3 mol PO per mole of PA [cf. Fig. 5(c)]. It vanishes altogether from spectrum of the product obtained at the ratio PA : PO equal to 1 : 8 [Fig. 5(d)]. Hence, as more and more PO oxide is introduced, the oxirane reacts with NH group of secondary amide formed by decomposition of trioxoimidazolidine ring to produce tertiary amide and

because of that the intensity reduces of the secondary amide band.

The thus outlined mechanism of the reaction of PA with excess PO is confirmed in ^{1}H-NMR spectra. Here again a reduction of intensity of the signals due to amide protons at 7.35 and 8.4 ppm is observed as the excess of PO is increased from 3 to 4 per mole of PA. No such signal can be found in the spectra of the product obtained with eightfold excess of PO. Furthermore, multiplets appear from methine group protons characteristic for the ester —CHO(CO)— (4.5 ppm) and the remaining oxypropylene groups (3.7 ppm), as well as the signal from methyl protons in —CH$_2$—O— and —N—CH$_2$— (3.3 ppm).

Hence, the reactions of the successive moles of PO take place by addition of a part of PO to hydroxyl
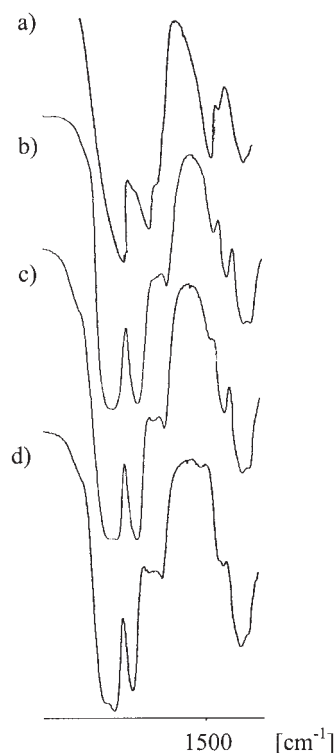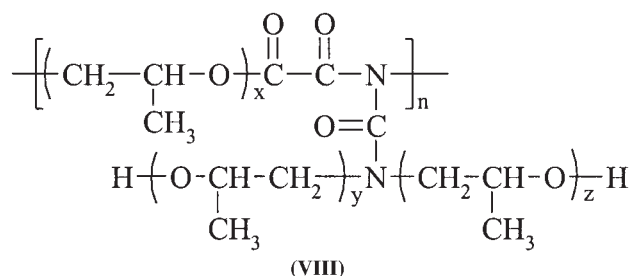

Figure 5 Fragments of IR spectra of the products of reaction of 1 mol of parabanic acid with (a) 2, (b) 3, (c) 4, and (d) 8 mol of propylene oxide. All reactions were carried out in the presence of catalyst (0.144 mol triethylamine/mol parabanic acid) at 40–45°C.

groups of BHPP, while the remaining part of PO reacts with the linear products of condensation, so that all excess becomes consumed in the reaction to yield compound (**VIII**):

$$\left[\left(CH_2-\underset{\underset{CH_3}{|}}{CH}-O\right)_x\underset{\underset{O=C}{||}}{\overset{\overset{O}{||}}{C}}-\overset{\overset{O}{||}}{C}-\underset{|}{N}\right]_n$$

H$\left(O\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH_2\right)_yN\left(CH_2\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}O\right)_z$H

(**VIII**)

where $x + y + z = m = 3$ through 8 and m is the number of moles of propylene oxide reacting with 1 mol of parabanic acid.

Another piece of evidence provides reactions of BHPP with PO (Table III, runs 21 and 22), where analogous polymeric products of decomposition of trioxoimidazolidine ring are formed. The reactions take place because BHPP is soluble in excess PO (similarly as the polymeric products).

From the analysis of ¹H-NMR, it follows that the products of ring opening obtained from PA and excess of PO at 30–40°C contain predominantly tertiary amide groups (cf. **VIII**), whereas the products obtained at a higher temperature, up to 80°C, contain products of the subsequent addition of PO to BHPP to yield the product (**IX**):

$$\left[\left(CH_2-\underset{\underset{CH_3}{|}}{CH}-O\right)_x\underset{\underset{O=C}{||}}{\overset{\overset{O}{||}}{C}}-\overset{\overset{O}{||}}{C}-\underset{|}{N}\right]_n$$

HN$\left(CH_2\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}O\right)_y$H
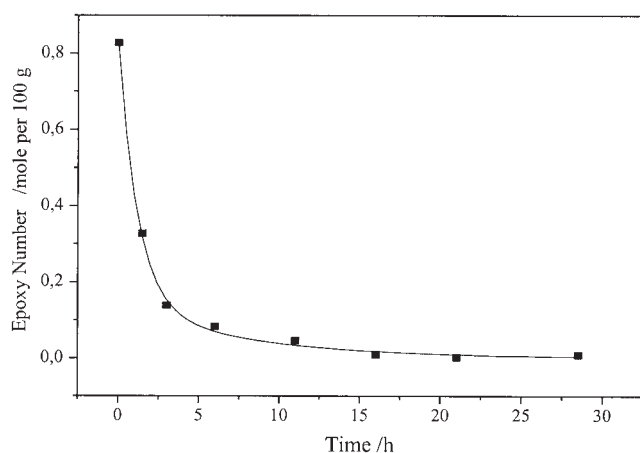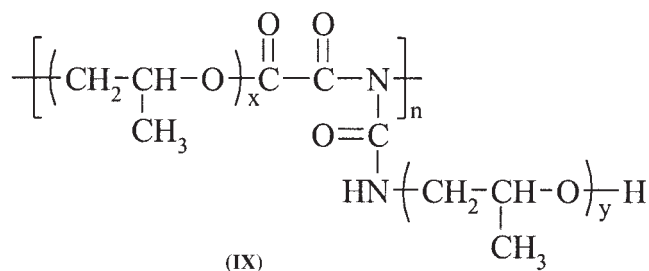
(**IX**)

Figure 6 The epoxy number in the reaction mixture consisting of parabanic acid and glycerin epichlorohydrin (mole ratio 1 : 4) versus reaction time.
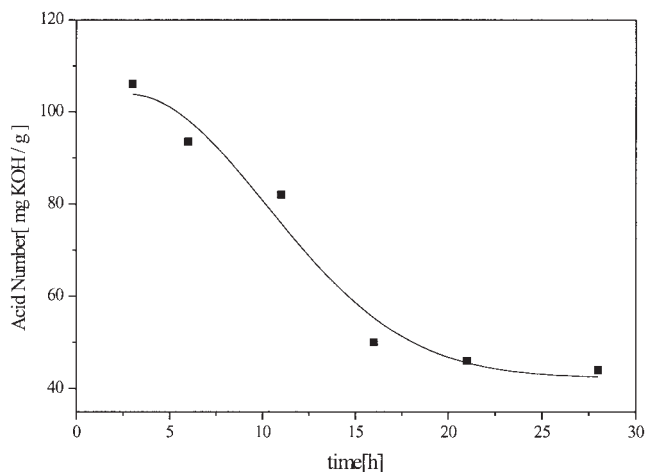
Figure 7 The acid number in the reaction mixture consisting of parabanic acid and glycerin epichlorohydrin (mole ratio 1 : 4) versus reaction time.

where x, y, and z have the same meaning as in structure (**VIII**).

The course of reactions of PA with excess ECH (Table III, run 23) was similar to those with PO. They were monitored be measuring EN (Fig. 6) and AN (Fig. 7). Taking into account the peculiar behavior of parabanic acid derivatives which react as they were monobasic acids, we expected AN not to drop down to zero, until the trioxoimidazolidine ring remained intact. The product of reaction of 1 mol PA with 4 mol ECH should have AN equal to 116 mg KOH/g. However, we have found that after 3 h of reaction AN was 106 and dropped down to 44 in the final product. This means that the reaction had to be accompanied by decomposition of the trioxoimidazolidine ring. The presence of Ist and IInd amide bands of secondary amide in IR spectra also confirms the conclusion. The small intensity of primary amide bands and the presence of signals due to amide protons in ¹H-NMR spectra suggests that the successive molecules of ECH react with secondary amide —NH group. Consequently, the structures analogous to those formed in reactions with propylene oxide of structures (**VIII**) and (**IX**) are the products of reactions.

CONCLUSION

1. To obtain N,N'-bis(2-hydroxyethyl) or N,N'-bis(2-hydroxypropyl) parabanate, one should carry out the addition of the respective oxiranes to parabanic acid at the stoichiometric molar ratios without a solvent at 35–40°C with at most 0.03 mol of TEA per mole of PA. N,N'-bis(3-chloro-2-hydroxypropyl) parabanate is most conveniently prepared at the stoichiometric molar ratio of reagents at 110–115°C in the absence of catalyst.

2. In reactions of 1 mol of PA with excess EO in DMF with TEA catalyst and at 60°C, one obtains a poly-

meric product as a result of the expected reaction between PA and oxirane, but accompanied by decomposition of trioxoimidazolidine ring. In one constitutional unit of the polymeric product, there are at most three oxyalkylene groups per one parabanic acid moiety. The same product is obtained in reactions of 1 mol PA with 2 mol oxirane if the optimal conditions for preparing N,N′-bis(2-hydroxyethyl) parabanate are not kept.

3. Reactions of successive moles of propylene oxide with the product of reaction of parabanic acid with at most 2 mol of PO may occur via subsequent addition of a part of oxirane to hydroxyl groups and another part to the amide groups in the linear product of opening trioxoimidazolidine ring until all PO is reacted.

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