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Polyhydroxyalkyl derivatives and polyetherols obtained from azacyclic compounds

Part I. REACTIONS WITH OXIRANES

Summary — The methods to synthesize polyhydroxyalkyl derivatives of azacycles and polyetherols with azacycles in reactions with oxiranes have been reviewed. These compounds are useful substrates for obtaining polymers of enhanced thermal stability like polyurethanes, polyesters or polyacrylates. The synthesis conditions, catalysts and solvents used for successful synthesis protocols for the substrates and chosen applications of substrates were presented.

Keywords: heterocyclic compounds with nitrogen atoms, oxiranes, alkylene carbonates, hydroxyalkylation, structure of products.

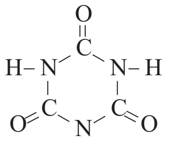
WIELOHYDROKSYALKILOWE POCHODNE I POLIETEROLE OTRZYMYWANE ZE ZWIĄZKÓW AZACYKLICZNYCH. Cz. I. REAKCJE Z OKSIRANAMI

Streszczenie — W pracy dokonano przeglądu metod otrzymywania wielohydroksyalkilowych pochodnych niektórych azacykli i polieteroli z pierścieniami zawierającymi atomy azotu, nadających się do otrzymywania tworzyw o zwiększonej odporności termicznej, m.in. takich jak poliuretany, poliestry i poliakrylany. Omówiono metodę hydroksyalkilowania melaminy, adeniny, kwasów izocyjanurowego, barbiturowego, moczowego i parabanowego za pomocą oksiranów (tlenek etylenu, tlenek propylenu i epichlorohydryna gliceryny) w środowiskach różnych rozpuszczalników organicznych. Przedstawiono warunki prowadzenia reakcji, najważniejsze katalizatory i rozpuszczalniki oraz wskazano możliwości zastosowania otrzymywanych związków.

Słowa kluczowe: związki herocykliczne z atomami azotu, oksirany, węglany alkilenowe, hydroksyalkilowanie, struktura produktów.

The presence of certain heterocyclic rings with nitrogen atoms in an organic polymer may significantly improve its thermal stability, which plays a crucial role in application of the polymers as thermal insulating materials. For instance in case of typical polyurethane foams, the upper temperature range of safe usage is usually considered to be 90—110 °C [1, 2]. This limitation can be avoided by applying a polyetherol component containing a thermostable heterocyclic ring with nitrogen atoms, such as 1,3,5-triazine [3], perhydro-1,3,5-triazine [4] or purine [5] ring. The mentioned derivatives start to decompose at temperatures above 300 °C. The same heterocyclic rings incorporated into the structure of polyurethanes, polyesters [6—8] or epoxy resins [9] also improve thermal stability of the polymers and additionally enhance their chemical resistance and stability. Polyurethane foams prepared from such a polyetherol withstand temperature reaching 200 °C and can permanently work at 140—150 °C, and, occasionally (for up to 30 min) at 800 °C [2]. The most known azacycles used for these purposes are: isocyanuric acid [formula (I)], barbituric acid [formula (II)], 5,5-diethylbarbituric acid [formula (III)], uric acid [formula (IV)], adenine [formula (V)], parabanic acid [formula (VI)] and melamine [formula (VII)].

The discussed azacycles are insoluble in most organic solvents except for dimethyl sulfoxide (DMSO) or to some extent in water (like isocyanuric acid, barbituric acid or melamine). Others are practically insoluble (uric acid, guanine and adenine), therefore their functionalization by a reaction in a solution is precluded. *N*-hydroxyalkyl derivatives of these azacycles are usually better soluble, readily react with hydroxyalkylating agents like neat oxiranes or alkylene carbonates. Thus mentioned azacycles can be used for modification of polymers after their conversion into hydroxyalkyl derivatives, which are able to react with acrylic and methacrylic acids, with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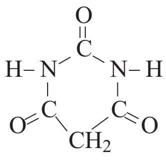
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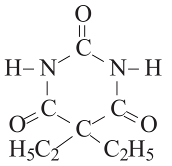
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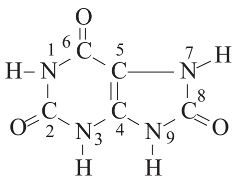

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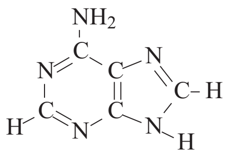
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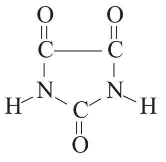
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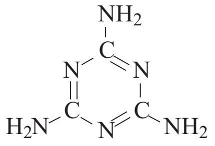
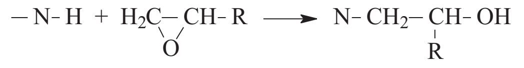

(VII)

isocyanates resulting in polyurethanes, with dicarboxylic acid and their anhydrides to form polyesters, or to modify epoxide, phenol-formaldehyde, or amine resins *etc.* [6—14].

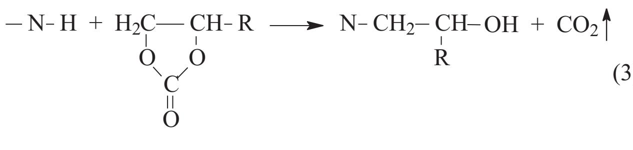
Hydroxyalkylation is a substitution of labile hydrogen with a hydroxyalkyl group. Usually the replaced hydrogen atom is bound to an oxygen, nitrogen or sulfur atom. The most often used hydroxyalkylation agents are formaldehyde, oxiranes (ethylene oxide and propylene oxide, epichlorohydrin of glycerol) and alkylene carbonates (ethylene or propylene carbonate).

Hydroxyalkylation of azacycles proceeds usually on a nitrogen atom of amine or an imide group:

$$-N\text{-}H + CH_2O \rightleftharpoons -N\text{-}CH_2OH \qquad (1)$$


$$-N\text{-}H + H_2C\underset{O}{\frown}CH\text{-}R \longrightarrow N\text{-}CH_2\text{-}\underset{R}{CH}\text{-}OH$$

(2)


$$-N\text{-}H + \underset{\underset{\underset{O}{\|}}{C}}{\underset{O\quad O}{H_2C-CH}}\text{-}R \longrightarrow N\text{-}CH_2\text{-}\underset{R}{CH}\text{-}OH + CO_2\uparrow$$

(3)

where: R = -H, $-CH_3$

The reaction needs the excess of hydroxyalkylation agent. At first instance the *N*-hydroxyalkylated derivatives are formed, which react later to form oligo- or polyetherols. The process can be conducted with three methods:

— in a straightforward reaction of azacycle with oxiranes,

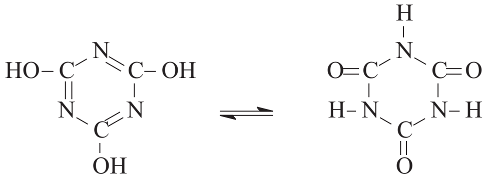
— by an initial reaction of azacycle with formaldehyde and later with oxiranes,

— in a straightforward reaction of azacycle with alkylene carbonates.

The methods of hydroxyalkylation of some azacyclic compounds as precursors of polyetherols are reviewed here, including the catalysts and solvents used for these processes, as well as trends and possibilities to employ the process.

ISOCYANURIC ACID

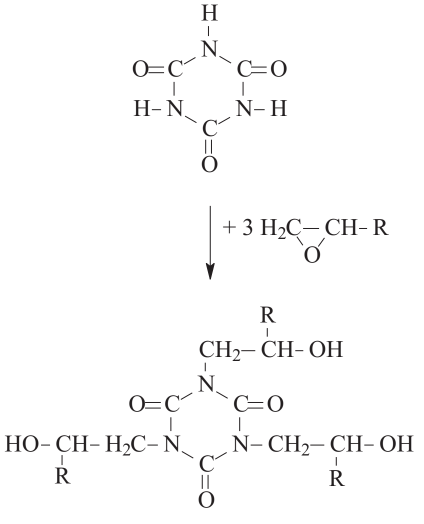
Isocyanuric acid [formula (I)] is a trifunctional organic acid of symmetric structure with no carboxylic groups. Acidity of the compounds comes from imide groups in their molecules [15]. Isocyanuric acid behaves as a monobasic one in aqueous solutions; its ionization constant is $1.8 \cdot 10^{-5}$ [16]. Isocyanuric acid has two limiting tautomeric structures [17]:


(4)

(VIII)

In the solid state and in acidic environment the compound has the triketonic structure [formula (I)]. Isocyanuric acid is a product of growing importance as a raw material in the synthesis of multifunctional monomers and polymers, additives to plastics, coatings, and paints. The reasons are that it is a cheap chemical, produced in a simple way, directly from urea and the products obtained from it are thermally stable.

The most common oxiranes, such as ethylene and propylene oxides, epichlorohydrin of glycerol react with isocyanuric acid in a sequence of reactions to form 1,3,5-tris-(hydroxyalkyl) isocyanurates [formula (IX) in eq. (5)] and semiproducts in various degrees of substitution. Actually


(5)

(IX)

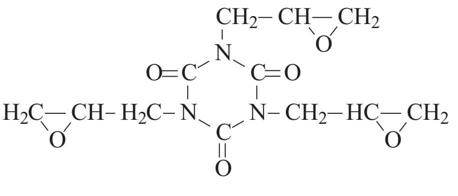
where: R = -H, $-CH_3$, $-CH_2Cl$

the reaction takes place in three stages and, unlike that with formaldehyde is irreversible [18] (eq. 5).

The first reports on the reactions of isocyanuric acid with oxiranes were published in the fifties of XX-th century. Due to functionality of the acid, the reaction products were non-crystalline solids (resins), comprising mono-, di- and tri-substituted compounds. It was concluded that in a reaction of 3 moles of ethylene oxide with 1 mole of isocyanuric acid, 1,3,5-tris(2-hydroxyethyl) isocyanurate [formula (IX) with R = H] is formed. Several methods of preparing 1,3,5-tris(2-hydroxyethyl) isocyanurate from isocyanuric acid and ethylene oxide have since been described, mostly in patents. The methods differed in the type of catalyst used (tertiary amines, alkali metal hydroxides, alcoholates), type of solvent [aliphatic or aromatic hydrocarbons, ketones, alcohols, dimethylformamide (DMF), dimethyl sulfoxide (DMSO)], or the reaction conditions [19—27]. Similarly, starting from isocyanuric acid and propylene oxide one obtains 1,3,5-tris(2-hydroxypropyl) isocyanurate [formula (IX) with R = CH_3] [28—32]. The product is again a resinous substance. In the reaction carried out in DMF at 115—125 °C at the molar ratio of isocyanuric acid to propylene oxide equal to 1:3 one obtains a resin containing 77 and 23 % of di- and tri-substituted derivative, respectively [18]. Japanese researchers [33] demonstrated that 1,3,5-tris(2-hydroxypropyl) isocyanurate is a solid (melting temperature T_m = 90.5 °C), similarly as 1,3,5-tris(2-hydroxyethyl) isocyanurate.

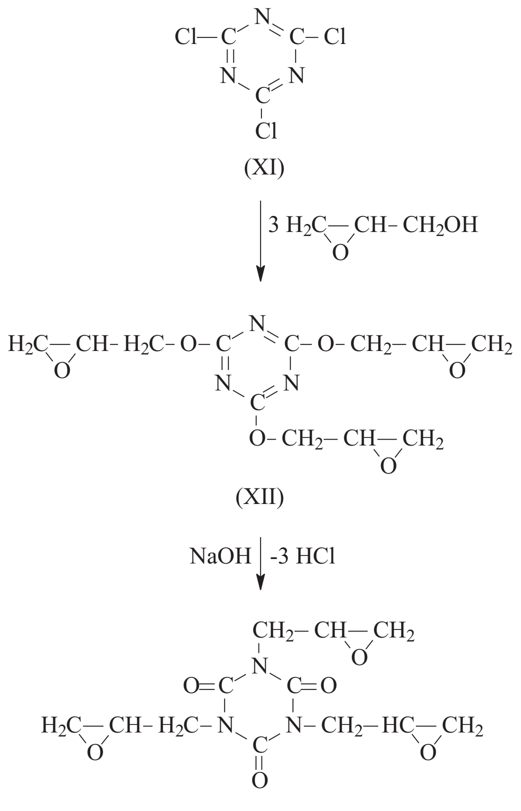
In a reaction of three moles of epichlorohydrin of glycerol with isocyanuric acid a resinous product was obtained that was a mixture of di- and tri-substituted derivatives of the acid [34]. Unlike for ethylene oxide or propylene oxide, the reactions with epichlorohydrin of glycerol are carried out with substantial excess of the latter reaching 15—20 moles per mole of isocyanuric acid or even 90 moles, in the presence of a large amount of basic catalyst, up to 15 wt. % of isocyanuric acid. Among the catalyst, amines, ammonium salts, and ion exchange resins were reported [35—38].

The studies on the reaction of isocyanuric acid with epichlorohydrin of glycerol concentrated on the feasibility of the subsequent dehydrochlorination of 1,3,5-tris(3-chloro-2-hydroxypropyl) isocyanurate obtained by addition of 3 moles of epichlorohydrin of glycerol to 1 mole of isocyanuric acid that leads to 1,3,5-triglycidyl isocyanurate [formula (X)] [38, 39]:



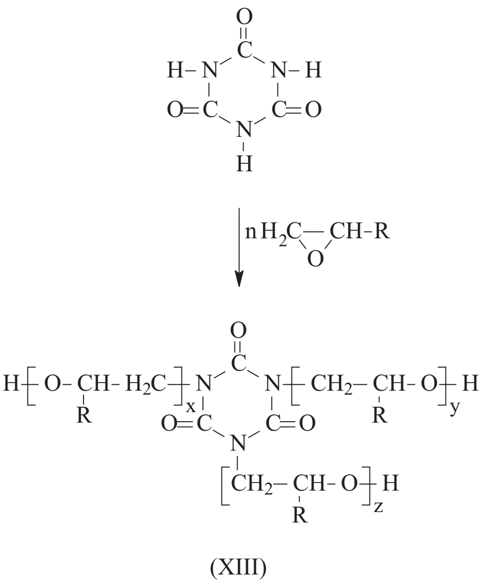
(X)

The product is a mixture of diastereoisomers [40, 41]. The isomers can be isolated by recrystallization from methanol (form α, T_m = 104 °C) and extraction with chloroform (form β, T_m = 156—157 °C) [42]. A method to synthesize triglycidyl cyanurate [formula (XII) in Scheme A], in the reaction of cyanuric chloride [formula (XI) in Scheme A] with glycidol has also been described [39].



Scheme A. Synthesis of triglycidyl cyanurate and rearrangement to isocyanurate

Triglycidyl cyanurate [formula (XII) in Scheme A] at elevated temperature tends to rearrange into isocyanurate given by formula (X) [43], which is commercially



(6)

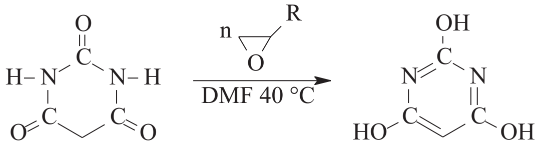
(XIII)

where: R = -H, $-CH_3$, $-CH_2Cl$, x + y + z = n important as a component of epoxy resins of improved thermal stability and a curing agent for epoxy and polyester resins, including powder coatings [44]. Its disadvantage is poor storage stability that depends on purity. The product of decomposition is 3-glycidyl-1,3-oxazolidin-2-one proposed as a reactive solvent or diluent for epoxy resins [45].

The reactions of isocyanuric acid or its derivatives with an excess of ethylene oxide or propylene oxide yield trifunctional polyetherols [formula (XIII) in eq. (6)] [46, 47] comprising in their structure thermostable perhydro-1,3,5-triazine ring that provides polyurethane foams with improved thermal stability.

BARBITURIC ACID AND ITS DERIVATES

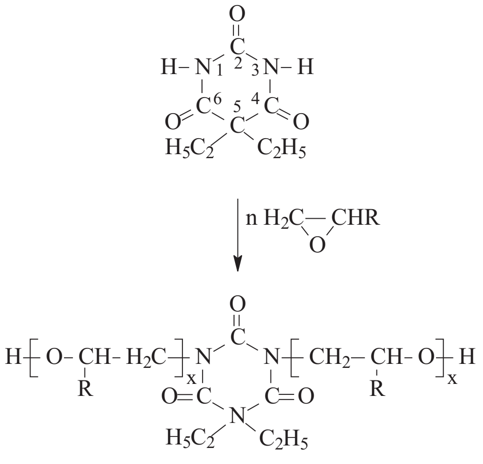
Barbituric acid [formula (II)] differs from isocyanuric acid by the presence of a carbon atom instead of nitrogen in the ring. The pyrimidine ring of barbituric acid is thermally stable. It decomposes starting from 270—280 °C. Barbituric acid dissolves in DMSO, DMF, dioxane and water. First acid dissociation constant corresponds to deprotonation of methylene group with $K_a = 1.26 \cdot 10^{-4}$ [48] analogous as that for 1,3-dimethylbarbituric acid [49]. Imide group has also acidic character, although much weaker, characterized by $K_a = 3.16 \cdot 10^{-13}$ [48]. Thus barbituric acid is a relatively strong acid [49], which becomes weaker when one alkyl substituent is present at C_5 [50]. In the solid state and in DMSO solution barbituric acid is known as triketone form [formula (II)] [51—55]. When barbituric acid is heated for several hours in DMF or DMSO at temperature above 100 °C, the thermodynamically favored tautomer is formed, *i.e.* 1,3-diazine-2,4,6-triol [formula (XIV) in eq. (7)] [56]. When barbituric acid attempted to react with excess of oxiranes, tautomer (XIV) is formed as early as at 40 °C, and leaves the solution as precipitate instead of expected conversion into oligoetherols. This may indicate the catalytic role of epoxies in the process:



(II) (XIV) (7)

where: R = H-, CH_3-

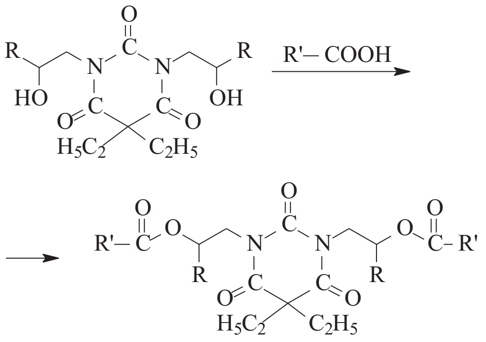
Presumably the catalytic action of oxiranes is based on proton transfer promotion and therefore they speed up the formation of trienolic form [56]. The enol form is a yellow solid, melting at 280 °C with decomposition. It is insoluble in organic solvents, in water it slowly returns into the triketonic form (during weeks). When hydrogens at C_5 are replaced with alkyl groups like in 5,5-diethylbarbituric acid [formula (III)] the tautomerization is not possible and renders such compound suitable substrate for synthesis of *N*-hydroxyalkyl derivatives [formula (XV) in eq. (8)] [57—60].



(8)

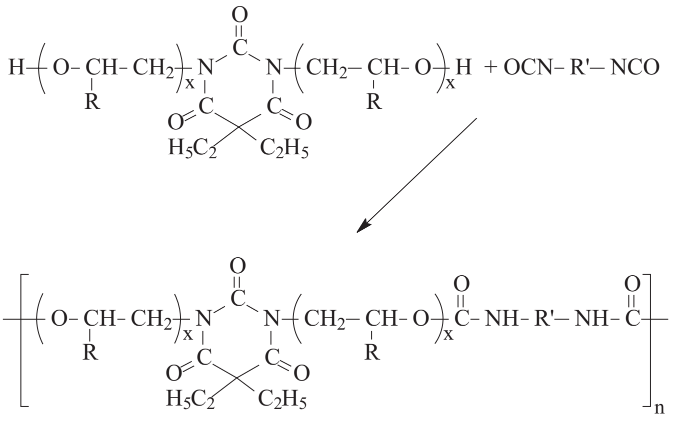
(XV)

This strategy enables the synthesis of new derivatives, *i.e.* esters [formula (XVI) in eq. (9)] and polyurethanes [formula (XVII) in eq. (10)] with a pyrimidine ring starting from 1,3-bis(hydroxyalkyl) derivatives of 5,5-diethylbarbituric acid with carboxylic acids and isocyanates [61, 62], respectively:



(9)

(XVI)



(XVII) (10)

The ester monomers [formula (XVI) where R′ = -CH=CH_2- or -C(CH_3)=CH_2] were used to obtain polymers in the radical polymerization. It has been found that the polymers with a pyrimidine ring have enhanced thermal stability and heat resistance. The structure of polyurethanes, their physical and phase transitions were elucidated. It has been found that they are thermally more stable than classic polyurethanes [63].

URIC ACID AND ADENINE

The simplest way of preparing polyetherols with purine rings would be the reaction of uric acid [formula (IV)] with oxiranes. Until 1999 no information on this reaction could be found in the literature. The reason is the lack of solvents of uric acid. It is insoluble even in DMSO or DMF and its solubility in water is only 0.5 g/dm^3 at 99 °C [64]. The solubility problem was overcome by preparing soluble hydroxymethyl derivatives of uric acid (vide supra).

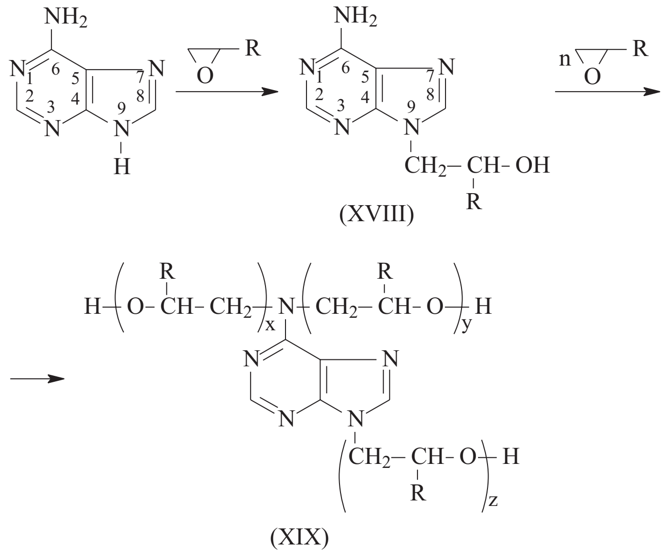
Another compound containing purine rings is adenine [formula (V)]. Reactions of adenine with oxiranes were carried out in DMSO (the best solvent of adenine) or in DMF at 90—95 °C with a triethylamine catalyst. Under these conditions propylene oxide reacted very slowly (46 h). With a DABCO catalyst (1,4-diaza[2.2.2]bicyclooctane) [65] the reaction in DMF was found to proceed more readily and, at the excess of oxiranes, it was possible to obtain purine ring containing polyetherols. This reaction is presented in Scheme B.

The most acidic character have the N(9) proton [66] and the reaction starts with substitution of this proton by oxirane. Initially a crystalline product: 2-(adenin-9-yl)ethanol [formula (XVIII), R = H in Scheme B] or 2-(adenin-9-yl)-1-methylethanol [formula (XVIII), R = CH$_3$] are formed. As more and more oxirane is introduced, amino group slowly starts to react and the product has the form of a semisolid brown resin [formula (XIX)] [65]. Amino groups become fully substituted when over 5-fold or 6-fold molar excess of ethylene oxide or propylene oxide, respectively, is used. Liquid resin is obtained only with 16-fold or 10-fold excess, respectively. Adenine melts at *ca.* 300 °C and its ring decomposes as high as at *ca.* 680 °C. Hence, its hydroxyalkyl derivatives have particularly good thermal stability and decompose at 440—480 °C [65].

The general difficulty to synthesize polyurethanes of enhanced thermal stability is their high viscosity and poor homogenization with typical isocyanates used in the synthesis.

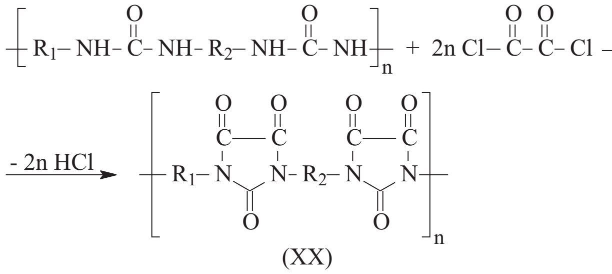
PARABANIC ACID

Parabanic acid of the systematic name imidazolidinetrione is a crystalline solid melting with decomposition at 242—243 °C [67]. In the solid state and in aqueous solutions it has the triketonic form shown as formula (VI) [68]. The acid is soluble in water, hot ethanol [69], methanol, DMF, and in DMSO [70]. In aqueous solutions the first ionization constant is 6.0 · 10^{-7} and the second 1.6 · 10^{-11} [68]. High decomposition temperature of parabanic acid makes this compound a suitable starting material in synthesis of high-molecular compounds of improved thermal stability. Interest in this compound as a monomer was negligible. Only its glycidyl derivative (*N*,*N'*-glycidyl parabanate) was reported as a component of preparations for cotton fabrics [9, 71]. Polymers with imidazolidine rings [formula (XX) in eq. (11)] were prepared not by using parabanic acid itself or its derivatives, but rather through ring closure polyreactions [72—75] or by modifying an existing polymer, such as polyurea [76—78]:



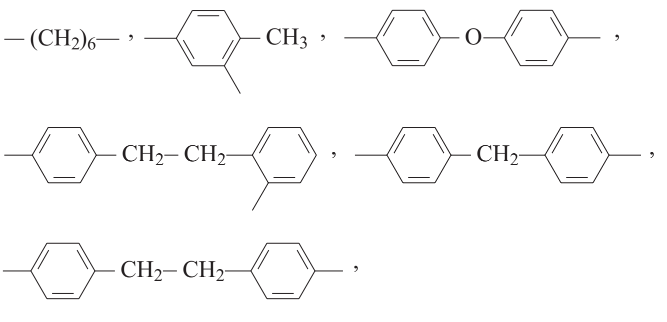
where: R = -H, CH$_3$; x + y + z = n + 1

Scheme B. The reaction of adenine with an excess of oxirane

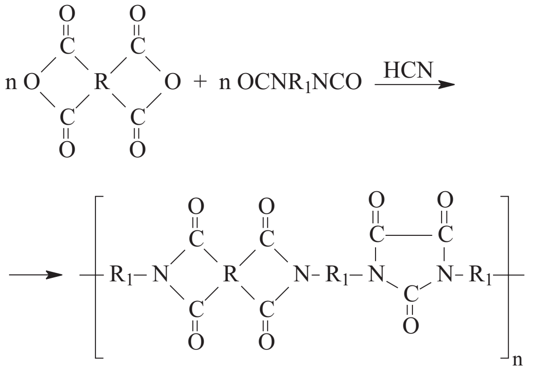


(11)

where: R$_1$ and R$_2$ standing for:



The polymers were also obtained in reactions of dianhydrides with diisocyanates carried out in the presence of cyanide ions [79, 80]:

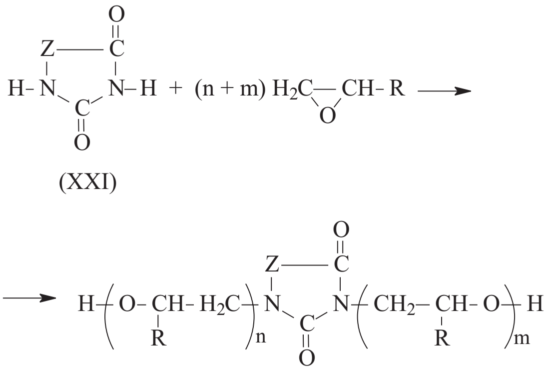


(12)

where: R, R_1 — aliphatic, aromatic of aliphatic/aromatic groups containing 4—40 carbon atoms

The resulting polymers of high thermal stability were used for manufacturing electro-insulating lacquers. Laminates and fibers obtained from the polymers were used for preparation of high modulus products, such as cable supports [80]. For these advantages, simple methods of synthesis of the materials, *i.e.*, monomers containing a ready to use trioxoimidazolidine ring were sought for.

Studies on the synthesis of hydroxyalkyl derivatives of parabanic acid and on their application as monomers started as recently as at the beginning of XXI century. The hydroxyalkylation was carried out using some oxiranes. Reactions of this type were described in the literature for compounds of the structures similar to that of parabanic acid [81—84], such as uracyl, dihydrouracyl, hydantoin and their derivatives of general formula (XXI) in eq. (13).

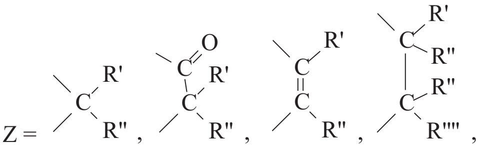


(XXI)

(13)

(XXII)

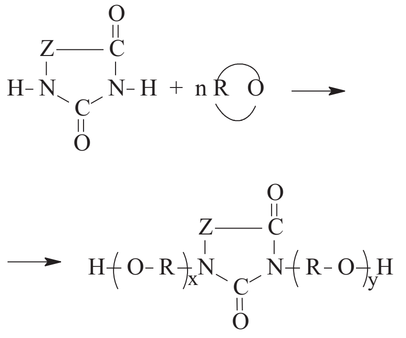
where: R = -H, $-CH_3$ and Z stands for



R', R'', R''', and R'''' denote -H, alkyl, cycloalkyl, or substituted phenyl

The reactions were carried out with ethylene oxide of propylene oxide in DMF [84] dioxane or halogenated hydrocarbons [85] using a small excess of oxiranes with respect to the number of >NH groups of a given compounds.

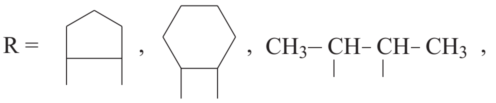
Tetraethylamonium chloride, tertiary amines, alkali metal halides (LiCl, NaCl) or Lewis' acids ($AlCl_3$, $SbCl_5$, $SnCl_4$, $FeCl_3$, $ZnCl_2$, BF_3) were used as catalysts [83—85]. To obtain compounds of structure (XXII), where n + m > 2 a single diol with a heterocyclic ring (n = m = 1) was used and oxirane molecules were then attached to the terminal OH groups. The resulting polyols turned out to be useful semiproducts in synthesis of polyesters or polyurethanes for manufacturing adhesives, coatings or laminates [84]. Heterocyclic compounds presented as formula (XXI) were also reacted with 2,3-epoxybutane, 1,2-epoxycyclopentane or 1,2-epoxycyclohexane to obtain alcohols (x = 0) or diols (x and y > 0) [86, 87] of formula (XXIII):



(14)

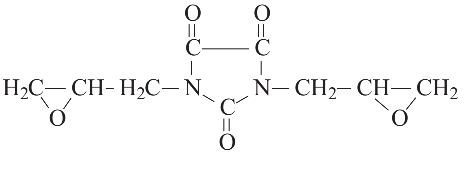
(XXIII)

where Z has the same meaning as in (XXI) and

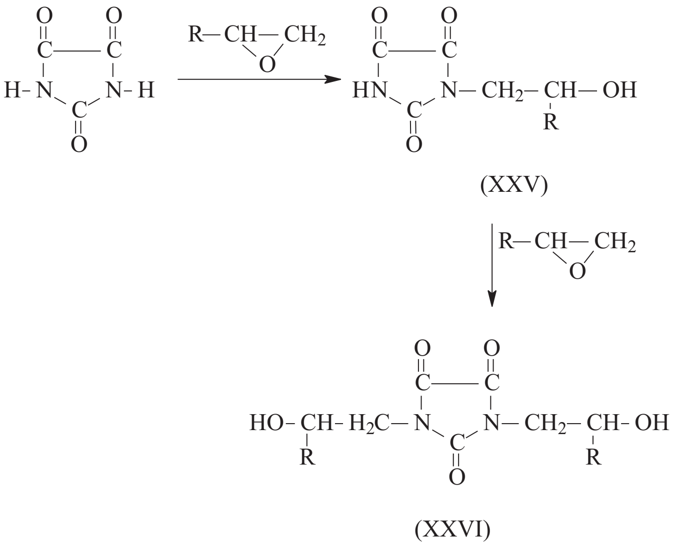


x + y = 1—30

The polyetherols were crosslinked with acid anhydrides to obtain coatings of good mechanical properties [84]. They were also used in manufacturing of laminates and molding or coating compositions [85] of excellent electromechanical properties [86—93]. The heterocyclic compounds mentioned above were reacted with epichlorohydrin of glycerol and, without isolating intermediate halogenohydrines with heterocyclic rings, they were further converted into respective glycidyl ethers [82, 83, 89—91]. The already mentioned *N,N'*-diglycidyl parabanate [formula (XXIV)] was obtained in this way in a reaction of parabanic acid with epichlorohydrin of glycerol [71].



(XXIV)

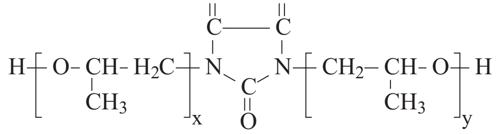


where: R = -H or $-CH_3$

Scheme C. The reaction of parabanic acid with oxirane

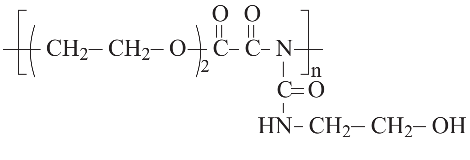
Products of this type were used for preparing epoxy resins of improved shelf storage time [91]. More recently, attempts were reported on preparation of diols in reactions of parabanic acid with ethylene oxide or propylene oxide. In reactions, presented in Scheme C, of equimolar quantities of the acid with respective oxiranes, *N*-(2-hydroxyethyl) hydroparabanate [formula (XXV), R = -H] or *N*-(2-hydroxypropyl) hydroparabanate [formula (XXV), R = $-CH_3$] were obtained, respectively, and at the molar ratio of the reagents equal 1:2, the respective products were *N,N'*-bis(2-hydroxyethyl) parabanate [formula (XXVI), R = -H] or *N,N'*-bis(2-hydroxypropyl) parabanate [formula (XXVI), R = $-CH_3$] [94].

The reactions were carried out at 35—40 °C either without any catalyst and solvent or in a DMF solution with tertiary amines as catalysts. It was found that in reactions of parabanic acid with excess of ethylene oxide or propylene oxide any polyetherols of the formula (XXVII) cannot be obtained because of decomposition of the trioxoimidazolidine ring. In the case of ethylene oxide, the resulting products are polymeric materials with units containing formally three oxyethylene units per parabanic acid unit [formula (XXVIII)] irrespectively of reaction temperature and initial molar ratio [95].



(XXVII)

where: R = -H or $-CH_3$

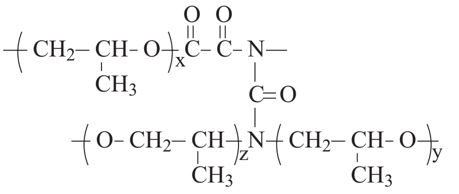


$$\left[\left(CH_2-CH_2-O\right)_2 \overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-\underset{\underset{\underset{HN-CH_2-CH_2-OH}{|}}{C=O}}{\underset{|}{N}}\right]_n$$

(XXVIII)

where: n — the number of moles of oxirane that reacted with one mole of parabanic acid

An increase in the amount of catalyst changes the structure of the polymer. The side chains 2-hydroxyethyl groups are then activated and a crosslinked product is obtained. In the reactions of parabanic acid with an excess of propylene oxide, secondary amide groups react with the oxirane and products containing mostly tertiary amino groups [formula (XXIX)] are obtained:



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

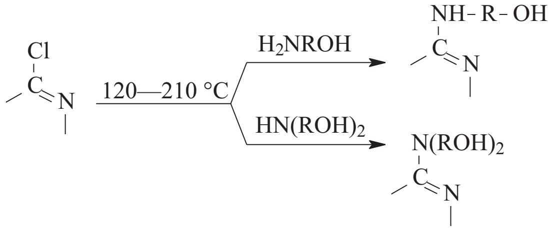
(XXIX)

where: x + y + z = n, n — the number of moles of propylene oxide reacting with one mol of parabanic acid

Different are the reactions of the acid at the excess of ethylene oxide. A polymer containing secondary amino groups precipitates from the reaction medium and does not react further with the oxirane, even at elevated temperature.

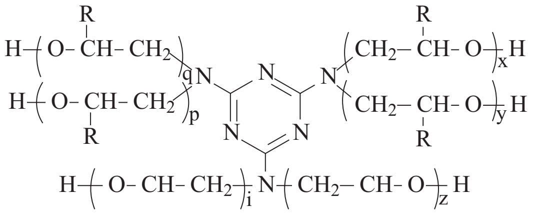
MELAMINE

1,3,5-triazine-2,4,6-triamine, better known as melamine [formula (VII)] is the amide of cyanuric acid. Melamine is a weak base with ionization constants in water at 25 °C equal to $K_1 = 1.1 \cdot 10^{-9}$ and $K_2 = 1.0 \cdot 10^{-11}$ [96]. All six hydrogen atoms of melamine are capable of reacting. They can either be substituted (*e.g.* in alkylation or acylation reactions) or take part in addition [15]. The last type of reaction is a reaction with oxiranes. The hydroxyalkyl derivtives of melamine cannot be obtained directly. They are formed when a small amount of oxirane is used (at melamine:oxirane molar ratio from 1:1 to 1:6), however they are contaminated with unreacted melamine, and therefore difficult to separate [97]. Fortunately they can be prepared in the reaction of respective aminoalcohols with cyanuric chloride [98—100], presented in Scheme D.



Scheme D. The reaction of aminoalcohols with cyanuric chloride

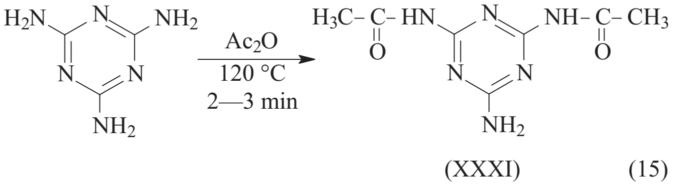
Patent literature on these compounds concentrates mostly on the products obtained with the molar excess of oxirane exceeding six [101—103]. When 6-molar or more excess of oxirane in relation to melamine is used the oligo- and polyetherols of the general formula (XXX) are formed:



(XXX)

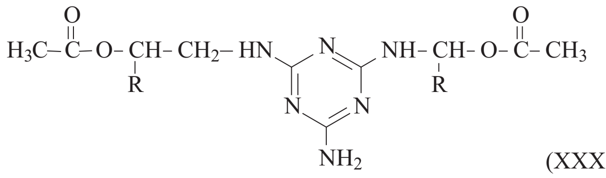
where: x + y + i + z + p + q = n, n — number of equivalents of oxirane per equivalent of melamine

Liquid or resinous substances of hydroxyl number 200—300 mg KOH/g are obtained. The catalysts claimed are oxides or hydroxides of metals of I and II group of the periodic table, most often potassium hydroxide. The latter, however, is not the most effective catalysts because of its limited solubility in organic solvents (including DMSO). Furthermore, dark-brown products are obtained in its presence, displaying high viscosity. The reaction of melamine with oxiranes studied in DMSO and DMF solution, the best solvent of melamine. All these disadvantages were overcome when alkylammonium hydroxides were applied, such as tetrabutylammonium [104] or tetraethylammonium [105] hydroxides, that dissolve in organic solvents much better than potassium hydroxide. Detailed study on the course of reaction and composition of products was described in [106]. The hydroxyl groups from derivatives of melamine are more reactive than amino groups. These reactions lead to formation of etherol chains at expense of unreacted amino groups of melamine. Consequently, the resulting polyetherols have somewhat longer etherol sequence substituting the first amino proton and a shorter etherol sequence substituting the second amino proton [*i.e.*, in formula (XXIX) x > y, q > p, i > z). While seeking 1,3,5-triazine containing compounds better soluble in organic solvent than melamine, attempts were made to apply diacetylmelamine as a starting material for preparation of polyetherols [107]. It is prepared by reacting 1 mole of melamine with two moles of acetic anhydride [108]:



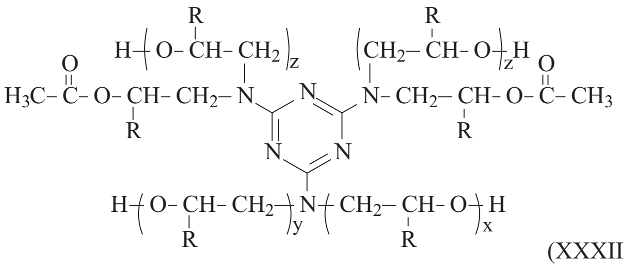
(XXXI) (15)

The reactions of diacetylmelamine [formula (XXXI)] with ethylene oxide or propylene oxide are accompanied by nucleophilic intramolecular rearrangement that alter the structure of polyetherols [104] with respect to the anticipated basing on the structure of diacetylmelamine. Hence, in the reaction of 1 mole of diacetylmelamine with two moles of ethylene oxide *N,N'*-bis(acetyloxyethyl)melamine [formula (XXXII), R = H] rather than *N,N'*-diacetyl-*N,N'*-bis(2-hydroxyethyl)melamine is formed:



(XXXII)

The reaction of one mole of diacetylmelamine with two moles of propylene oxide proceeds in the same way. Further moles of oxirane first react with primary and then with secondary amino groups yielding tetra-functional polyetherols given by formula (XXXIII) [109]:



(XXXIII)

where: R = -H, -CH$_3$; x + y + 2z = n - 2
n – number of equivalents of oxirane per equivalent for diacetylmelamine

CONCLUSIONS

The polyetherols of azacyclic compounds like isocyanuric or 5,5-diethylbarbituric acid, melamine and its derivatives can be obtained by excessive hydroxyalkylation. These polyetherols are useful for synthesis of polymers of enhanced thermal stability. The hydroxyalkylation agents can be oxiranes like ethylene oxide propylene oxide or glycerol epichlorohydrin.

The basic difficulty in synthesis of polyetherols is the lack of solvents for manufacturing purposes of previously mentioned azacyclic compounds, which are not soluble in oxiranes, but only to a lesser extent in DMSO and DMF.

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