

Hydroxyalkylation of Barbituric Acid. I. Hydroxymethyl Derivatives of Barbituric Acid—Precursors of Polyetherols with a Pyrimidine Ring

Anna Ślęczka, Jacek Lubczak

Rzeszów University of Technology, Department of Organic Chemistry, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland

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ABSTRACT: The reaction of barbituric acid with formaldehyde at variable molar ratios was studied. The structure of the products was elucidated using $^1\text{H-NMR}$ and IR spectroscopy as well as acidic number and formaldehyde percentage analysis. The products were potential substrates for the synthesis of linear and multifunctional

polyetherols with a pyrimidine ring by reaction with oxiranes. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 3468–3478, 2006

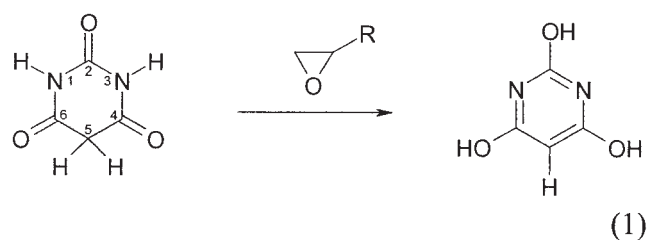
Key words: addition polymerization; oligomers; structure-property relations; resins

INTRODUCTION

Melamine, isocyanuric acid, and uric acid are easily hydroxymethylated with formaldehyde.^{1–3} Hydroxymethylated derivatives can then be used in reaction with oxiranes such as ethylene or propylene oxide for the synthesis of polyetherols containing triazine, perhydrotriazine, and purine rings, respectively.^{4–6} The incorporation of those into polyurethanes or polyesters gives the polymers high thermal stability.^{7,8} However, melamine, isocyanuric, and uric acids are insoluble in most solvents. Therefore, to obtain polyetherols from them by reaction with oxiranes, it was necessary to functionalize these azacyclic substrates with formaldehyde. Their hydroxymethylated derivatives were soluble in organic solvents, including oxiranes.^{3–5}

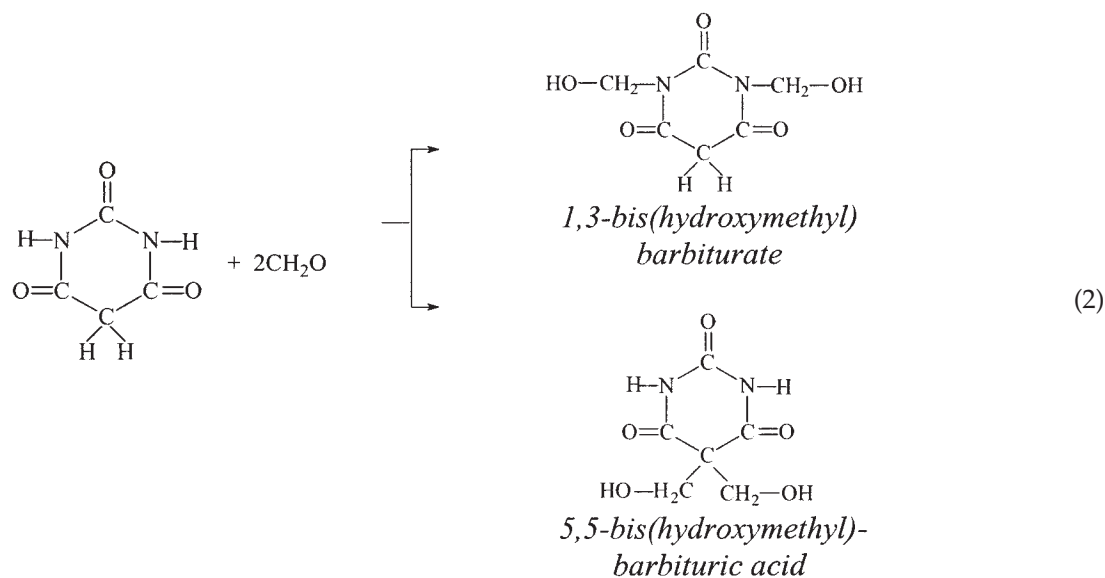
The pyrimidine ring of barbituric acid (BA) is thermally stable. Between 270°C and 280°C, it starts to decompose. BA dissolves in DMSO, DMF, dioxane, and water. Unfortunately, it cannot be used for syn-

thesis of polyetherols in straightforward reaction with ethylene or propylene oxides because it undergoes tautomeric conversion into trienolic form in these conditions:



The latter is insoluble in oxiranes and does not react with them further.⁹ We attempted to avoid this problems in obtaining appropriate substrates for polymers with a pyrimidine ring by obtaining hydroxymethylated derivatives of BA, which are able to react further with oxiranes. We anticipated that BA would react with formaldehyde at both the nitrogen and methylene carbons to give *N*- and *C*-hydroxymethyl derivatives, respectively:

Correspondence to: Jacek Lubczak (jml@prz.rzeszow.pl).



There are no data on such compounds despite previous study of the reaction between BA and its derivatives with formaldehyde.¹⁰ Recently, the kinetics and mechanism of the reaction of BA with salicylic and benzoic aldehydes was studied.¹¹ It also was found that the equimolar reaction between 5-ethylbarbituric acid and formaldehyde in slightly acidic conditions at 60°C led to C-hydroxymethyl derivative.¹²

In this article we describe the successful attempts to obtain *N*- and *C*-hydroxymethyl derivatives of BA by reaction with formaldehyde. The products were soluble in organic solvents and can be used to synthesize bi- and tetrafunctional polyetherols with pyrimidine rings.

EXPERIMENTAL

Syntheses

Reactions of BA with formaldehyde

In a series of syntheses, 12.8 g (0.1 mol) of BA (pure, BDH, Laboratory Supplies, Poole, UK) and an appropriate amount of 36% formalin (pure, POCH, Gliwice, Poland) to reach a 1 : 1–1 : 10 molar ratio were placed in a three-necked 100-cm³ round-bottomed flask equipped with a thermometer, a mechanical stirrer, and a reflux condenser. The mixture was heated at 96°C for 2.5 h if the solid did not disappear or only for 10 min after the BA dissolved. Then the reaction mixture was cooled to room temperature and poured into 200–500 cm³ of acetone. The precipitate was formed, which was filtered off, washed with acetone, and dried at 30°C in vacuum to a constant mass. When no precipitate was formed, the water was distilled off in

vacuum ($p = 13.33$ hPa; $t = 20^\circ\text{C}–60^\circ\text{C}$) to get resinlike products. The reactions at 25°C were conducted for 12 h using 5% formaldehyde. Water was then partially removed from the mixture at room temperature in vacuum. The resulting mixture was poured into acetone, and products were isolated as solid, transparent resins.

Syntheses were conducted at 20°C (with 5% formaldehyde) and at 50°C (with 36% formalin) using the lowest molar excess formaldehyde necessary for the dissolution of BA (1:2) and at 96°C using a 1:4 molar ratio. The reaction time was 10 min after dissolution of BA, in which case the reaction mixtures were not poured into acetone. Instead, the products were obtained as creamy foam solids after the water was removed.

Synthesis of 5-ethyl-5-(hydroxymethyl)barbituric acid

To a three-necked flask were added 7.6 g (0.048 mol) of 5-ethylbarbituric acid (obtained as described in Boehm¹³) and 28.8 g of 5% formaldehyde (0.048 mol). Solidifying of the product was observed after 5 min of exothermic reaction.

Analytical methods

Acidic number was determined by the alkacymetric method in anhydrous products obtained by the reaction of BA with formaldehyde. The weakly bound

TABLE I
Conditions of Preparation of Hydroxymethyl Derivatives of Barbituric Acid Separated by Precipitation with Acetone

Entry	Temperature (°C)	Initial BA: CH ₂ O molar ratio	Time (h)	CH ₂ O content in product (%CH ₂ O mass)		BA:CH ₂ O molar ratio of product	Acidic number (mgKOH/g)	
				calc. ^a	found		calc.	found
1	96	1 : 1	2.5	19.0	26.2	1 : 1.5	323.2	238.3
2	96	1 : 2	2.5	31.9	33.8	1 : 2.2	289.2	205.0
3	96	1 : 3	2.5	41.3	32.8	1 : 2.1	257.3	181.1
4	96	1 : 4	2.5	48.4	45.0	1 : 3.5	240.8	159.6
5	20	1 : 1 ^b	12	19.0	24.3	1 : 1.4	330.0	335.3
6	20	1 : 2 ^b	12	31.9	27.2	1 : 1.6	318.8	202.8
7	20	1 : 3 ^b	12	41.3	37.4	1 : 2.5	276.4	189.2
8	20	1 : 4 ^b	12	48.4	37.5	1 : 2.6	272.3	187.8

^a Calculations were performed assuming that all formaldehyde used was in the product.

^b 5% CH₂O in water solution.

formaldehyde (as hydroxymethyl groups) was determined in product using the iodometric method.¹⁴ The ¹H-NMR spectra (80-MHz TESLA spectrometer, type BS586A; Czechoslovakia) were recorded in d₆-DMSO solvent (with hexamethyldisiloxane internal standard), whereas the IR spectra were obtained in KBr pellets or capillary films (PARAGON 1000 FTIR instrument, Perkin Elmer).

Thermal analysis of the products was performed according to a dynamic method using a derivatograph by the F. Paulik, J. Paulik, L. Erdey system (MOM, Hungary). The recording parameters were: sample mass of 100 mg, temperature range of 20°C–1000°C, registering time of 100 min, 1 : 10 DTA amplification, and 1 : 15 DTG amplification.

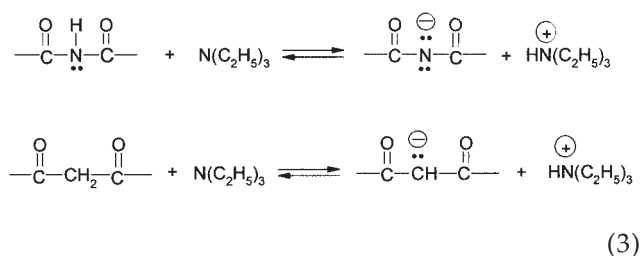
RESULTS AND DISCUSSION

Reaction features and product analysis

BA dissolves in formalin already at room temperature provided that the initial BA : CH₂O molar ratio is 1 : ≥2. It also dissolves in 5% formaldehyde solution within 10–15 min when twofold molar excess formaldehyde is applied. Dissolution is accompanied by heat release. Products of the reaction are soluble in water except for those products obtained from BA : CH₂O 1 : 1 reaction mixtures. Water-soluble products can be precipitated with acetone. This method of isolation is especially useful for lower hydroxymethyl derivatives of BA, obtainable from BA : CH₂O mixtures with 1 : ≤4 ratios. During such a workup, no elimination of formaldehyde from substrate occurs. When a higher molar excess of CH₂O is used, the products obtained are soluble in acetone, in which case the products can be isolated by vacuum distillation of water at tempera-

tures below 60°C. Simultaneously, removal of weakly bound formaldehyde (as hydroxymethyl groups) takes place. Thus, the final BA : CH₂O ratio in the product can be lower than the starting ratio in the reaction mixture (see Table I).

Initially, the reactions were monitored by ¹H-NMR of products isolated successfully by precipitation with acetone. There were two resonances from acidic hydrogen in the BA spectrum: at about 11 ppm from imide —NH protons and at 3.4 ppm from the methylene group in the ring. They both disappeared from the spectrum after the addition of triethyloamine (TEA) because of their acidic character, according to the reaction:



The intensity of imide proton resonance decreased upon the reaction of BA with one equivalent of CH₂O at 96°C. Simultaneously, the resonance at 5.1 ppm attributed to methylene protons, N—CH₂OH, appeared.⁴ Still, the resonance at 3.4 ppm in this product was preserved, suggesting that the ring methylene group remained almost untouched; however, the low-intensity resonance at 2.0–2.1 ppm from C₅—CH₂OH protons indicated that substitution at C₅ also occurred in these conditions as a minor reaction. In the ¹H-NMR spectrum of the product of the reaction of BA with 2 equivalents of CH₂O (Fig. 1), the intensity of the resonance at 5

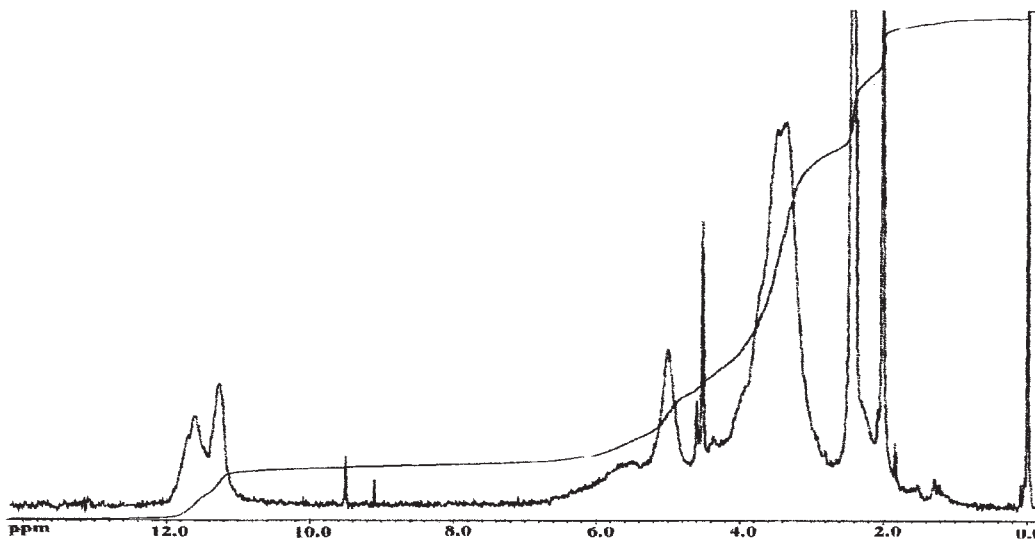
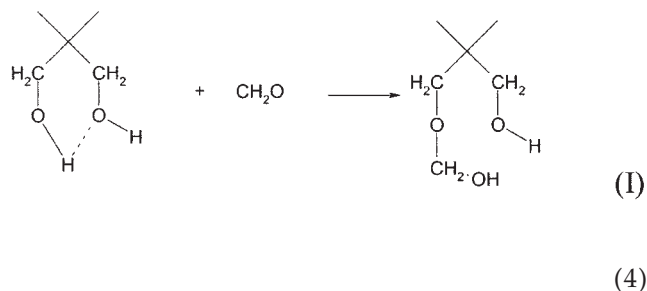


Figure 1 $^1\text{H-NMR}$ spectrum of the product of the reaction of 1 mol BA with 2 mol CH_2O at 96°C .

ppm increased considerably, showing more *N*-hydroxymethyl groups. In addition, resonance at 5.7 ppm appeared, which was attributed to a $-\text{OH}$ proton from the *N*-hydroxymethyl group.⁴ Simultaneously, the intensity of the resonance centered at 2.1 ppm increased, indicating that substitution at C_5 had taken place. Integration of the resonances belonging to the $\text{N}-\text{CH}_2\text{OH}$ and $\text{C}_5-\text{CH}_2\text{OH}$ groups provided the percentages of substitution, which were 54.5 mol % *N* substitution and 45.5 mol % *C* substitution, that is, 1.2 equivalents of formaldehyde was built into $\text{N}-\text{CH}_2-\text{OH}$, and 1 mol formaldehyde was incorporated as $\text{C}_5-\text{CH}_2\text{OH}$ (the ratio of the BA : CH_2O in the product was 1 : 2.1). Another spectral feature of this product was the appearance of two low-intensity resonances, at 4.65 ($-\text{N}-\text{CH}_2\text{O}-\text{CH}_2-\text{N}-$) and at 4.50 ppm ($\text{N}-\text{CH}_2-\text{N}-$ or/and $-\text{C}-\text{CH}_2\text{O}-\text{CH}_2-\text{C}-$). Their presence suggests that during the addition of formaldehyde the mutual condensation of *N*- and C_5 -hydroxymethyl groups occurred.

In the spectra of products obtained with a higher molar excess of CH_2O at 96°C , decreased intensity of the imide and ring methylene proton resonances was observed, which means that the addition of formaldehyde occurred at both the *N* and *C* centers. Unexpectedly, in the spectrum of the product obtained from the BA: CH_2O 1:4 system, the resonance centered at 2.1 ppm disappeared with simultaneous growth of a new resonance at 3.7 ppm. This can be interpreted to the formation of chelate (I) as a result of disubstitution with hydroxymethyl groups at C_5 . Six-membered, stable chelate (I) is characterized by methylene proton resonance at 2.1 ppm. When a larger amount of form-

aldehyde was used, the chelate (I) was further converted:

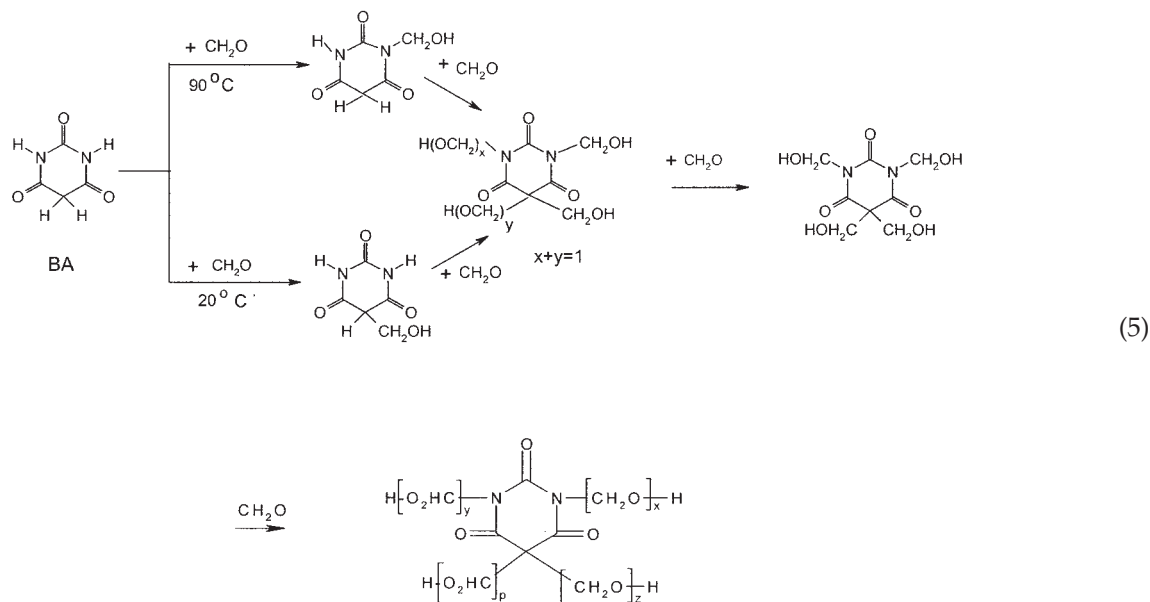


Evidence that the origin of the resonance at 2.1 belonged to methylene protons of $\text{C}_5-\text{CH}_2\text{OH}$ was the observation that in the $^1\text{H-NMR}$ spectrum of the product obtained from 5-ethylbarbituric acid and formaldehyde at 20°C , the resonance at 3.7 ppm attributed to $\text{C}_5-\text{CH}_2-\text{OH}$ appears. In this derivative no further addition of formaldehyde was possible because of the ethyl substituent at C_5 , thus precluding the formation of chelate (I).

The $^1\text{H-NMR}$ spectrum of the product obtained from an equimolar BA : CH_2O mixture at room temperature showed that the imide proton resonance had high intensity (Fig. 2). The product resonance at 2.1 ppm appeared, clearly indicating the reaction of formaldehyde with C_5 . The low intensity of the resonance at 5.1 ppm suggests that in these conditions the reaction of the imide groups with formaldehyde was not efficient. The spectrum of the product obtained with a twofold excess of CH_2O at room temperature showed the growing intensity of the resonance at 2.1 ppm (number of $\text{C}_5-\text{CH}_2\text{OH}$ groups increased). Simultaneously, the intensity of the $-\text{NH}$ resonance de-

creased, and a new signal from the methylene protons of the *N*-hydroxymethyl group appeared. Integration provided 57 mol % C_5-CH_2OH , with the rest made up of *N*-hydroxymethyl protons (0.9 mol C_5-CH_2OH and 0.7 mol $N-CH_2OH$ groups).

Thus, the reaction path depended on the conditions of the process; at room temperature the methylene group of the acid ring primarily reacted, whereas at 96°C the imide group is was primary site of formaldehyde attack:



where $x + y + z + p = n$ and n is the number of attached formaldehyde units.

At intermediate temperatures both processes occurred. The 1H -NMR spectral picture provided good corroboration of the findings from IR spectral monitoring. In the IR spectra of the products obtained at room temperature, the stretching vibrations of $-NH$ and $-OH$ were observed above 3200 cm^{-1} (Fig. 3). In

the course of the consecutive addition of formaldehyde, the $-NH$ bands disappeared (Fig. 4). In the spectra of the products obtained at 96°C, the band from $-NH$ was found only in the product obtained from the 1 : 1 BA : CH_2O mixture.

When a large excess of formaldehyde was used (6 or more equivalents of CH_2O per mole BA), the products were separated by removal of water under vacuum.

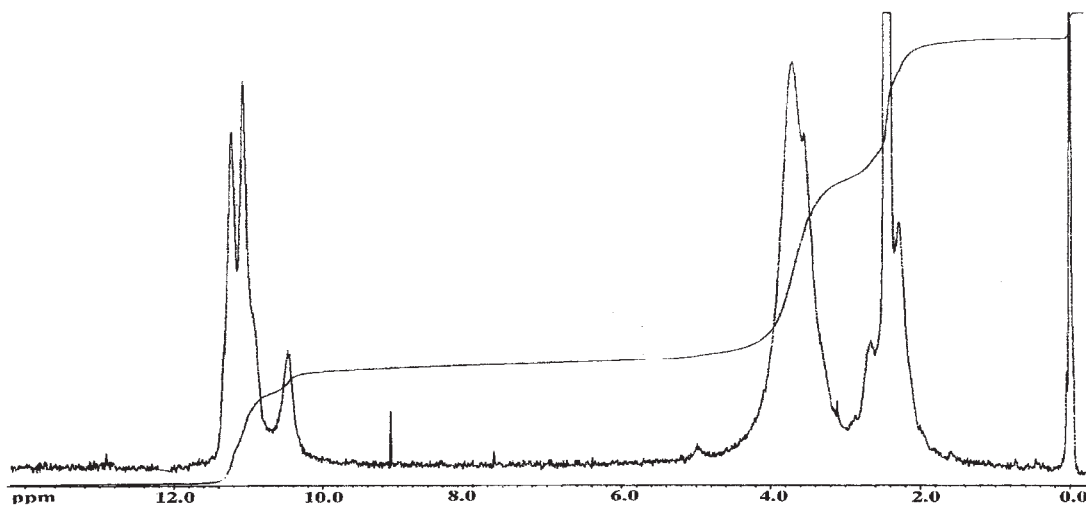


Figure 2 1H -NMR spectrum of the product of the reaction of 1 mol BA with 1 mol CH_2O at 20°C.

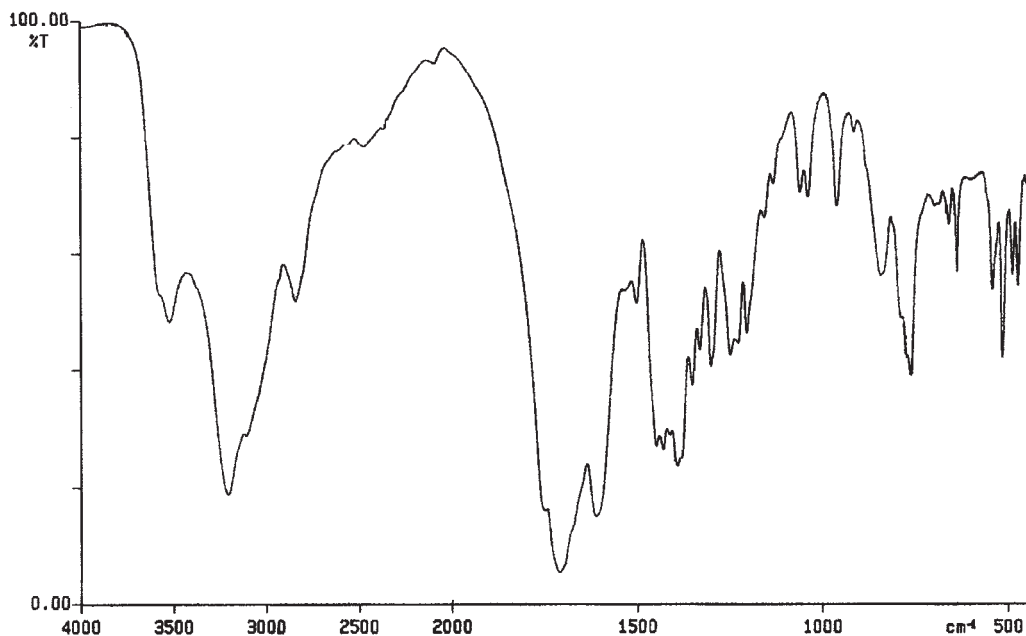


Figure 3 IR spectrum of the product of the reaction of 1 mol BA with 1 mol CH₂O at 20°C.

Regardless of the temperature of synthesis, the resonances from the imide protons in the ¹H-NMR spectra of the products almost completely disappeared (Fig. 5). Instead, resonances from the *N*-hydroxymethyl (5.1 ppm), *C*-hydroxymethyl (3.7 ppm), and semiacetal groups of condensation products (at 4.50–4.65 ppm) were observed. Thus, the formaldehyde was consecutively attached to *N*- and *C*-hydroxymethyl groups with the formation of semiacetals.

This was further shown by analysis of the weakly bound formaldehyde (as hydroxymethyl groups) in semiproducts of addition from the 1 : 6 and 1 : 10 systems (Table II). The number of formaldehyde groups was often smaller than calculated because that part of the formaldehyde was distilled off in vacuum.

Interesting information on the stability of hydroxymethyl groups in aqueous solutions was provided by determination of the acidic number (AN) of the prod-

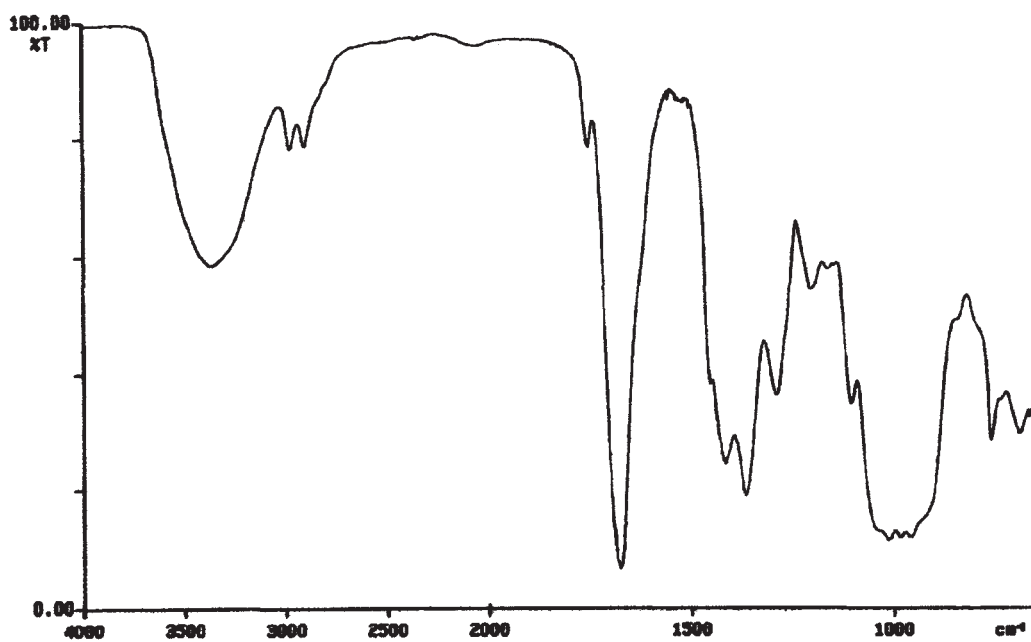


Figure 4 IR spectrum of the product of the reaction of 1 mol BA with 6 mol CH₂O at 50°C.

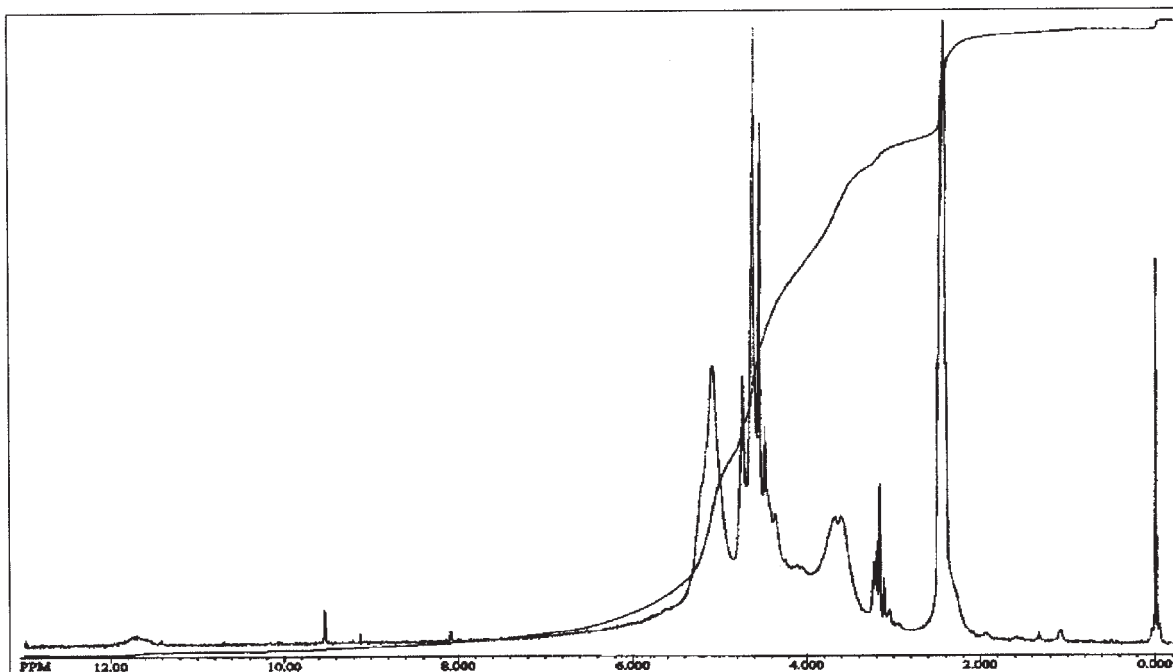


Figure 5 $^1\text{H-NMR}$ spectrum of the product of the reaction of 1 mol BA with 6 mol CH_2O at 50°C .

ucts (Tables I and II). The acidic number of BA equaled 435 mg KOH/g ($\text{AN}_{\text{calcd.}} = 438 \text{ mg KOH/g}$), indicating that in titration conditions the BA was a one-proton acid. The determinations of AN for products of hydroxymethylation produced values much larger than zero (even for products obtained from the BA : CH_2O 1 : >4 system, that is, when all the acidic imide and methylene protons should have been substituted). Assuming that every hydroxymethyl derivative of BA is unibasic, the experimental values of AN were about 30%–35% lower than the calculated ones. This suggests that one of the functional groups of BA is acidic enough and that formaldehyde is weakly

attached to its conjugated base. A methylene group has such properties.^{15,16} That formaldehyde was able to split from C_5 in aqueous solutions and release formaldehyde was determined analytically.

If the reaction was conducted at an initial BA: CH_2O molar ratio of 1 : 4 or 1 : 3 at 96°C (Table II) and water removed under reduced pressure ($p = 13.33 \text{ hPa}$) at temperatures below 60°C or between 60°C and 100°C on a rotary evaporator ($p = 26 \text{ hPa}$), a product with approximately 33.5 wt % formaldehyde was obtained. This demonstrates the presence of two hydroxymethyl groups in the product. The $^1\text{H-NMR}$ unambiguously indicated that the main product of the reaction in

TABLE II
Conditions of Preparation of Hydroxymethyl Derivatives of Barbituric Acid Separated by Removal Water under Reduced Pressure

Entry	Temperature ($^\circ\text{C}$)	Initial BA: CH_2O molar ratio	Time (min)	CH ₂ O content of product (%CH ₂ O mass)		BA: CH_2O molar ratio of product	Acidic number (mgKOH/g)	
				calc. ^a	found		calc.	found
1	96	1:3	150	31.9	33.5	1:2.1	298.4	185.5
2	96	1:4	150	31.9	33.6	1:2.1	298.4	187.4
3	96	1:10	150	70.1	60.8	1:6.6	131.1	92.4
4	50	1:2	10	31.9	31.0	1:2.0	298.4	221.2
5	50	1:4	5	48.4	45.8	1:3.5	226.2	160.0
6	50	1:6	120	58.4	55.3	1:5.3	201.8	132.6
7	20	1:2 ^b	5	31.9	31.1	1:2.0	298.4	211.4
8	20	1:10	720	70.1	66.1	1:8.3	148.1	101.8

^a Compare to Table I.

^b Compare to Table I.

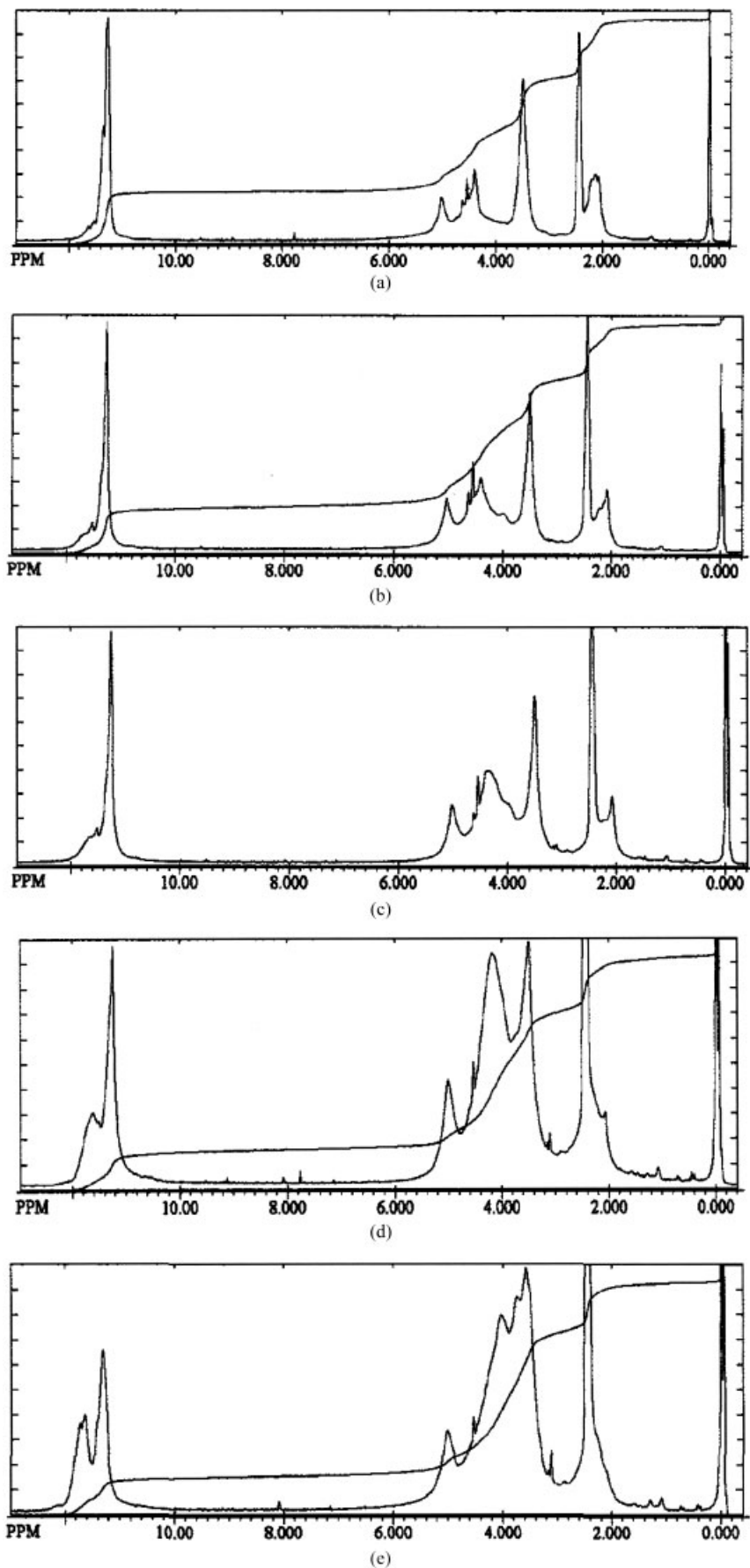


Figure 6 $^1\text{H-NMR}$ spectrum of the product of the reaction of 1 mol BA with 2 mol CH_2O : (a) at 20°C , (b) exposed to $\text{d}_6\text{-DMSO}$ at 90°C for 15 min, (c) exposed to $\text{d}_6\text{-DMSO}$ at 90°C for 30 min, (d) exposed to $\text{d}_6\text{-DMSO}$ at 90°C for 90 min, (e) exposed to $\text{d}_6\text{-DMSO}$ at 90°C for 240 min.

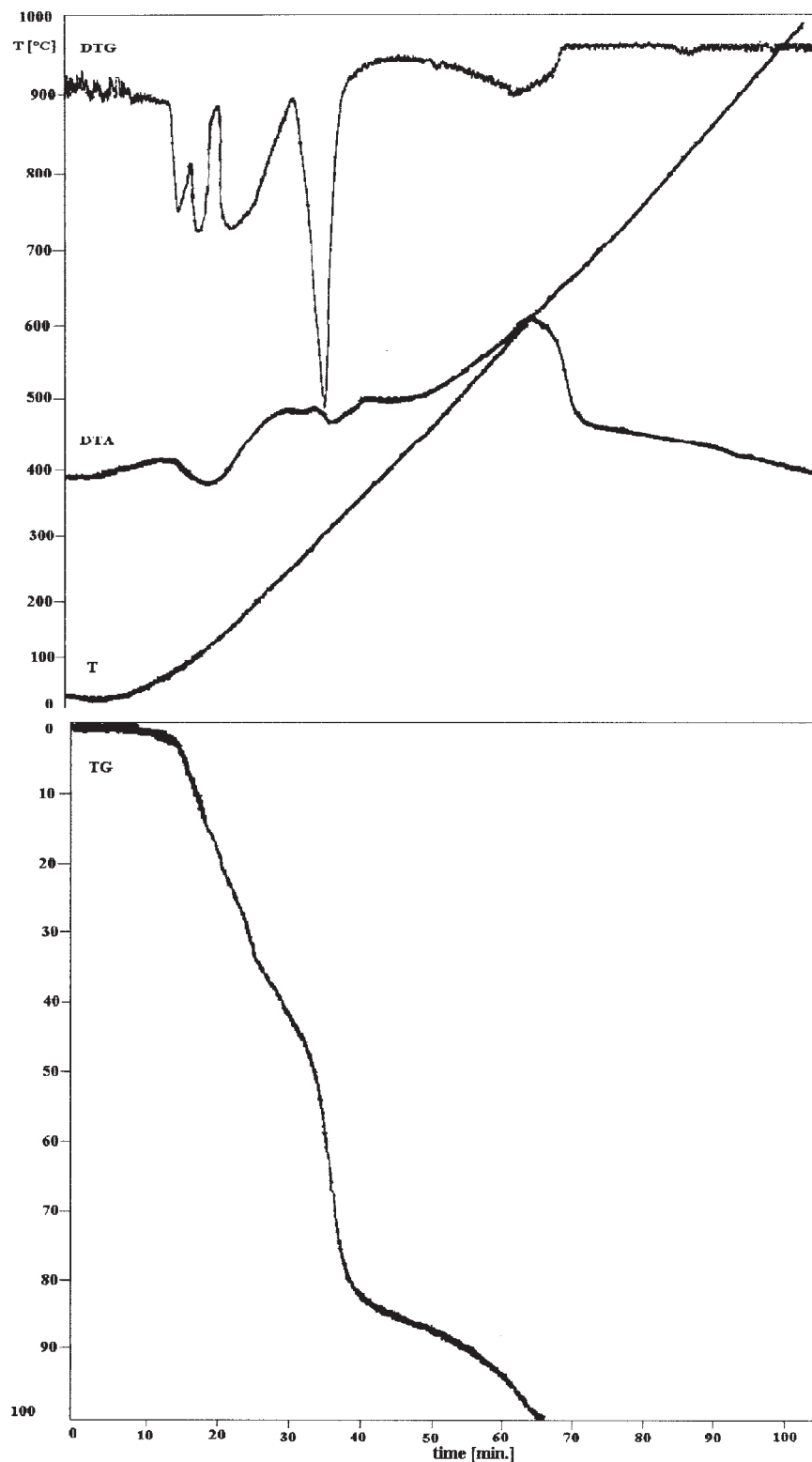
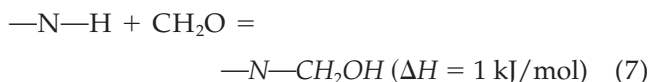
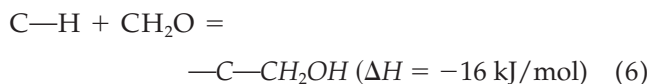


Figure 7 Results of thermal decomposition of the product of reaction of 1 mol barbituric acid with 6 mol formaldehyde.

these condition was 1,3-bis(hydroxymethyl)barbiturate. In contrast, the $^1\text{H-NMR}$ spectrum of the product obtained at 50°C from the 1 : 2 system and separated by vacuum removal of water showed that the formal-

dehyde had been eliminated from the product, and formaldehyde reacted with both the N and the C_5 centers (with resonances at 5.1 and 2.1 ppm both present). On the basis of the integration of the corre-

sponding resonances of the *N*- and *C*-hydroxymethyl group protons (1.1 : 0.9), it could be concluded that the reactivity of the methylene and imide groups was similar. If water was distilled from the 1 : 2 mixture (CH_2O added as 5% aqueous solution) at room temperature, the main product, identified on the basis of its $^1\text{H-NMR}$ spectrum, was 5,5-bis(hydroxymethyl) barbituric acid. The enthalpies of reaction calculated from the bond energies



indicated that the preferred reaction was hydroxymethylation of methylene protons, and indeed it has been shown in this study that this reaction already was occurring at room temperature.

Analysis of the $^1\text{H-NMR}$ spectra of *C*-hydroxymethyl derivatives of BA heated to 90°C in d_6 -DMSO and stored at this temperature for 3 h indicated that isomerization of 5,5-bis(hydroxymethyl)barbituric acid to 1,3-bis(hydroxymethyl)barbituric acid occurred. It was accompanied by diminishing of $\text{C—CH}_2\text{—OH}$ resonance at 2.1 ppm with a simultaneous increase in the intensity of the resonance at 5.1 ppm attributed to $\text{N—CH}_2\text{—OH}$ protons. At the same time, the resonance at 11 ppm belonging to the N—H proton appeared that showed evidence that imide groups were blocked with formaldehyde [Fig. 6(a–e)].

The same behavior was found for *C*-hydroxymethyl derivatives of BA dissolved in d_6 -DMSO at room temperature and then stored for several months at ambient temperature.

Thermal analysis of the products of reaction between BA and formaldehyde was applied in order to determine thermal stability of these compounds. DTA curve for the product obtained from 1 : 2 BA : CH_2O at 96°C showed, in addition to the peak corresponding to pyrimidine ring cleavage (at 280°C – 290°C), two endothermic peaks, in the ranges of 65°C – 75°C and 145°C – 160°C . Both were related to mass loss, the first indicating slight loss of mass, and the second showing major loss of mass. They corresponded to formaldehyde release from C_5 - and *N*-hydroxymethyl groups. Similar peaks were observed for the product obtained from 1 : 2 BA : CH_2O at room temperature; however, the derivatogram showed that mass loss corresponding to cleavage of *N*-hydroxymethyl group (145°C – 160°C) was less pronounced. An additional endothermic peak at 120°C – 130°C was present in the thermogravimetric curve of the product obtained from the 1 : ≥ 5.3 BA : CH_2O system originating from cleavage of semiacetal groups (Fig. 7).

Thus, the reaction of BA with excess formaldehyde can be optimized for synthesis of the 1,3-bis(hydroxymethyl) derivative; this needs to be obtained from BA : CH_2O at a ratio of 1 to 2.6–2.8. If the product contains more than two formaldehyde groups (it depends on the distillation regime), the product should be exposed to heating to 90°C until the appropriate amount of formaldehyde has been lost. Such a workup results in cleavage of the *C*-hydroxymethyl groups, leaving the *N*-hydroxymethyl ones.

Perspectives on application of hydroxymethyl derivatives

Hydroxymethyl derivatives of BA obtained from the 1 : 4 BA : CH_2O system at 96°C were bifunctional compounds with two *N*-hydroxymethyl groups, and they had good solubility in DMSO, DMF, and water. Our preliminary investigation showed that these derivatives can be successfully used for synthesis of polyetherols containing a barbituric ring in reactions with oxiranes. Polyetherols are convenient substrates for obtaining linear polymers such as polyurethanes or polyesters with a pyrimidine ring in the main chain.

With the aim of producing products soluble in oxiranes, we reacted BA with formaldehyde at an initial ratio of 1 : 6, resulting in formation of a resinlike product after removal of the water. The product contained not only *N*- and C_5 -hydroxymethyl but also semiacetal $\text{O—CH}_2\text{OH}$ groups.

Our preliminary study indicated that after introducing this product to a slight amount of water [up to 5% (w/w)] and catalyst (triethylamine), liquid mixtures were obtained that were easily miscible with oxiranes with gentle heating (to 40°C – 50°C), and a reaction with ethylene oxide or propylene oxide occurred, resulting in formation of tetrafunctional polyetherols with a pyrimidine ring. These polyetherols could then be used together with isocyanates to obtain polyurethane foams that had high thermal resistance.

Details about the analysis and the properties of products obtained in the oxirane reactions with hydroxymethylated derivatives of BA will be reported separately.

CONCLUSIONS

1. Formaldehyde reacted with BA involving imide and ring methylene groups to produce *N*- and/or *C*-hydroxymethyl derivatives of BA. The relative reactivity could be optimized by the parameters of synthesis; at room temperature the primary site of formaldehyde substitution was methylene carbon, whereas at 96°C mainly an imide proton was substituted. At

50°C formaldehyde reacted with both the methylene and imide functions of BA.

2. Hydroxymethylation of BA enabled bi- and tetrafunctional derivatives with an alcohol character to be obtained. These were able to react further with oxiranes to form polyetherols with a pyrimidine ring. It should be mentioned that straight hydroxyalkylation of BA with oxiranes is impossible because BA tautomerizes into a trienol form that is insoluble in these conditions.
3. The new polyetherols can be used for synthesis of new polymers containing a pyrimidine ring.

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