# New method of synthesis of oligoetherols with pyrimidine ring from barbituric acid and glycidol (*Rapid Communication*)

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**Abstract**: Barbituric acid (BA) cannot be used for synthesis of oligoetherols in a straightforward reaction with ethylene oxide (EO) or propylene oxide (PO) or alkylene carbonates because it undergoes tautomeric conversion into the tri-enolic form. The latter is insoluble in oxiranes and alkylene carbonates and does not react with them further. This obstacle was eliminated by initial functionalization of BA with glycidol (GL) leading to hydroxyalkyl derivatives of BA. The hydroxyalkyl derivatives of BA dissolve easily in oxiranes or in alkylene carbonates like ethylene (EC) or propylene (PC) carbonates and react with them to give oligoetherols with enhanced thermal stability.

**Keywords**: barbituric acid, glycidol, oligoetherols, structure, properties.

## Nowa metoda syntezy oligoeteroli z pierścieniem pirymidynowym z zastosowaniem kwasu barbiturowego i glicydolu

**Streszczenie**: Do syntezy oligoeteroli przeznaczonych do otrzymywania termoodpornych polimerów w reakcjach hydroksyalkilowania nadmiarem oksiranów [tlenku etylenu (EO), tlenku propylenu (PO)] lub węglanów alkilenowych nie może być stosowany kwas barbiturowy (BA), ponieważ związki alkilujące katalizują reakcje jego tautomeryzacji do formy trienolowej, która jest nierozpuszczalna we wspomnianych czynnikach hydroksyalkilujących i nie reaguje z nimi. Trudności te wyeliminowano dzięki zastosowaniu w reakcji glicydolu (GL), który umożliwia otrzymywanie hydroksyalkilowych pochodnych BA o zwiększonej funkcyjności, w porównaniu z wyjściowym kwasem. Opracowana metoda nie wymaga używania toksycznych rozpuszczalników, ponieważ otrzymane pochodne rozpuszczają się w oksiranach i węglanach alkilenowych [węglan etylenu (EC) lub węglan propylenu (PC)] oraz reagują bezpośrednio z nimi dzięki czemu otrzymuje się oligoeterole o zwiększonej termoodporności.

**Słowa kluczowe**: kwas barbiturowy, glicydol, oligoeterole, struktura, właściwości.

High temperature of decomposition of a pyrimidine ring (270—280 °C) [1] makes barbituric acid (BA) a good candidate to obtain diols or multifunctional oligoetherols by reaction with oxiranes or alkylene carbonates and further to obtain thermally resistant polymers [2—6]. BA cannot be used for synthesis of oligoetherols in a straightforward reaction with ethylene or propylene oxides because it undergoes tautomeric conversion into the tri-enolic form, which is insoluble in oxiranes and does not react with them further [7]. Our previous studies have shown that BA does not react with alkylene carbonates for the same reason and probably therefore there is lack of literature reporting on application of BA for obtaining oligoetherols. We have explored another route to hydroxyalkyl derivatives of BA, based on the reaction of BA with formaldehyde [4]. Tetra(hydroxymethyl) derivatives of BA can be applied for the synthesis of polymers with a pyrimidine ring, because they dissolve well in oxiranes and react with them to give oligoetherols. The foams obtained from these oligoetherols are remarkably thermally stable due to the presence of pyrimidine rings [5]. The disadvantage of hydroxymethyl derivatives of BA is migration of formaldehyde from hydroxymethyl groups into the end of oxyalkyl chain upon their reaction with oxiranes [6] and release of HCHO during the synthesis of polyurethane foams (PURF) and undesired, non-controlled foaming. Therefore, the methods of synthesis of oligoetherols with a pyrimidine ring with exclusion of formaldehyde are still the matter of interest. Such syntheses as described here straightforward reaction of BA with a hydroxyalkylating agent would be especially useful. The GL was the good candidate as hydroxyalkylating reagent.

## EXPERIMENTAL PART

### Materials

The following materials were used in this work:

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— barbituric acid (BA, pure, BDH, Laboratory Supplies, UK);

— glycidol (GL, pure, Sigma-Aldrich);

— triethylamine (TEA, pure, Avocado),

— ethylene oxide (EO), propylene oxide (PO), ethylene carbonate (EC) and propylene carbonate (PC) (all pure, Fluka).

### Syntheses involving oxiranes

To the pressure reactor equipped with a mechanical stirrer, reflux condenser, and thermometer there were introduced 12.8 g (0.1 mol) of BA and 29.6 g (0.4 mol) of GL. The mixture was heated at 130 °C for 3 h. Then 2 $cm^3$ of TEA and 46.4 g (0.8 mol) of PO were added. The synthesis was conducted at 90 °C and 500 kPa pressure for about 20 h.

### Syntheses involving alkylene carbonates

To the three-necked round bottom 250 $cm^3$ flask, equipped with mechanical stirrer, reflux condenser, and thermometer, 42.4 g of the product obtained from BA and GL (0.1 mol) and 70.4 g (0.8 mol) of EC or 81.6 g (0.8 mol) of PC as well as 0.77 g (in the case of EC) or 1.10 g (in the case of PC) of $K_2CO_3$ as a catalyst were introduced. In another reactions EC and PC were used stepwise: first 52.8 g (0.6 mol) of EC was reacted and then 40.8 g (0.4 mol) of PC was added. The mixture was stirred and heated at 150—165 °C until alkylene carbonates reacted to the end.

### Analytical methods

The reaction between BA and GL and alkylene oxides or carbonates was followed by measuring of the content of unreacted epoxide groups (according to PN-EN ISO 3001:2002 standard) and the content of unreacted carbonate using the $Ba(OH)_2$ method [8].

Elemental analyses for C, H, N, were done with EA 1108, Carlo-Erba analyzer.

The $^1H$ NMR spectra were recorded at 500 MHz Bruker UltraShield in DMSO-$d_6$ with HMDS as internal standard.

IR spectra were registered on PARAGON 1000 FTIR Perkin Elmer spectrometer in ATR technique. MALDI-ToF spectra of products were obtained on Voyager-Elite Perceptive Biosystems (US) mass spectrometer equipped with nitrogen laser working at 337 nm. The method of laser desorption from matrix was used with 2,5-hydroxybenzoic acid in THF at 1 mg/$cm^3$ concentration. The samples were diluted with methanol to concentration of 1 mg/$cm^3$, followed by addition of 10 mg/$cm^3$ solution of NaI in acetone. Therefore in some cases the molecular ion weights were increased by the weight of $Na^+$ and $CH_3OH$.

Thermal analysis of the product of reaction BA with GL was performed in a crucible at 20—600 °C temperature range, about 200 mg sample, under the air atmosphere with TGA/DSC 1 derivatograph (Mettler).

Refractive index, density, viscosity, and surface tension of oligoetherols were determined with Abbe refractometer, picnometer, Höppler viscosimeter (BHZ, Prüfgerate-werk, Germany) and by the detaching ring method, respectively.

## RESULTS AND DISCUSSION

BA reacts with GL upon heating to 100 °C. The exothermic reaction does not require any catalyst. In order to avoid the precipitation of the enolic form of BA the molar ratio of BA:GL was maintained at the level at least 1:4. Nevertheless, the enolic BA appears initially and upon prolonged heating it dissolves in the reaction mixture and the obtained final product is clear, semi-solid orange resin. In the IR spectrum of the product the oxirane ring band and the NH bonds of BA valence and deformation bands (initially observed at 3200—3090 and 1370—1340 $cm^{-1}$) are absent. This clearly leads to the conclusion that imide groups of BA react with GL. Also the methylene group (BA) deformation band at 810 $cm^{-1}$ disappears indicating the involvement of the methylene hydrogens in the reaction between BA and GL. Concomitantly, the bands assigned to I- and II- order -OH groups appear at 1034 and 1103 $cm^{-1}$ as well as broad band at 3320 $cm^{-1}$. The keto group is preserved in the ring as it was confirmed by the presence of valence band at 1634 $cm^{-1}$.

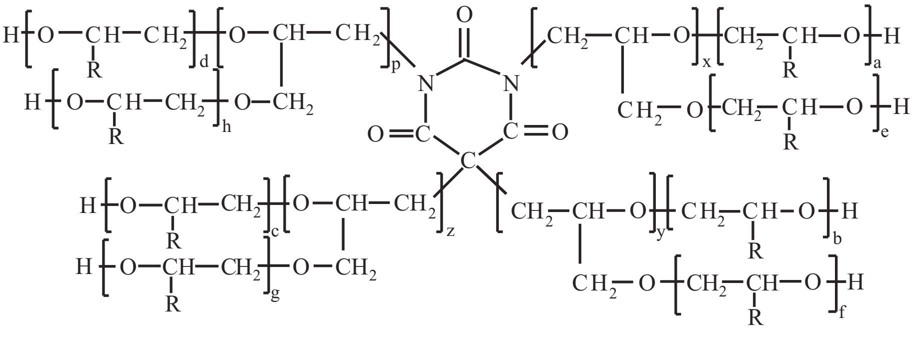
The analysis of $^1H$ NMR spectra of products also confirmed the reaction of imide groups of BA with GL by the disappearance of the -N**H** resonance at *ca.* 11.0 ppm. The enolic form is absent in the products as it can be concluded from the absence of olefinic resonance at *ca.* 8 ppm. Moreover, the multiplets at 3.7—3.2 ppm attributed to methylene and methine protons of aliphatic chain appear.

The structure of products was confirmed by MALDI-ToF mass spectra. The interpretation of MALDI-ToF spectrum for the product of reaction between 1 mole of BA and 4 moles of GL is presented in Table 1. The series of peaks differing of m/z = 74 units occur, indicating the consecutive incorporation of oxyalkylene units into oligomers (signals 9, 14, 19, 24, 27, 30, 33 and 35). Specifically, in the products obtained in the case of molar ratio of BA:GL = 1:4 several derivatives of variable substitution level of BA with GL are present. From the mass spectra we could also conclude that elimination of water from the products occurs, by the presence of series of peaks corresponding to molecular ions of the masses lower than 18 m/z units in comparison with the main products (signals 6, 10, 13, 21, 26 and 29). The percentage of elimination products was so low that only traces of them could be detected by the $^1H$ NMR spectra. The product obtained for molar ratio of BA:GL = 1:4 was not suitable for synthesis of PURFs due to high viscosity rendering the formation of homogeneous mixture with isocyanates impossible.

**Table 1. Interpretation of MALDI-ToF spectrum of reaction product obtained from 1 mole of BA and 4 moles of GL**

| Signal number | Signal position m/z | Relative signal intensity, % | The molecular ion structure | Calculated molecular weight |
|---|---|---|---|---|
| 1 | 127.9 | 29.0 | BA | 128 |
| 2 | 153.9 | 23.0 | BA+ $Na^+$ | 151 |
| 3 | 185.0 | 37.5 | BA + Gl[a] – $H_2O$[b] + $H^+$ | 185 |
| 4 | 203.0 | 17.0 | BA + GL + $H^+$ | 203 |
| 5 | 241.0 | 37.5 | BA + GL + $H_2O$ + $Na^+$ | 243 |
| 6 | 259.0 | 100.0 | BA + 2GL – $H_2O$ + $H^+$ | 259 |
| 7 | 316.3 | 33.3 | BA + 2 GL + $H_2O$ + $Na^+$ | 317 |
| 8 | 333.1 | 52.0 | BA + 2GL + $CH_3OH$ + $Na^+$ | 331 |
| 9 | 351.1 | 31.2 | BA + 3GL + $H^+$ | 351 |
| 10 | 358.4 | 12.5 | Ba + 3 GL – $H_2O$ + $Na^+$ | 355 |
| 11 | 369.1 | 10.0 | BA + 3GL + $H_2O$ + $H^+$ | 369 |
| 12 | 399.1 | 20.0 | BA + 3GL + $CH_3OH$ + $H^+$ | 400 |
| 13 | 407.1 | 29.8 | BA + 4GL – $H_2O$ + $H^+$ | 407 |
| 14 | 425.1 | 41.2 | BA + 4GL + $H^+$ | 425 |
| 15 | 443.1 | 8.3 | BA + 4GL + $H_2O$ + $H^+$ | 443 |
| 16 | 455.1 | 7.5 | BA + 4GL + $CH_3OH$ | 456 |
| 17 | 473.1 | 8.3 | BA + 4GL +$CH_3OH$ + $H_2O$ | 474 |
| 18 | 481.2 | 16.7 | BA + 4GL + $CH_3OH$ + $Na^+$ | 479 |
| 19 | 499.2 | 27.1 | BA + 5GL + $H^+$ | 499 |
| 20 | 517.1 | 10.0 | BA + 5GL + $H_2O$ | 517 |
| 21 | 535.1 | 6.2 | BA + 5GL – $H_2O$ + $CH_3OH$ +$Na^+$ | 535 |
| 22 | 547.1 | 8.3 | BA + 5GL + $CH_3OH$ + $H_2O$ | 548 |
| 23 | 555.2 | 8.3 | BA + 5GL + $CH_3OH$ + $Na^+$ | 553 |
| 24 | 573.2 | 18.7 | BA + 6GL + $H^+$ | 573 |
| 25 | 591.1 | 10.4 | BA + 6GL + $H_2O$ + $H^+$ | 591 |
| 26 | 609.1 | 6.4 | BA + 6GL – $H_2O$ + $CH_3OH$ + $Na^+$ | 609 |
| 27 | 647.2 | 11.2 | BA + 7GL + $H^+$ | 647 |
| 28 | 665.2 | 9.8 | BA + 7GL + $H_2O$ + $H^+$ | 665 |
| 29 | 683.1 | 6.0 | BA + 7GL – $H_2O$ + $CH_3OH$ + $Na^+$ | 683 |
| 30 | 721.2 | 7.9 | BA + 8GL + $H^+$ | 721 |
| 31 | 739.2 | 6.9 | BA + 8GL + $H_2O$ + $H^+$ | 739 |
| 32 | 757.2 | 5.2 | BA + 8GL + $CH_3OH$ | 757 |
| 33 | 795.2 | 6.2 | BA + 9GL + $H^+$ | 795 |
| 34 | 831.2 | 5.4 | BA + 9GL + $CH_3OH$ | 831 |
| 35 | 869.2 | 3.6 | BA + 10GL + $H^+$ | 869 |
| 36 | 887.2 | 4.2 | BA + 10GL + $H_2O$ + $H^+$ | 887 |

[a] GL — oxyalkylene unit from glycidol. [b] "– $H_2O$" means that the product undergoes water elimination in the course of the reaction.



(I)

R = H, $CH_3$

**T a b l e 2. The results of elemental analysis and physical properties (measured at 20 °C) of products of reactions between BA, GL, EC and PC (or PO)**

| Molar ratio of BA:GL:EC:PC (or PO) | Element content, wt % | | | | | | Refractive index | Density, g/cm$^3$ | Viscosity, N·s/m$^2$·10$^3$ | Surface tension, N/m·10$^3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | calculated | | | found | | | | | | |
| | % N | % C | % H | % N | % C | % H | | | | |
| 1:4:0:0 | 6.60 | 45.28 | 6.60 | 6.80 | 45.12 | 6.72 | -a) | - | - | - |
| 1:6:0:0 | 4.90 | 46.15 | 7.00 | 4.80 | 46.24 | 7.49 | - | - | - | - |
| 1:4:8:0 | 3.60 | 49.48 | 7.73 | 3.58 | 49.79 | 8.03 | 1.4768 | 1.2585 | 67 343 | 46.3 |
| 1:4:0:8 | 3.37 | 53.49 | 10.43 | 3.51 | 53.41 | 10.46 | 1.4896 | 1.1689 | 60 867 | 45.6 |
| 1:4:6:4 | 3.04 | 52.17 | 8.26 | 3.09 | 52.57 | 8.47 | 1.4965 | 1.2081 | 45 259 | 41.9 |
| 1:4:0:(8) | 3.15 | 54.05 | 8.56 | 3.30 | 53.72 | 8.30 | 1.4889 | 1.1739 | 39 127 | 41.0 |

a) Products are semisolid resins, for which determinations cannot be performed at the room temperature with the methods used here.

For products of reaction of BA with GL, PO, EC or PC the elemental analysis was performed and physical properties were determined. The results are listed in Table 2. Large excess of GL (up to 18 moles per 1 mole of BA) did not significantly decrease viscosity, however the obtained resin was well miscible with EO and PO at 80—90 °C and reacted with them in absence of solvents and in presence of TEA to form multifunctional oligoetherols of low viscosity. Alkylene carbonates could be used instead of oxiranes. The latter syntheses could be done in the presence of $K_2CO_3$ catalyst. The elemental analytical results correspond to Formula (I).

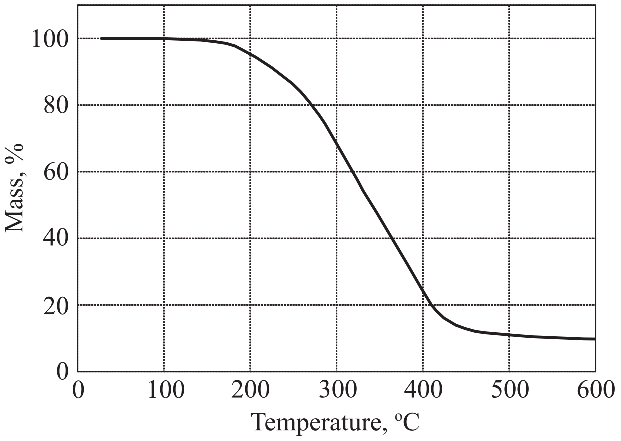


**Fig. 1. Thermal analysis of product of reaction obtained for reagents with molar ratio of BA:GL = 1:4**

Products of BA with GL reaction as well as obtained oligoetherols have enhanced thermal resistance. The thermogravimetric curve of this product obtained for molar ratio of BA:GL = 1:4 is presented in Fig. 1. Their 10 % decomposition initiated at *ca.* 235 °C, while the temperature of maximum decomposition was within 340 °C. Classic oligoetherols used for obtaining of thermostable PURFs start to decompose at the temperature over 170 °C [9]. The values of viscosities and surface tension indicate that oligoetherols can be successfully used as polyol components for obtaining of PURFs.

## CONCLUSIONS

The new method of synthesis of stable hydroxyalkyl derivatives of BA and oligoetherols with a pyrimidine ring was elaborated. The hydroxyalkyl derivatives of BA were obtained by reaction of BA with excess GL (1:4 molar ratio). The reaction was conducted without solvent and catalyst. The obtained semiproducts were then *in situ* applied to obtain thermally resistant oligoetherols by reaction with alkylene carbonates or oxiranes.

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