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SYNTHESIS OF 2-HYDROXYPROPYL-1,3-*bis*-ESTEROSULPHOIMIDES OF SACCHARIN-5- AND -6-CARBOXYLIC ACID

E.T.Aslanova, T.A.Aslanov, A.A.Mammadova, B.A.Mammadov, D.R.Nurullayeva

Institute of Polymer Materials of Azerbaijan National Academy of Sciences

ipoma@science.az

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The interesterification reaction of the ethyl (I) and isopropyl (II) ethers of sulphoimides of saccharin-5- and -6-carboxylic acids with glycerine has been studied. The corresponding 2-hydroxypropyl-1,3-*bis*-esterosulphoimides of saccharin-5-and-6-carboxylic acids have been synthesized. They have been characterized by elemental analysis and method of the IR spectroscopy. It has been elucidated that in use of 10% PbO catalyst per mass of glycerine a yield of purposeful product reaches its greatest value – 82 and 85% depending on used saccharin: (-5-) or (-6-).

Keywords: *alkyl ethers, saccharin-carboxylic acids, sulphoimide, glycerine.*

Introduction

It is known that the ethers of trimellitic and pyromellitic acids are the monomers for preparation of thermo- and radiation-resistant polymers [1].

In the literature there are data about synthesis of diesterodisulphoimides by interesterification of the methyl ether of sulphoimides of saccharin-monocarboxylic acids by aliphatic and aromatic glycols [2, 3].

In this paper the interesterification reaction of the ethyl and isopropyl ethers of sulphoimides of saccharin-5- and -6-carboxylic acid with glycerine is described.

The aim of this work is the synthesis of new monomers on the basis of sulphoimides of saccharin-5- and -6-carboxylic acids for their further application during preparation of thermostable polymers.

Experimental

Synthesis of the alkyl ethers (ethyl- and isopropyl-) of sulphoimides of saccharin-5- and -6-carboxylic acids. The synthesis of the ethyl or isopropyl ethers of saccharin-5- and -6-carboxylic acids was carried out by heating of mixture consisting of 22.7 (0.1 mol) saccharin-5- and -6-carboxylic acid, 240 ml of absolute ethanol or isopropyl alcohol and 18 ml concentrated sulphuric acid. It was boiled with reflux condenser equipped with chlorocalcium tube to complete water separation and preparation of homogeneous transparent solution, which was cooled and poured into 600 ml distilled ice water. For ethyl

ethers: T_{melt} (I) = 129°C. T_{melt} (II) = 139–140°C. For isopropyl ethers: T_{melt} (I') = 145°C. T_{melt} (II') = 153–154°C.

Synthesis of 2-hydroxypropyl-1,3-*bis*-esterosulphoimides of saccharin-5-(a) and -6-(b) carboxylic acids. The mixture of 25.4 g (0.1 mol) of the ethyl ether of sulphoimide of saccharin-5- and -6-carboxylic acids and 4.9 g PbO in 49.6 g (0.5 mol) of 1,2,3-propantriol (glycerine) at mixing was heated to 124–126°C for 3–4 h. The reaction mass was dissolved in acetone and isolated by distilled water.

The prepared grayish-white crystalline product was dried at room temperature and brought to constant mass in vacuum. The product on the basis of sulphoimide of saccharin-5-carboxylic acid have T_{melt} (a) = 149–151°C.

The product on the basis of sulphoimide of saccharin-6-carboxylic acid corresponded to T_{melt} (b) = 158–160°C.

There have been analogously synthesized the above-mentioned compounds on the basis of isopropyl ether of sulphoimides of saccharin-5- and -6-carboxylic acids.

The boiling temperature of glycerine and solvents corresponded to the literary data [4].

The IR spectra were taken on IR-Fourier microscope LUMOS (firm BRUKER Germany) in the range of wave frequencies 600–4000 cm⁻¹ on the crystal diamond.

Results and discussion

With the aim of synthesis of the new reaction ability monomers in the first stage there

have been prepared the alkyl ethers (ethyl- and isopropyl-) of saccharin-5- and -6-carboxylic acids on scheme:

In the second stage by interesterification of the prepared ethers by glycerine 2-hydroxypropyl-1,3-*bis*-estersulphoimides of saccharin-5- and -6-carboxylic acids have been prepared:

As a result of interesterification there have been prepared 2-hydroxypropyl-1,3-*bis*-estersulphoimides of saccharin-5-(*a*) and -6-(*b*) carboxylic acids having ester and sulphoimide groups in their composition [5].

During carrying out of interesterification of the alkyl ethers of saccharin-5- and -6-carboxylic acids with glycerine PbO has been used as the catalyst. It has been elucidated from obtained data that a yield of the purposeful products mainly depends on quantity of the used catalyst. It has been established by test way that in use of 10% PbO catalyst per mass of glycerine a yield of 2-hydroxypropyl-1,3-*bis*-estersulphoimides of saccharin-5- and -6-carboxylic acids reaches its greatest value – to 82% (*a*) and 85% (*b*).

It has been established that with increase of a number of hydrocarbons in ether group of sulphoimides of saccharin-5 and 6-carboxylic

acids the interesterification reaction occurs at lower temperatures.

The composition and structure of 2-hydroxypropyl-1,3-*bis*-estersulphoimides of saccharin-5-(*a*) and -6-(*b*)carboxylic acids have been determined by elemental analysis and IR spectroscopy.

The physical constants of the products (*a*) and (*b*) are presented in Table. It has been detected that in the IR spectra of these compounds there are the absorption bands in the fields of 1300–1250 cm⁻¹ and 1100 cm⁻¹ corresponding to the valence vibrations of C–O–C ester group, and also the absorption bands in the field of 1720 cm⁻¹ characteristic for >C=O– group in esters. In addition, there are the absorption bands in the fields of 1730, 1370, 1180 and 3000–2840 cm⁻¹ characteristic respectively for >C=O groups of SO₂ and >NH saccharin cycle [6].

Physical constants of 2-hydroxypropyl-1,3-*bis*-estersulphoimides of saccharin-5-(*a*) and -6-(*b*) carboxylic acids

Compound	Brutto formula	Found, % Calculated, %				M	$T_{\text{melt}},$ °C	Yield, %
		C	H	N	S			
<i>a</i>	C ₁₉ H ₁₄ O ₁₁ N ₂ S ₂	43.85	2.60	5.45	12.07	510	149–151	82
<i>b</i>		44.74	2.74	5.49	12.57		158–160	85

Conclusions

1. The interesterification reaction of the ethyl and isopropyl ethers of sulphoimides of saccharin-5- and -6-carboxylic acids with glycerine has been studied. The corresponding 2-hydroxypropyl-1,3-bis-esterosulphoimides of saccharin-5- and -6-carboxylic acids have been synthesized.
2. It has been established that at use of 10% PbO catalyst for mass of glycerine a yield of the purposeful product reaches its greatest value – to 82 and 85% depending on used saccharin: (-5-) or (-6-).
3. The synthesized 2-hydroxypropyl-1,3-bis-esterosulphoimides of saccharin-5-(a) and -6-(b) carboxylic acids are of interest for their use as the monomers at preparation of linear and highly branched sulphoimide-containing polymers and also as

the hardener-plasticizer of epoxy diene resins.

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SAXARİN-5- VƏ -6-KARBON TURŞULARININ 2-HİDROKSİPROPİL-1,3-bis-EFİROSULFİMİDLƏRİNİN SİNTEZİ

E.T.Aslanova, T.A.Aslanov, A.A.Məmmədova, B.A.Məmmədov, D.N.Nurullayeva

Saxarin-5- və -6-karbon turşularının etil və izopropil efirosulfimidlərinin qliserinlə yenidən efirləşməsi reaksiyası öyrənilmişdir. Saxarin-5- və -6-karbon turşularının müvafiq 2-hidroksiopropil-1,3-bis-efirosulfimidləri sintez edilmişdir. Onlar element analizi və İQ spektroskopiya üsulu ilə xarakterizə edilmişdir. Məlum olmuşdur ki, qliserin kütləsinə nisbətən 10% PbO katalizatoru istifadə etdikdə alınan məhsulun çıxımı tərkibindən asılı olaraq ən yüksək həddə – 82% və 85%-ə çatır.

Açar sözlər: *alkil efirləri, saxarin-karbon turşuları, sulfimid, qliserin.*

СИНТЕЗ 2-ГИДРОКСИПРОПИЛ-1,3-бис-ЭФИРОСУЛЬФОИМИДОВ САХАРИН-5- И -6-КАРБОНОВЫХ КИСЛОТ

Э.Т.Асланова, Т.А.Асланов, А.А.Мамедова, Б.А.Мамедов, Д.Р.Нуруллаева

Изучена реакция переэтерификации этиловых и изопропиловых эфиров сульфоимидов сахарин-5- и -6-карбоновых кислот с глицерином. Синтезированы соответствующие 2-гидроксипропил-1,3-бис-эфиросульфоимиды сахарин-5- и -6-карбоновых кислот. Они охарактеризованы элементарным анализом и методом ИК-спектроскопии. Выяснено, что при использовании 10% катализатора PbO на массу глицерина выход целевого продукта достигает в зависимости от использования сахараина (-5-) или (-6-) своего наибольшего значения – до 82 и 85% соответственно.

Ключевые слова: *алкиловые эфиры, сахарин-карбоновые кислоты, сульфоимид, глицерин.*