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About Selective Methods of Synthesis of 6-*tert*-Butyl-2-methylphenol and 6-*tert*-Butyl-2,4-dimethylphenol

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Abstract—Vapor phase catalytic methylation with methanol of 2-*tert*-butylphenol at the temperature 280–300°C proceeds selectively with formation of 6-*tert*-butyl-2-methylphenol. Elevating reaction temperature above 300°C leads to formation of 2,6-dimethylphenol. Reaction of 2-*tert*-butylphenol with methanol in alkaline medium in the presence of zinc oxide is shown to lead initially to formation of a mixture of calixarenes and methylenebisphenols that at elevated temperature exert splitting leading in future to 6-*tert*-butyl-2,4-dimethylphenol. Obtaining it in this reaction from 2,2'-methylenebis-(6-*tert*-butyl-4-methylphenol) proceeds selectively. Pathways of the reductive methylation of methylenebisphenols with methanol in alkaline medium is considered.

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Derivatives of 6-*tert*-butyl-2-methylphenol (**I**) are the basic compounds in the chemistry of sterically hindered phenol [1]. Therewith, their antioxidant activity and volatility is higher when compared with the derivatives of 2,6-di-*tert*-butylphenol [2]. Combination of these properties is mostly expressed in 6-*tert*-butyl-2,4-dimethylphenol (**II**) that is used for stabilization of rocket fuel and as thernostabilizer for polyethylene and polyamides [2, 3].

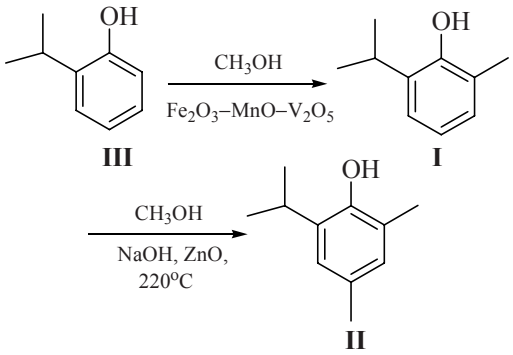
To the moment on the basis of *tert*-butyl-substituted methylphenols has ben created a series of remedies. Proceeding from compound **II** is obtained oxymetazoline [4]. For the reliable synthesis of this remedy should be used compound **II** and products of its bromomethylation of high purity grade [5]. Therefore the actuality of development of highly selective methods for the synthesis of compounds **I** and **II** is obvious. This situation required revision of known methods and development of new pathways of their preparation.

The known selective method of synthesis of compound **I** by reduction of 4-bromo-6-*tert*-butyl-2-methylphenol is interesting only theoretically [6]. The process of *ortho*-*tert*-butylation of 2-methylphenol with isobutylene in the presence of aluminum 2-methylphenoxide commonly is used as a basis for the technology of synthesis of compound **I**. The process requires temperature not higher than 100°C and leads to formation of a mixture containing 90% of compound **I** and 10% of 2-methyl-4-*tert*-butylphenol isomer **IV** [7]. Somewhat higher selectivity of the process has been achieved when the components reacted at the temperature below 80°C [8]. Due to similarity in boiling points, purification of compound **I** from compound **IV** technologically is wery complicated, therefore practically is used the product with content 90% of main component **II**. A modification of catalyst for improving the ratio of compound **II** and isomer **IV** has been proposed but did not give significant results [9].

Another method for the synthesis of copound **I** that is studied in this work consists in methylation of 2-*tert*-butylphenol with methanol using highly effective catalyst of the phenol *ortho*-methylation which has been used formerly for the synthesis of 2,6-dimethylphenol [10] and 2-methyl-1-naphthol [11], consisting of finely grinded alloy of the oxides Fe_2O_3, V_2O_5, and MnO in the ratio (43–50):(42–50):(8–6). The process

of methylation of 2-*tert*-butylphenol with methanol proceeds in gas phase in a flow type steel reactor in stationary layer of the catalyst by passing the vapors in the mole ratio 1:3. The reaction temperature is varied in the range from 270 to 325°C . The flow rate of the reagents passing through the catalyst layer is varied from 0.3 to 1.2 h^{-1}. From the catalyzate was removed methanol by evaporation and resudue was analyzed by GLC. The results are listed in the table.

From the table is seen that formation of compound **I** in this catalytic variant occurs in the temperature range 280–305°C. Further increase in temperature at the contact of the feeding mixture with the catalyst leads to the process of replacement of *tert*-butyl group in 2-*tert*-butylphenol and in compound **I** by methyl group with formation finally of 2,6-dimethylphenol. Comparison of results of the experiments 2 and 3 in the table obviously indicates to positive effect of decrease in the feeding solution flow rate and decrease in it of the 2-*tert*-butylphenol concentration. Actually, at increase in the ratio 2-*tert*-butylphenol : methanol to 1:5 in the experiment 3 a catalyzate is obtained containing after removing the solvent 90% of compound **I**.



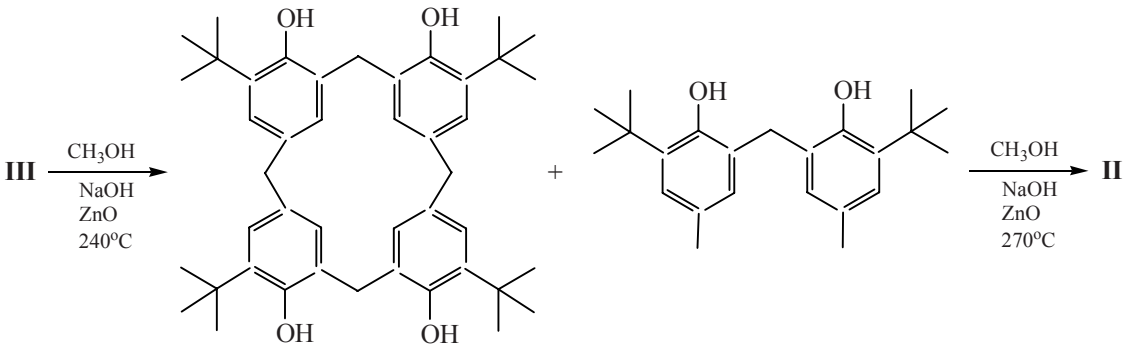
To avoid transformation of compound **I** into compound **II** we applied another catalytic system that promotes *para*-methylation of phenols [12]. At the heating in an autoclave the methanol solution of compound **III** in the presence of alkali and zinc oxide we obtained a reaction mixture which after usual treatment contained 95% of compound **II** that allows to use it without further purification as an intermediate in the syntheses of biologically active compounds. Thus, at the consecutive use of the catalysts for the *ortho*- and *para*-methylation of phenol we succeeded in the synthesis of compound **II** with acceptable purity.

As is known, pure enough compound **II** has been obtained successfully by reaction of isobutylene with 2,4-dimethylphenol in the presence of aluminum 2,4-dimethylphenoxide [13]. As catalysts in this process is used concentrated H_2SO_4 [14], ion exchange resins in acid form [15], and phosphoric acid [16]. However, accessibility of 2,4-dimethylphenol remains problematic. It is known that for the synthesis of compound **II** can be used a mixture of 2,4- and 2,5-xylenols **II** [17]. The knowledge about this method that includes several chemical steps obviously emphasizes the necessity of searching new selective and economically advantageous methods of synthesis of compounds **I** and **II**.

As known, in the process of methylation of 2-*tert*-butylphenol in alkaline medium is formed a reaction mixture that contains predominantly compound **II** [18]. We for first time showed that in the course of this reaction initially occurs formation of exocalix[4]arenes and methylenebisphenols mixed with condensed compounds with more complicated structure.

Catalytic methylation of 2-*tert*-butylphenol with methanol

Run no.	Reation conditions			Formed gas mass, g h^{-1}	Product content, wt %				Conversion of 2-*tert*-Bu-phenol, %	Selectivity on 2-*tert*-Bu-phenol, %
	T, °C	Flow volume rate, h^{-1}	2-*tert*-Bu-phenol feeding, g h^{-1}		2-*tert*-Bu-phenol	2-Me-6-*tert*-Bu-phenol	2,6-xyleol	H_2O		
1	280	1.2	20.8	–	63	30	–	–	37	81
2	290	1.2	20.8	0.01	49	45.6	–	–	51	89.2
3	290	0.6	10.4	0.04	14	75.4	7.4	1.5	85.4	91.1
4	305	1.2	20.8	0.06	26	66.7	4.9	2	73.2	93.5
5	305	0.3	5.2	0.12	39	52.6	6.1	5	61	86.5
6	325	0.7	12.2	0.16	3.7	60	33	2	96	72.4



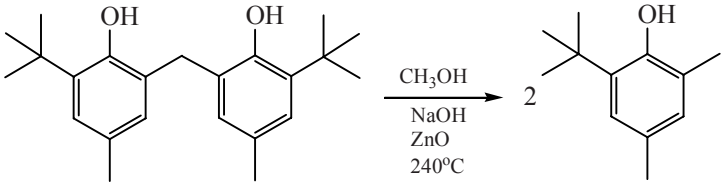
IV **V**

Calixarene **IV** was isolated from the reaction mixture in 10% yield. The presence in the mixture up to 40% of calixarenes that are effective polyolefins light stabilizers, and of methylenebisphenols well known as polymer thermostabilizers allowed us to study the mixture obtained and to recommend it as a new type of polyfunctional additive for producing coverings based on polyethylene with thermal and light stability [19].

At elevating the methylation temperature to 270–290°C occurs splitting of compounds **IV** and **V** as well as oligomeric phenols with formation of a mixture of phenol derivatives containing by the data of GLC up to 60% of compound **II**. Thus compound **II** can be synthesized in one technological step from 2-*tert*-butylphenol, but due to complex composition of the mixture its isolation in pure state brings new problems.

As is know, 2-*tert*-butylphenol forms Mannich base exclusively in *ortho*-position to its hydroxyl group [20]. We studied the route of the synthesis of compound **II** by reduction with hydrogen of the formed 2-*N,N*-dimethylaminomethyl-6-*tert*-butylphenol in the presence of Pd/C. However, this approach turned to be not enough selective due to side reactions of hydrogenization of the aromatic ring and cyclization involving nitrogen atom.

The most effective method of synthesis of compound **I**, in our opinion, is use of 2,2'-methylenebis(6-*tert*-butyl-4-methylphenol) **V** as the initial compound.



V **II**

As known, reaction of 4,4'-methylenebis(3,5-di-*tert*-butylphenol) with methanol in the presence of sodium methoxide under pressure at temperature 200°C yields products containing 85% of *tert*-butyl-4-methylphenol [21]. We decided to examine a principal possibility of application of this method to the synthesis of compound **II** from compound **V** taking into account that the latter is an accessible product of large tonnage domestic manufacturing and is 4-fold cheaper than 2,4-dimethylphenol.

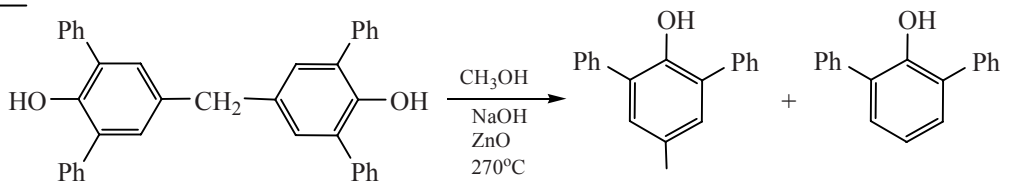
Noteworthy that the problem of selection of catalysts for splitting methylenebisphenols has not be studied so far, and one should search for its solution taking into account enhanced lability of hydrogen atoms in the methylene fragment and in steric closeness to this fragment of hydroxy groups that probably capture the catalyst initially. Earlier we have found that zinc oxide catalyzes such processes that occur in alkaline medium [12]. Therefore for the synthesis of compound **II** starting with compound **V** we propose to carry out the splitting of methylenebisphenol in alkaline medium in the presence of methanol and with ZnO as a catalyst.

Actually, upon heating in an autoclave at the temperature 240–250°C of methanol solution of compound **V** with alkali and catalytic additive of zinc

oxide we obtained a reaction mixture that after removing the catalyst, solvents and water afforded a product containing 95% of compound **II** and in the residue the low volatile parent compound **V**. One simple distillation of this product gave pure compound **II**. By this way we succeded to solve the problem of accessibility of compound **II** for the purposes of technological application in required amounts and of high purity grade.

At the consideration of the mechanism of formation of methylphenols from methylenebisphenols earler was presumed that thermolysis of the initial methylenebisphenols is the key process leading to formation of highly reactive methylenquinones, but they could not be identified in the reaction mixture [22].

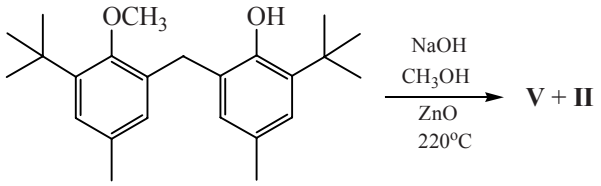
We obtained direct evidences of proceeding of the thermolysis of methylenebisphenols in alkaline medium with formation in approximately equal amounts of the derivatives of phenol and methylphenol for two compounds: for 4,4'-methylenebis-2,6-diphenylphenol **VI** and for the ether **IX** obtained from the compound **V**.



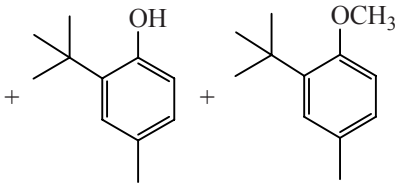
VI **VII** **VIII**

At the treatment in autoclave of compound **VI** with alkaline methanol at 270°C for 7 h we obtained a reaction mixture containing by the data of GLC 45% of compound **VII** and 32% od 2,6-diphenylphenol **VIII**, from which with 34% yield was obtained 2,6-diphenyl-4-methylphenol **VII**.

We decided to examine another method of synthesis of methylphenols from the methylenebisphenols taking into account a possibility of premilinary *O*-methylation of the former.



IX



X **XI**

At the treatment in autoclave of the methanol solution of ether **IX** in the presence of alkali proceeded two processes. Initially ether **IX** is hydrolyzed with formation of methylenebisphenol **V** and then bisfenol **V** exerts thermal splitting leading to compounds **II** and **X** in approximately equal amounts. The reaction mixture contained also traces of compound **XI** while biphenyl and stilbene derivatives were absent. From these observations follows that the mechanism of methylenebisphenol splitting after its preliminary *O*-methylation is doubtful. For us was unexpected that hydrolysis of ether **IX** in alkaline medium at elevated temperature proceeds readily.

At the comparison of conditions for the reductive thermolysis of compounds **V** and **VI** is seen that the presence of electron-releasing substituents in the structure of methylenebisphenol increases noticeable the probability of their splitting. The same is confirmed by us at the study of kinetics of thermolysis: we found that the activation energy of the reaction of thermolysis of methylenebisphenols contained *tert*-butyl groups is approximately a half of the value obtained for the compound **VI** [23, 24].

EXPERIMENTAL

The chromatomass spectrometric analysis is carried out on a Hewlett-Packard instrument, the set includes gas chromatograph HP 5890 series 11 and mass-selective deterctor HP 5971. Capillary column HP5MS 30 m × 0.25 mm × 0.25 μm, carrier gas helium. For the monitoring composition of reaction mixtures is used a gas chromatograph Tsvet. Melting points are measured on a Koffler device. The product composition of methylation of 2-*tert*-butylphenol is elucidated on a liquid phase chromatograph with consecutive diode matrix and mass-selective detector (an Agilent system

1100 Series LS/MSD). The mass-selective detector (a G1946C model) is used in the regime of chemical ionization (CI) at atmospheric pressure. Scanning of ions with *m/z* up to1000 allowed to detect molecular masses of all components in the mixture, their quantitative contents were determined by measuring peaks areas and simultaneously by the GLC method. Identification of methylenebisphenol and calixarenes was carried out on individual samples isolated by column chromatography with reverse phase Zorbax Rx-C-18, using a methanol–water mixture as eluent.

6-*tert*-Butyl-2-methylphenol (I). *a*. 50 g of 2-(*N*,*N*-dimethylaminomethyl)-6-*tert*-butylphenol was loaded to an autoclave containing 5 g of 4% Pd/C. The autoclave was blown with hydrogen, pressure was increased to 5 MPa and the autoclave was rotated for 11 h at 130ºC. The reaction mixture obtained contains 76–84% of 6-*tert*-butyl-2-methylphenol, 3–6% of parent compound and a series of other products. The product **I** was isolated by distillation in a vacuum, fraction 25–30 g was collected with bp 90–100ºC (1–2 mm Hg), that contains 95% of compound **I**.

b. A tubular flow type stainless steel reactor was used, with external heating, tube 14 mm diameter and 700 mm length. To the reactor was loaded 30 cm^3 of catalyst with granules 1–2 mm prepared by fusing Fe, Mn and V oxides. A solution of 2-*tert*-butylphenol in methanol (ratio 1:5 mol) was contacted with the catalyst at the flow volume rate 0.6 h^{-1} at temperature 290°C. The produced catalyzate was evaporated and oily substance was isolated that contains by the data of GLC 90% of 2-methyl-6-*tert*-butylphenol **I**, 3% of parent 2-*tert*-butylphenol, 2% of 2,6-dimethylphenol. The oil was distilled in a vacuum, a fraction bp 90–100ºC (1 mm Hg) was collected. This fraction by the data of GLC contains 97% of 6-*tert*-butyl-2-methylphenol. Yield of compound **I** of such purity is 80%.

4,4'-Methyleme-bis-(2,6 -diphenylphenol) (VI). A mixture of 30 g of 2,6-diphenylphenol and 1.8 g of paraform in 146 ml of formic acid was heated with stirring at the temperature 130°C (in bath) for 2.5 h. The precipitate dropped was filtered off, washed with water and crystallized from $CHCl_3$–methanol 1:1 mixture. 4,4'-Methylenebis-(2,6-diphenylphenol) **VI**, 20.3 g, with mp 198-200°C was obtained. From the filtrate 5.2 g portion of **VI** with mp192–196°C was isolated.

2,6-Diphenyl-4-methylphenol (VII). A mixture of 10 g of methylenebisphenol **VI**, 50 ml of methanol, 5.0 g of granulated NaOH and 0.5 g of ZnO was loaded to the autoclave 0.1 l volume and heated with stirring at the temperature 270°C for 7 h. From the reaction mixture (8. g) by extraction with hexane was isolated 7.5 g of a product containing by the data of GLC 45% of 2,6-diphenyl-4-methylphenol **IX** and 32% of 2,6-diphenylphenol, and some other components. By extraction with hexane 3.5 g of a mixture containing 70% of compound **VII** was isolated. After crystallization of this mixture from ethanol was obtained 2.0 g (yield 34%) of 2,6-diphenyl-4-methylphenol **VII**, mp 73–75°C . ^{1}H NMR spectrum (CCI_4, δ, ppm): 2.30 s, (3H, CH_3); 4.95 s (^{1}H, ArOH); 6.96 s (2H, ArH); 7.2–7.5 m (10H, 2Ph).

6-*tert*-Butyl-2,4-dimethylphenol II. *a.* To a Vishnevskii autoclave 1 l volume equipped wit a stirrer was loaded 50.0 g (0.31 mol) of 6-*tert*-butyl-2-methylphenol **I**, 50 g of NaOH, 5 g of ZnO and 0.5 l of methanol. After sealing the autoclave was heated at working stirrer for 8 h at the temperature 210–220ºC. After cooling to 60°C , methanol was distilled off. To the residue was added 200 ml of petroleum ether and 200 ml of water, organic layer was separated and evaporated, and 53 g of 95% purity compound **VII** was isolated that when necessary was purified by distillation in a vacuum collecting a fraction bp 100–103°C (3 mm Hg). 48 g (0.26 mol) of 98% 6-*tert*-butyl-2,4-dimethylphenol **I** was isolated, yield 84%.

b. To a dry steel rotating autoclave 5 l volume was loaded 600 g (1.76 mol) of 2,2-methylene-bis-(6-*tert*-butyl-4-methylphenol) **V**, 3400 ml of anhydrous methanol, 300 g of NaOH and 30 g of ZnO. The mixture was heated at the 250°C for 8 h. The autoclave was then cooled, and liquid part was decanted. In the autoclave remained a solid white residue that without a treatment was used repeatedly as a catalyst. From the liquid part the methanol excess was distilled off and to the residue was added 2 l of water and 300 ml of petroleum ether. The mixture was carefully stirred and then layers were separated. The organic layer was washed with cold water and the solvent was evaporated in a vacuum. Finally was obtained 620 g (3.59 mol) of yellowish oil containing by the data of GLC 95% of 2,4-dimethyl-6-*tert*-butylphenol (yield 94%). This product was further used in syntheses without additional purification.

c. To a steel autoclave 0.1 l capacity was loaded 4 g of 6-*tert*-butyl-2-(2'-methoxy-3'-*tert*-butyl-5'-methyl-

benzyl)-4-methylphenol **V**, 4 g of NaOH and 30 ml of methanol, and the mixture was treated at the autoclave rotation at the temperature 220°C for 4 h. After cooling the content was extracted with ether, the extract was washed with water and evaporated. 3 g of dark liquid was obtained that contained by the GLC data 48% of 2,2-methylene-bis-(6-*tert*-butyl-4-methylphenol), 20% of 6-*tert*-butyl-4-methylphenol and 22% of 6-*tert*-butyl-2,4-dimethylphenol. By the method of chromato-mass spectrometry in the reaction mixture was also identified 1.5% of parent ether **V** and 0.5% of 2-*tert*-butyl-4-methylanisol.

Synthesis of calix[4]arene V. To a rotating steel autoclave 0.25 l capacity was loaded 20 g of 2-*tert*-butylphenol, 150 ml of methanol, 20 g of NaOH, and 3 g of ZnO, and the mixture was heated at rotation at the temperature 250°C for 15 h. After cooling, the reaction mixture was neutralized with hydrochloric acid and extracted with methyl-*tert*-butyl ether. Solvent was evaporated and 18 g of labile oil was obtained from which was distilled off in a vacuum a fraction 6 g, bp 110–125°C (10 mm Hg) containing mainly 6-*tert*-butyl-2,4-dimethylphenol, and bottom residue remained.

The bottom residue composition was determined by the method of liquid chromatography on an Agilent 1100 device with a mass-selective detector. Below are listed the components with the following data for each one: retention time in column (min), content in the mixture (%) and molecular mass. 6-*tert*-Butyl-4-(4'-hydroxybenzyl)-2-methylphenol, 1.75(5), 256; 2,4'-methylene-bis(2-*tert*-butylphenol), 2.45(5), 312; 2-(5'-*tert*-butyl-3'-methyl-4'-hydroxybenzyl)-6-*tert*-butylphenol, 2.72(6), 326; 4,4'-methylene-bis(2-*tert*-butylphenol), 3.49(4), 312; 4-(5'-*tert*-butyl-3'-methyl-4'-hydroxybenzyl)-6-*tert*-butylphenol, 3.97(10) , 326; compound **VI**, 4.55(10), 340; 2-(6'-*tert*-butyl-4'-hydroxybenzyl)-4-(3"-*tert*-butyl-5"-methyl-2"-hydroxybenzyl)-6-*tert*-butylphenol, 5.29(8) 488; 2,4-бис-(5'-*tert*-butyl-3'-methyl-4'-hydroxybenzyl)-6-*tert*-butylphenol, 6.13'(5), 502; a compound with the structure of calixarene **IV** but containing only three *tert*-butyl groups, 7.45(10), 592; calixarene **IV**, 8.47(18), 648; a compound isomeric to the calixarene **IV**, 8.77(4) 648; compounds 3% each with the molecular masses 650, 664, 768 and 812.

The bottom residue 12 g was dissolved at boiling in 40 ml of ethanol and white precipitate dropped upon cooling was filtered off. Complex of 5,11,17,23-tetra-*tert*-butyl-4,12,16,24-tetrahydroxycalix[4]arene **IV,** 2 g (10%) and one ethanol molecule was obtained, mp 262°C . The ^{1}H NMR spectrum [in $(CD_3)_2SO$], δ, ppm: 8.34 s (4H, Ar–OH), 6,70 s (4H, Ar–H), 6.58 s (4H, Ar–H), 4.28s (^{1}H, OH), 3.74 s (4H, $-CH_2-$), 3.59 s (4H,CH_2), 3.40 q (2H,CH_3CH_2OH), 1.36 s (36H, C_4H_9-*t*), 1,08 t (3H, CH_3CH_2OH). At short time heating of a sample of this complex at the temperature 100°C calixarene **V** was obtained, mp 278–282°C. Found: *m/z* 648.42201. $C_{44}H_{56}O_4$. Calculated: *m/z* 648.41783. Melting pouint and ^{1}H NMR spectrum of the sample **V** coincided completely with the published data [20].

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