THE ALKYLATION OF PHENOLS BY COMPOUNDS

WITH MIXED FUNCTIONS

COMMUNICATION 1. THE ALKENYLATION OF m-CRESOL BY ALLYL ALCOHOL

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The alkenylphenols are of considerable interest as antioxidants, and also as starting products for the preparation of elastic materials and insecticides. However a description of their synthesis by the alkenylation of phenols by unsaturated alcohols has thus far been limited to the work of Niederl [1], Chichibabin [2], Losev [3] and co-workers. Niederl [1] has reported that he separated 3-methyl-6-isopropenylphenol in good yield from the products of the alkenylation of m-cresol by allyl alcohol in the presence of sulfuric acid in the cold. Later, Losev, Smirnova and Ryadneva [3] reported that on alkenylating phenol by allyl alcohol under these conditions they only obtained a tar from which they were unable to separate individual constituents by fractional distillation. Chichibabin [2] used phosphoric acid in the alkenylation of phenol by allyl alcohol. He obtained a substituted phenol to which he ascribed the propenylphenol structure. Losev, Smirnova and Ryadneva [3], who carried out the reaction at 70°, believe that they separated out o-isopropenylphenol, with a small admixture of the para isomer. However in the papers of Chichibabin [2] and Losev [3] no evidence is presented to show the structure of the phenols which they prepared.

We studied the alkenylation of m-cresol by allyl alcohol in the presence of a number of acid catalysts: phosphoric acid, zinc chloride deposited on aluminum oxide, and cationite KU-1 which is a sulfonated phenol-formaldehyde resin activated by hydrochloric acid. In all the experiments with phosphoric acid and zinc chloride deposited on aluminum oxide that were carried out at 150 and 175°, allyl-m-cresol was obtained as the ortho- and paraisomers. The neutral reaction products were 2,6-dimethylcoumaran:



On alkenylation of m-cresol by allyl alcohol in the presence of KU-1 at a temperature of 95°, we only obtained 3-methyl-6-allylphenol. In the neutral fraction of the products of catalysis, besides 2,6-dimethylcoumaran, the allyl ether of m-cresol was detected. The structure of the allyl-m-cresols was determined by preparing phenoxy derivatives of the methyl ethers, and also by the oxidation of the latter to the corresponding methoxyphthalic acids. The structure of the radical in allyl-m-cresol was demonstrated by the hydrogenation of 3-methyl-6-allylphenol to 3methyl-6-n-propylphenol. In addition we carried out an independent synthesis of 3-methyl-6-allylphenol by the rearrangement of the allyl ether of m-cresol. As was shown in one of the papers [4], using the allyl ether of phenol as an example, this rearrangement is not accompanied by isomerization of the radical, which was determined by the use of labeled atoms. In order to explain the reaction mechanism, we carried out the alkenylation of the methyl ether of m-cresol by allyl alcohol in the presence of phosphoric acid at 75°:



In this case the course of the reaction is such that the intermediate formation of an ether is excluded. Inasmuch as no para isomer is formed during the rearrangement of the ether under the conditions we used, although it does occur on the direct alkenylation of m-cresol, one may assume that the reaction goes simultaneously in two directions: by means of C-alkenylation and O-alkenylation. Meanwhile the O-alkenylation product becomes rearranged to the ortho isomer with subsequent cyclization to 2,6-dimethylcoumaran. Favorable to the acceptance of such a mechanism is the fact that, on rearrangement of the allyl ether of m-cresol, there is formed, as the principal product of cyclization, a product which is identical with the diethylcoumaran which is separated from the products of direct alkenylation:



The absence of the para isomer and the presence of a considerable quantity of the allyl ether of m-cresol among the products of catalysis in the experiment with KU-1, permits one to assume that direct alkenylation of the nucleus did not occur in this case.



EXPE RIMENTAL

The original m-cresol boiled at 86-87° (10 mm) and had $n^{20}D$ 1.5390 and d^{20}_{4} 1.0334. Allyl alcohol: b. p. 95-96° (760 mm); $n^{20}D$ 1.4136 and d^{20}_{4} 0.8578.

The following were tried as catalysts: zinc chloride (20%) deposited on aluminum oxide, commercial orthophosphoric acid, sp. gr., 1.74, and cationite KU-1. The alkenylation of m-cresol by allyl alcohol in the presence of zinc chloride deposited on aluminum oxide, was carried out in an electrically heated rocking autoclave. The reactions in the presence of phosphoric acid and of KU-1 were carried out in a flask equipped with a mechanical stirrer, a reflux condenser, a thermometer and a dropping funnel.

The results of the experiments on alkenylating m-cresol in the presence of these catalysts are shown in Table 1. In all the experiments the original reagents were taken in equimolecular ratios. On the completion of each experiment the products of catalysis were separated from the catalyst and divided into phenolic and neutral fractions by treatment with a 10% solution of caustic soda. Table 2 shows the properties of the substances we separated, which were obtained in experiments with the different catalysts. The phenolic fraction of the products of catalysis was a mixture of the isomers of allyl-m-cresols.

Catalyst	Quantity of catal- yst in $\frac{\eta_0}{0}$ of wt. of reactants	Temp., °C	Length of expt., hrs.	Yield of catalyst in % of wt. of reactants	Total yield of alkenylation prods.		Yield of neutral prods. as % of cresol reacted			Yield of ally1- m-cresols (based on m-cresol reacted)	
					% of theoret.	√₀ of m- cresol reacted	total yield	allyl ether of m -cresol	2,6-di- methy1- coumaran	o- isomer	P- isomer
$ZnCl_2/Al_2O_3$ Same $^{*} ^{*} ^{*}$ H_3PO_4 Same $^{*} ^{*}$ KU-1	$ \begin{array}{c} 10 \\ 10 \\ 200 \\ 100 \\ 100 \\ 20 \end{array} $	100 150 175 75 75 95 95	8 8 8 8 8 8 12	95,0 93,5 91,8 94,2 91,0 89,0 73,0	5,722,047,045,027,039,07,5	$ \begin{array}{c} 19\\62,6\\71,6\\70,4\\66,6\\61\\53,5\end{array} $	$16,2 \\ 16,6 \\ 26,6 \\ 3,8 \\ 3,3 \\ 17 \\ 31$	3 0,5 Trace 20,0	13,2 16,0 26,6 3,8 3,3 17,0 11,0	2,8 20,0 14,0 37,6 33,3 23,0 22,5	26,0 31,6 27,0 30,0 21,1 —

TABLE 1. Results of the Experiments on Alkenylating m-Cresol by Allyl Alcohol

TABLE 2. Properties of Compounds Separated from the Alkenylation of m-Cresol by Allyl Alcohol

No. of com - pound	Name	Catalyst	B. p. °C at 10 mm	n_{D}^{20}	d_4^{20}	MR	M.p. of phenoxy derivative,°C
I	3-Methyl-6-allyl- phenol	ZnCl ₂ /Al ₂ O ₃ H ₃ PO ₄ KU-1	106-108 107-108,5 105-107	$1,5415 \\1,5424 \\1,5420$	$1,0199 \\1,0205 \\1,0202$	$45,66 \\ 45,62 \\ 45,66$	87—88 87—87,5 87—88
II	3-Methyl-4-allyl- phenol	$ZnCl_2/Al_2O_3$ H_3PO_4	122 - 124 123 - 124	$1,5432 \\ 1,5430$	$1,0212 \\ 1,0214$	$\frac{45,69}{45,69}$	111—112,5 112—113
ш	Allyl ether of m-	KU~1	84-85	1,5203	0,9582	45,95	
IV	2,6-Dimethyl-	$ZnCl_2/Al_2O_3$ H_PO.	91,5 91-92	1,5280 1,5279	1,0082 1,0082	45,19	
	coumaran	KÜ-1	92-93	1,5300	1,0092	45,32	

For phenols (I) and (II) (Table 2) the methyl ethers were prepared and had the following properties: a) b. p. $107-109^{\circ}$ (14 mm); $n^{20}D$ 1.5282 and d^{20}_{4} 0.9724; b) b. p. $115-117^{\circ}$ (14 mm); $n^{20}D$ 1.5278 and d^{20}_{4} 0.9742. By the oxidation of the methyl ethers according to the method described by Karavaev, Bashkirov and Kraeva [5], 3-methoxy-terephthalic acid was obtained in the first case with m. p. $273-274^{\circ}$; according to the literature it melts at 274° [5]. From the oxidation product of the methyl ether of phenol (II), 4-methoxyphthalic acid with m. p. $158-160^{\circ}$ was separated; the same literature source showed a m. p. of 160° for it [5]. Thus, phenol (I) (see Table 2) is o-allyl-m-cresol, while phenol (II) is p-allyl-m-cresol.

Phenoxy derivatives were prepared from both of the allyl cresols. The melting point of the phenoxy derivative of 3-methyl-4-allylphenol (II) is 112-113° and corresponds with the value 113° given in the literature [6]. The melting point of the phenoxy derivative of 3-methyl-6-allylphenol (I) of 87-88° corresponds with the melting point of the phenoxy derivative of o-allyl-m-cresol prepared by the alkylation of m-cresol by allyl chloride [6], to which the authors, apparently, erroneously ascribe the structure of 3-methyl-2-allylphenol.

The hydrogenation of 3-methyl-6-allylphenol was carried out in an alcohol solution in the presence of Raney nickel at 40-42°. Nine g of 3-methyl-6-n-propylphenol, b. p. 112-113° (12 mm); $n^{20}D$ 1.5265 and d^{20}_4 1.0016 was obtained from 15 g of 3-methyl-6-allylphenol. For 3-methyl-6-n-propylphenol the literature shows: b. p. 115-117° (13 mm); $n^{20}D$ 1.5261 [6].

<u>Rearrangement of the allyl ether of m-cresol.</u> The allyl ether of m-cresol was prepared by the method of Claisen [7]; its properties were – b. p. 84-85° (10 mm); $n^{20}D$ 1.5185 and d^{20}_4 0.9625 and correspond with those shown in the literature [8]. In order to carry out the rearrangement, 28 g of the allyl ether of m-cresol was mixed with

50 g of orthophosphoric acid and heated at 75° for eight hours. From this 18 g of 2,6-dimethylcoumaran, b. p. 92-93° (10 mm); $n^{20}D$ 1.5278 and d^{20}_{4} 1.0084, and 0.5 g of 3-methyl-6-allylphenol, b. p. 105-108° (10 mm); $n^{20}D$ 1.5422. The remaining fraction of the products of catalysis consisted of a polymerization product and tarry material.

<u>The alkenylation of 3-methylanisole.</u> 3-Methylanisole was prepared by the Gattermann method [9]; m. p. 175-176° (760 mm); $n^{20}D$ 1.5169 and d^{20}_{4} 0.9720. Forty g (0.33 M) of 3-methylanisole was mixed with 100 g (1 g mole) of orthophosphoric acid; to this mixture, which was warmed to 75°, was gradually added 19 g (0.33 M) of allyl alcohol over the course of two hours. The reaction yielded 6 g of the methyl ether of 3-methyl-6-allylphenol, b. p. 105-107° (14 mm); $n^{20}D$ 1.5269 and d^{20}_{4} 0.9760. By oxidizing it according to the method described by Karavaev, Bashkirov and Kraeva [5], 3-methoxyterephthalic acid, m. p. 273-274° was obtained. The neutral fraction of the products of catalysis in all cases (see Table 2) was 2.6-dimethylcoumaran, b. p. 91.5° (10 mm); $n^{20}D$ 1.5280; d^{20}_{4} 1.0082. The properties of this 2.6-dimethylcoumaran correspond with the properties of dimethylcoumaran which we prepared by the rearrangement of the allyl ether of m-cresol. On alkenylating m-cresol by allyl alcohol over KU-1 a fraction was obtained – b. p. 84-85° (10 mm); $n^{20}D$ 1.5203; d^{20}_{4} 0.9582, whose properties were close to those of the product we synthesized from the allyl ether of m-cresol (see above).

SUMMARY

1. As a result of a study of the alkenylation of m-cresol by allyl alcohol in the presence of acid catalysts – phosphoric acid, zinc chloride deposited on aluminum oxide, and cationite KU-1, conditions were found which gave a yield of products of alkenylation that reached 47% of the theoretical.

- 2. The reaction products are isomeric allyl-m-cresols and 2,6-dimethylcoumaran.
- 3. The reaction mechanism of the alkenylation of m-cresol by allyl alcohol was explained.

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