CONDENSATION OF METHALLYL ALCOHOL WITH PHENOL

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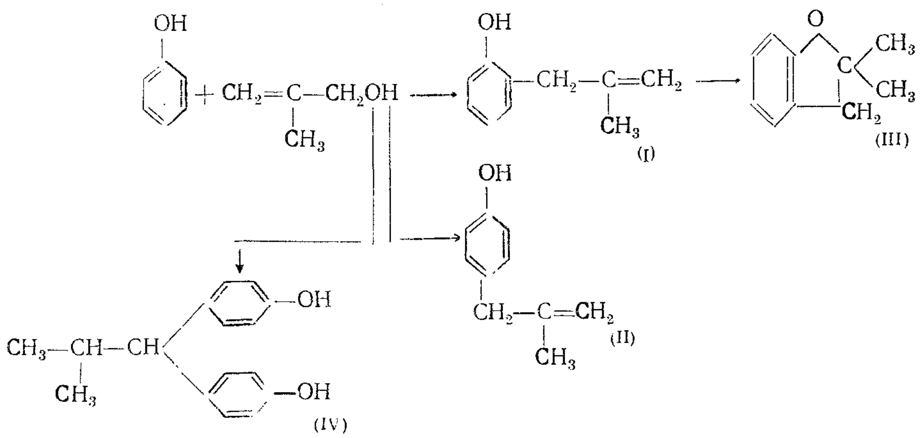
Present data in the patent literature indicate that alkenyl phenols can be used as raw material for the manufacture of rapidly drying varnishes.

Alkenyl phenols, chromans, and coumarans are used in the manufacture of plastics. They are used as antioxidants for gasolines and are the starting materials for preparing elastic materials, insecticides [1], and lubricating oil additives.

Certain chromans and courmarans possess insecticidal, fungicidal, and herbicidal properties, and are also used as medicinal materials [2].

Developing research on the alkenylation of phenols in the presence of a cation-exchange resin, we studied the condensation of phenol with methallyl alcohol.

The condensation scheme of phenol with methallyl alcohol can be representd in the following way:



Both acidic and neutral compounds are present in the reaction products. Acidic compounds were identified as o- and p-methallyl-phenols (I) and (II) and also as 2-methyl-1,1-bis[14-hydroxyphenyl]-propane (IV).

The neutral portion of monosubstitution products of phenol is 2,2-dimethyl-2,3-dihydrobenzofuran (III) or 2,2-dimethylcoumaran (Table 1).

The ratio of o- and p-isomers is approximately 1:4.5, which follows from results of vacuum distillation of a mixture of o- and p-isomers and from chromatographic analysis data.

The bisphenols were distilled as a viscous yellow liquid at 190-210°C (3 mm). Bisphenol (IV) was isolated in a yield of about 30% after recrystallization from benzene.

Conditions for obtaining maximum yields of monosubstitution products of phenol and bisphenols (Table 2) were found as a result of the investigation.

The starting methallyl alcohol was obtained in a yield of 51-53% by reduction of methylacrolein with lithium aluminum hydride. Methallyl alcohol was distilled at 111-114° and had a refractive index of n_D^{20} 1.4242. Bromine

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TABLE 1. Physicochemical Properties of the Isolated Compounds

Compound	bp, °C	Refractive index n_D^{20}	Density ρ_4	bp, °C	Elementary composition, %				Note
					found		calculated		
					C	H	C	H	
p-Methallylphenol	128—130/10 mm	—	—	49—50	80,87	8,23	81,2	8,12	$R_f = 0,42$
o-Methallylphenol	85—115/10 mm	1,5470	1,031	—	—	—	—	—	MR_D found 45,4 MR_D calculated 46,24
2,2-Dimethylcoumaran	89—91/17 mm	1,5162	0,99	—	81,56	8,444	81,2	8,12	$R_f = 0,73$ MR_D found 45,1 MR_D calculated 44,98
2-Methyl-1,1-bis[14-hydroxyphenyl] propane	190—210/3 mm	—	—	152	79,44	7,47	79,3	7,43	$R_f = 0,29$

TABLE 2. Effect of Experimental Conditions on Yield of Monosubstituted Phenols and Bisphenols (Reaction time 6 h, Ratio of Phenol : Methallyl Alcohol 5 : 1)

Temperature, °C	Amount of catalyst, %	Content in catalyzate, wt. %		Yield of monosubstituted phenols, % of theor.
		monosubstituted phenols	bisphenols	
100	5	0,5	99,5	—
80	10	1	99,0	—
100	10	12,5	87,5	10,4
100	20	26,8	73,2	18,2
100	30	21,4	78,6	13,4
100	40	19,2	80,8	11,6
80	20	18,7	81,3	11,0
96—97 benzene	20	26,6	73,4	17,0
120	20	38,4	61,6	21,3
124 (toluene)	20	42,7	57,3	23,2

number: found 213.3; calculated 222. Literature data: bp 114.49°C,* refractive index n_D^{20} 1.4255, density ρ_4^{20} 0.8515 [3].

Purity of methallyl alcohol was confirmed by chromatography.

Condensation of phenol with methallyl alcohol was carried out according to the method for allyl alcohol [4].

In a four-necked flask fitted with a stirrer, thermometer, reflux condenser, and dropping funnel were placed 51.5 g of phenol and 12 g of KU-2 cation-exchange resin. Methallyl alcohol (9 g) was added in drops at 100°C. Stirring of the reaction mixture was continued for 6 h.

The obtained catalyzate was distilled under vacuum.

Phenol was distilled at 76°C (14 mm). The residue was distilled into fractions: first fraction (3.0 g) at 82-135°C (10 mm) and the second fraction (8.2 g) at 190-210°C (3 mm). The first fraction contained 2,2-dimethylcoumaran and o- and p-methallylphenols. The monosubstituted phenols from several experiments were combined, dissolved in diethyl ether, and treated with an aqueous solution of potassium hydroxide to separate acidic and neutral products.

The basic extracts were acidified with a 10% HCl solution. The separated layer of acidic compounds was extracted with ether and dried over anhydrous magnesium sulfate. The acidic and neutral products were distilled under vacuum from a Claisen flask with a fractionating column.

Isomerization of Methallyl Alcohol in the Presence of KU-2 Cation-Exchange Resin. As was noted above, bisphenols are formed upon reaction of methallyl alcohol with phenol. Their formation is possible only in the case if methallyl alcohol is isomerized into isobutyraldehyde in the presence of the cation-exchange resin. Isomerization of methallyl alcohol into isobutyraldehyde is observed in the presence of acidic catalysts [5].

It was established that heating methallyl alcohol in xylene solution in the presence of KU-2 cation-exchange resin at the boiling point of xylene forms isobutyraldehyde. The latter was isolated and identified via the 2,4-dinitrophenylhydrazone, mp 179-180°C.

LITERATURE CITED

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