CATALYTIC SYNTHESIS OF ALLYLAROMATIC HYDROCARBONS

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N. I. Shuikin and N. A. Pozdnyak

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

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The allylaromatic hydrocarbons: allylbenzene, allyltoluene and allyltetralin may prove to be interesting monomers for the preparation of a new type of rubbers and other polymers. The preparation of some of them has been attempted previously. Thus, a small amount of allylbenzene was obtained by Huston [1] in the alkenylation of benzene with allyl alcohol in the presence of aluminum chloride, and by McKenna and Sowa [2] in the presence of boron trifluoride. Simons and Archer [3] obtained diphenylpropane as the main reaction product of the alkenylation of benzene with allyl alcohol in the presence of either hydrobromic or sulfuric acid. In the alkenylation of benzene and toluene with allyl alcohol in the presence of ferric chloride, Nazarova and Tsukervannik [4] obtained allylbenzene and allyltoluene in a yield of 32 and 35%, respectively. However, in the presence of this catalyst, the authors observed the addition of hydrogen chloride to the formed allylaromatic hydrocarbons. In the presence of phosphoric acid, Tsukervannik [5] obtained allyltoluene in 10% yield and diallyltoluene in 40% yield. Shuikin and co-workers [6] studied the alkenylation of m-cresol with allyl alcohol in the presence of phosphoric acid, zinc chloride deposited on aluminum oxide, and cationite KU-1. The yields of the o- and p-allyl m-cresols, based on reacted m-cresol, reached 33.3 and 30%, respectively.

In this paper we studied the alkenylation of benzene, toluene and tetralin with allyl alcohol in the presence of zinc chloride at 110-140°

$$\mathrm{ArH} + \mathrm{CH_2{=}CHCH_2OH} \xrightarrow[\mathrm{ZnCl_2}]{110-140^\circ} \mathrm{ArCH_2CH{=}CH_2}.$$

We studied the effect of the temperature, molar ratios of the components and the reaction time on the yield of the alkenylaromatic hydrocarbons. It was observed that the alkenylation with allyl alcohol in the presence of zinc chloride does not go at a temperature below 110°, for which reason the alkenylation of benzene was run in undecane solution. Under the optimum conditions found by us, we obtained allylbenzene, allyltoluene and allyltetralin in 50, 72.9 and 60% of the theoretical yield, respectively, when based on taken allyl alcohol.

EXPERIMENTAL

The constants of the benzene, toluene, tetralin and allyl alcohol taken for the alkenylation agreed with the literature data. In each experiment we took 7.3 g (0.125 mole) of allyl alcohol and 19.5 g (0.125 mole) of zinc chloride. The amounts of the taken aromatic hydrocarbons are given in Table 1.

The alkenylation of benzene was run in undecane solution, which was taken in the amounts indicated in Table 1. The mixture, composed of undecane, allyl alcohol, zinc chloride and 5 g of benzene, was heated to 110°, after which, with stirring and heating, the remainder of the benzene was added at such a rate that the reflux temperature of the mixture did not drop below 108-110°. After adding all of the benzene, the stirring and heating was continued until the temperature of the reaction mixture reached 120°. After cooling, the reaction mass was decomposed with water, the hydrocarbon layer was separated and, after drying over calcium chloride, it was distilled through a column with an efficiency of 40 theoretical plates. When the reaction was run for 1 h in undecane solution the yield of allylbenzene was 50% of theory, when based on allyl alcohol.

The alkenylation of toluene was run in n-nonane solution and also without it (see Table 1). The reaction was run by heating the mixture of components up to 120° for 1-3 h. It was shown that when the toluene was diluted with

TABLE 1. Alkenylation of Aromatic Hydrocarbons with Allyl Alcohol

Amount of aromatic hydrocarbon, g	Molar ratio hydrocarbon : alcohol	Amount of solvent, ml	Temp., °C	Time, h	Yield of allylaromatic hydrocarbons, % of theory
Alkenylation of benzene.					
19,5	2 : 1	20	108—110	3	40,5
9,8	1 : 1	40	108—120	0,25	33,8
9,8	1 : 1	40	108—120	2,5	40,5
14,7	3 : 2	40	110—120	1,0	50,0
Alkenylation of toluene					
23,0	2 : 1	—	108—120	2,0	45,5
23,0	2 : 1	—	108—125	3,0	45,5
23,0	2 : 1	13	115—120	2,0	72,9
23,0	2 : 1	26	115—120	2,0	54,5
23,0	2 : 1	26	115—120	1,0	53,0
Alkenylation of tetralin					
16,5	1 : 1	—	165—170	1,0	9,3
16,5	1 : 1	—	140	1,0	18,6
33,0	2 : 1	—	140	0,5	46,5
33,0	2 : 1	—	140	0,25	42,0
50,0	3 : 1	—	140	0,5	51,0
50,0	3 : 1	—	140	0,25	60,0
50,0	3 : 1	—	120	1,0	18,6

TABLE 2. Properties of Allylaromatic Hydrocarbons

Name of allylaromatic hydrocarbon	B. p., °C (p in mm of Hg)	n_D^{20}	d_4^{20}	*MR*	
				found	calcd.
Allylbenzene	156—158 (748)	1,5090	0,8950	39,41	39,69
Allyltoluene	180—182,5 (746)	1,5125	0,8889	44,59	44,31
Allyltetralin	258—260 (746)	1,5415	0,9644	56,13	56,0

a small amount of n-nonane, and the reaction is run for 2 h, the yield of allyltoluenes reaches 72.9% of theory, when based on allyl alcohol. The position of the allyl group in the benzene ring was determined by infrared spectroscopy. The spectra were taken using an IKS-14 instrument and a KBr prism, in the 700-1200 and 1600-1900 cm^{-1} regions. Based on the obtained spectrum, it is possible to assume that the main alkenylation product of toluene under our conditions is o-allyltoluene (frequencies: 1835, 1766, 1737, 742 cm^{-1}), containing small amounts of the m- and p-isomers (frequencies: 771, 785, 805, 836 cm^{-1}).

The alkenylation of tetralin was run without a solvent in an excess of tetralin. When the molar ratio of tetralin to allyl alcohol was 3 : 1, and the mixture was heated at 140° for 15 min, we obtained allyltetralin in 60% yield, based on allyl alcohol (see Table 1). By means of infrared spectroscopy it was shown that the allyl group in the allyltetralin is found in the 6 position. The properties of the obtained allylaromatic hydrocarbons are given in Table 2. By means of the ultraviolet spectra, taken in the 200-300 mμ region on a recording EPS-2 spectrometer, it was established that the products of alkenylation with allyl alcohol are allylaromatic hydrocarbons. From allyltoluene and allyltetralin we prepared the copolymers with butadiene, which exhibited the properties of elastomers.

The ultraviolet spectra were taken by V. A. Petukhov, the infrared spectra were taken by G. K. Gaivoronskaya and the copolymerization with butadiene was run by T. D. Nagibina, for which the authors wish to thank them sincerely.

SUMMARY

1. A simple method was developed for obtaining allylaromatic hydrocarbons by the alkenylation of benzene, toluene and tetralin with allyl alcohol in the presence of zinc chloride. The yields were respectively 50.0, 72.9, and 60.0% of theory, when based on allyl alcohol.

2. Allyltetralin and allyltoluene are easily copolymerized with butadiene, forming elastomers.

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