CONDENSATION OF CHLOROBENZENE AND o-CHLOROTOLUENE WITH ALLYL ALCOHOL

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In a study of the reaction of haloalkylated aromatic compounds with haloolefins in the presence of sulfuric acid [1], chlorobenzene and, particularly, bromobenzene were found to have a low activity in this reaction. The maximum yield of the products of the condensation of chlorobenzene with methallyl chloride was 25.3%, while with bromobenzene it was only 3.5%.

In the present work we have studied the condensation of chlorobenzene and o-chlorotoluene with allyl alcohol in the presence of titanium tetrachloride and zinc chloride. The reaction was carried out in order to obtain haloalkenylaromatic compounds which may be interesting monomers for the synthesis of elastomers and other polymers. The condensation of the chloroaromatic compounds with allyl alcohol in the presence of titanium tetrachloride gave 1-chlorophenyl-2-chloropropane and 1-(2-chlorotolyl)-2-chloropropane with yields of 29.8 and 55.5%, respectively. The formation of the haloalkylaromatic compounds apparently takes place in accordance with the mechanism that we proposed previously [2]

$$C_6H_5Cl + CH_2{=}CHCH_2OH \xrightarrow{TiCl_4} C_6H_4Cl\cdot CH_2CH{=}CH_2$$

$$CH_3C_6H_4Cl + CH_2{=}CHCH_2OH \xrightarrow{TiCl_4} CH_3C_6H_3Cl\cdot CH_2CH{=}CH_2$$

The resulting allylaromatic compounds add hydrogen halide under the experimental conditions, forming the corresponding haloalkyl compounds

$$C_6H_4Cl\cdot CH_2CH{=}CH_2 \xrightarrow{HCl} C_6H_4Cl\cdot CH_2CHCl\cdot CH_3$$

$$CH_3C_6H_3Cl\cdot CH_2CH{=}CH_2 \xrightarrow{HCl} CH_3C_6H_3Cl\cdot CH_2CHCl\cdot CH_3$$

The dehydrochlorination of the haloalkyl compounds obtained by boiling them with a saturated alcoholic solution of KOH gave the propenylaromatic compounds with yields of 80-85%. The condensation of chlorobenzene with allyl alcohol in the presence of zinc chloride gave allylchlorobenzene with a yield of 23.5%

$$ClC_6H_5 + CH_2{=}CHCH_2OH \xrightarrow[120^\circ]{ZnCl_2} ClC_6H_4CH_2CH{=}CH_2$$

EXPERIMENTAL

The condensation was carried out at various molar ratios, temperatures, and times.

Condensation of Chlorobenzene with Allyl Alcohol. In the presence of $TiCl_4$, the main reaction product was 1-chlorophenyl-2-chloropropane. The influence of the temperature was studied at molar ratios of the components of 2 : 1 : 1, and at temperatures between —10 and 30°.

As can be seen from Fig. 1 (curve 1), the optimum temperature for this reaction is 20°. A change in the molar ratio at this temperature in the direction of increasing or decreasing the excess of chlorobenzene leads to a reduction in the yield of 1-chlorophenyl-2-chloropropane. The optimum conditions for its formation are: temperature 20°, molar ratio of chlorobenzene to allyl alcohol to $TiCl_4$ = 2 : 1 : 1, time 1 h. The yield of 1-chlorophenyl-2-chloropropane is 29.8% of theoretical. When 1-chlorophenyl-2-chloropropane was boiled with a three-fold amount of saturated aqueous caustic potash for 5 h, propenylchlorobenzene was obtained with a yield of 85%. The characteristics of the compounds obtained are given in Table 1.

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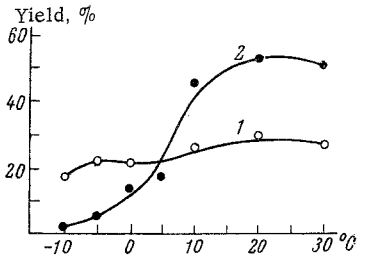

Fig. 1

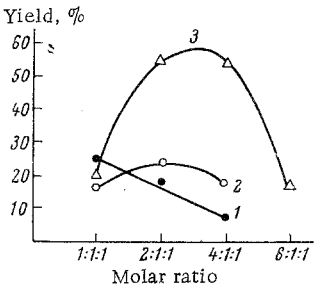

Fig. 2

Fig. 1. Influence of the temperature on the yield: 1) 1-chlorophenyl-2-chloropropane; 2) 1-(2-chlorotolyl)-2-chloropropane (molar ratio 2 : 1 : 1, time 1 h).

Fig. 2. Influence of the molar ratio of the components on the yield: 1) 1-chlorophenyl-2-chloropropane at —5°, time 1 h; 2) 1-chlorophenyl-2-chloropropane at 20°, time 30 min; 3) 1-(2-chlorotolyl)-2-chloropropane at 20°, time 30 min.

TABLE 1. Properties of the Compounds Obtained*

Name	Empirical formula	B.p., °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR		Cl, %		Iodine No.	Unsaturateds, %
					found	calc.	found	calc.		
1-Chlorophenyl-2-chloropropane	$C_9H_{10}Cl_2F_3$	120-122 (10) 195-205 (732)	1.5335	1.1667	50.05	49.89	36.52	37.50	—	—
Propenylchlorobenzene	$C_9H_9ClF_4$	85 (10) 185-195 (738)	1.5652	1.0747	45.77	44.56	22.58	23.25	162.7	95.8
Allylchlorobenzene	$C_9H_9ClF_4$	93 (6)	1.5288	1.0521	44.51	44.56	23.35	23.23	—	—
1-(2-Chlorotolyl)-2-chloropropane	$C_{10}H_{12}Cl_2F_3$	124-125 (5) 315-320 (738)	1.5375	1.1445	55.17	54.5	34.59	34.91	—	—
Propenyl-2-chlorotoluene	$C_{10}H_{11}ClF_4$	100-102 (9)	1.5630	1.0627	50.76	49.18	22.9	21.27	142.9	93.4

*The exaltation of the molecular refraction confirms the assumed position of the double bond in the chain with respect to the aromatic nucleus. The compounds given in Table 1 have been obtained for the first time; they apparently consist of mixtures of position isomers.

When chlorobenzene was condensed with allyl alcohol in the presence of zinc chloride, allylchlorobenzene was obtained. Allyl alcohol was added to a mixture of chlorobenzene and zinc chloride at the boiling point (not below 120° C) in proportion as it reacted. The best results were obtained at a molar ratio of chlorobenzene to allyl alcohol to $ZnCl_2$ of 2 : 1 : 1, a temperature of 124-129°, and a time of 30 min.

Condensation of o-Chlorotoluene with Allyl Alcohol. The condensation of o-chlorotoluene with allyl alcohol was carried out in the presence of $TiCl_4$. This gave 1-(2-chlorotolyl)-2-chloropropane. The influence of the temperature on the yield of this compound is shown by curve 2 in Fig. 1. The influence of the molar ratio (o-chlorotoluene to allyl alcohol to $TiCl_4$) is shown by curve 3 of Fig. 2.

The optimum conditions for the preparation of 1-(2-chlorotolyl)-2-chloropropane that we found are a temperature of 20° and a molar ratio between 2 : 1 : 1 and 4 : 1 : 1. Its yield amounted to 55.5% of theoretical, calculated on the allyl alcohol taken. The dehydrochlorination of the 1-(2-chlorotolyl)-2-chloropropane gave propenyl-2-chlorotoluene.

CONCLUSIONS

1. The condensation of chlorobenzene and o-chlorotoluene with allyl alcohol has been investigated.

2. Conditions for the preparation of 1-chlorophenyl-2-chloropropane and 1-(2-chlorotolyl)-2-chloropropane with yields of 29.8 and 55.5%, respectively, have been found. The dehydrochlorination of these compounds gives propenylchlorobenzene and propenylchlorotoluene with yields of 80-85%.

LITERATURE CITED

1. A. D. Petrov, V. N. Gramenitskaya, A. S. Lebedeva, and G. I. Nikishin, Neftekhimiya, 2, 776 (1962).
2. N. I. Shuikin, N. A. Pozdnyak, T. P. Dobrynina, and G. K. Shostakovskaya, Neftekhimiya, 6, 199 (1966).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of the first issue of this year.
