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Reactivity of Allyl Aryl Ethers in Diene Condensation with Hexachlorocyclopentadiene

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Abstract—The reactivity of allyl aryl ethers in the diene condensation with hexachlorocyclopentadiene was studied. The reactivity of aryl allyl ethers and product yield in this reaction significantly decreases when electron-withdrawing groups are introduced into the benzene ring. The reactivity is also influenced by the temperature, reaction time, and the molar ratio of the diene and dienophile.

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The diene synthesis is widely used for the preparation of organic compounds utilized in various industries as insecticides, plastics, additives for lubricating oils, etc.

The reaction of the diene synthesis using hexachlorocyclopentadiene as a diene is of interest. The compounds based on it are used in the manufacture of the highly heat- and flame-resistant polyether resins, additives to lubricants, insecticides, pesticides, plasticizers, etc. [1–4].

Due to the presence of the electronegative chlorine atoms, hexachlorocyclopentadiene has an electron-accepting diene system. Therefore it possesses the electron-withdrawing properties and can react easily with the nucleophiles.

We have previously performed the diene condensation of hexachlorocyclopentadiene with allyl aryl ethers [5], which occurred by the general scheme of the diene synthesis in accordance with the Alder rule [6] of "the maximal saturation accumulation" to form the *endo*-adducts, 5-aroxymethyl-1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hept-2-enes. In recent years, a number of studies appeared [7–11] on the reactivity of hexachlorocyclopentadiene in the diene condensation with various dienophiles.

This work presents the results on the investigation of the reactivity of hexachlorocyclopentadiene in the diene condensation with allyl aryl ethers. In the reactions performed in the standard conditions the compound reactivity corresponds to the reaction products yield, since the yield to a certain extent is proportional to the rate constant logarithm.

The comparative studies of the condensation of hexachlorocyclopentadiene with allyl aryl ethers were performed in the uniform conditions, at the same concentrations of the reactants, temperature, and the reaction time. The condensation was carried out at 160°C for 6 h at the diene–dienophile ratio of 1:1. In all the experiments 0.1 mol (27.3 g) of hexachlorocyclopentadiene was taken. The results of the comparative study of the diene condensation of hexachlorocyclopentadiene with allyl aryl ethers are given in Table 1.

As seen from the data in Table 1, the highest yield was observed in the case of condensation of hexachlorocyclopentadiene with allyl *o*-tolyl ether (74.1%). It was found that the yield of the adduct does not depend on the structure of the alkyl substituent in the aromatic ring. However, the nature of the substituent in the aromatic ring of allyl aryl ehters has a significant influence on their reactivity. The yield of the reaction product decreases significantly with introducing the electron-withdrawing groups (NO_2, Cl) into the aromatic ring. Taking into account the electron-withdrawing nature of hexachlorocyclopenta-

Table 1. Effect of the substituents in the dienophile on the condensation adduct yield

Experimental parameter	Allyl aryl ether				
	o-tolyl	*p*-butylphenyl	*p*-octylphenyl	*p*-nitrophenyl	2,4,6-trichlorophenyl
Reactant amount, g	14.8	19.0	24.6	17.9	23.7
Yield, %:					
allyl aryl ether	8.6	10.5	13.4	16.3	26.8
hexachlorocyclopentadiene	16.1	15.5	14.8	25.6	30.9
loss	1.2	1.3	0.8	1.1	1.2
Yield of the condensation adduct relative to the ether, %	74.1	72.7	71.0	57.0	41.1

Table 2. Effect of the reaction temperature on the condensation adduct yield

Experimental parameter	Temperature, °C						
	130	140	150	160	170	180	190
Yield, %:							
condensation product	37.7	51.4	61.9	70.2	71.9	75.2	74.8
allyl *o*-tolyl ether	13.0	7.9	4.3	1.4	0.7	–	–
hexachlorocyclopentadiene	48.2	39.5	32.4	27.0	26.0	23.3	23.7
loss	1.1	1.2	1.4	1.4	1.4	1.5	1.5
Yield of the condensation adduct relative to the ether, %	50.0	68.0	81.3	92.0	91.7	90.3	84.2
Residue, %	–	–	0.7	1.1	3.5	9.2	14.8

Table 3. Effect of the reaction time on the condensation adduct yield

Experimental parameter	Reaction time, h						
	1	2	3	4	5	6	7
Yield, %:							
condensation product	21.5	30.1	51.3	60.5	67.6	70.3	71.8
allyl *o*-tolyl ether	18.7	15.4	8.0	4.8	2.3	1.4	0.8
hexachlorocyclopentadiene	58.8	53.5	39.6	33.5	28.7	27.0	26.0
loss	1.0	1.0	1.1	1.2	1.4	1.3	1.4
Yield of the condensation adduct relative to the ether, %	28.5	39.9	67.6	79.6	88.8	92.0	91.7
Residue, %	–	–	0.4	0.4	0.7	1.1	3.3

Table 4. Effect of the components molar ratio on the condensation adduct yield

Experimental parameter	Diene–dienophile molar ratio			
	1:1	1.5:1	2:1	3:1
Hexachlorocyclopentadiene taken for the reaction, g	27.3	40.9	54.6	81.9
Yield, %:				
condensation product	74.1	70.3	59.5	43.3
allyl *o*-tolyl ether	8.6	1.4	–	–
hexachlorocyclopentadiene	16.1	27.0	39.7	0
loss	1.2	1.3	0.8	0.7
Yield of the condensation adduct relative to the ether, %	73.7	92.0	96.6	98.0
Residue, %	0.4	1.1	1.4	1.5

diene, this fact reaffirms the general principle [12], which states that the reaction rate decreases as the differences in the polar nature of diene and dienophile decreases, and vice versa. Thus, in the case of condensation of hexachlorocyclopentadiene with allyl *p*-nitrophenyl ether and allyl 2,4,6-trichlorophenyl ether the yield of the adduct reduces to 57 and 41.1%, respectively.

The yield of the product of diene condensation depends on the temperature, reaction time, and the diene–dienophile molar ratio. The condensation with allyl *o*-tolyl ether was studied as an example.

Effect of the temperature on the yield of the condensation adduct was studied in the range of 130–200°C at the constant reaction time (6 h) and the molar ratio of hexachlorocyclopentadiene (40.9 g) and allyl *o*-tolyl ehter (14.8 g) of 1.5:1. Below the studied temperature range, the reaction proceeds very slowly and requires a long time to afford the adduct in a quantitative yield. Above this temperature range (200–220°C) the rearrangement occurs of allyl aryl ethers into the allylphenols and the tarring of the condensation products with an increase in the yield of the polymer residue. The results of the temperature effect on the yield of the condensation adducts are given in Table 2.

As seen from the data of Table 2, the increase in the reaction temperature to 150°C leads to the formation of polymer residue. A further increase in the temperature to 170–200°C leads to an increase in the yield of the condensation adduct, but simultaneously the yield of polymer residue increases up to 14.8%. The optimal condensation temperature is 160°C, at which the adduct is formed in the highest yield (92%) without a significant increase in the yield of the polymer residue.

Another important factor affecting the yield of the condensation adduct is the reaction time. In order to study the effect of the reaction time on the adduct yield, we performed a series of experiments changing the reaction time from 1 to 8 h at 160°C at the diene–dienophile molar ratio of 1.5:1. The results of the study are given in Table 3.

These data show that the yield of the reaction adduct is maximal (92%) when the condensation proceeds for 6 h. Further increase in the reaction time has no significant effect on the yield, but there is an increase in the polymer residue yield up to 3.3%.

In the diene synthesis the components molar ratio is also of a great importance. The influence of the diene–dienophile molar ratio was investigated at the condensation temperature of 160°C and the reaction time of 6 h. The results of this study are presented in Table 4.

When a stoichiometric diene–dienophile ratio is 1:1 the adduct yield equals 73.7% with respect to the taken allyl *o*-tolyl ether. An increase in the diene–dienophile molar ratio to 1.5:1 leads to an increase in the reaction product yield up to 92%. A further increase in the diene–dienophile molar ratio to 2:1 and 3:1 results in an increase in the condensation products yield. Apparently, an excess of hexachlorocyclopentadiene provide the homogeneity of the reaction mixture and acts as a solvent for the dienophiles. This results in an increase in the adduct yields. However, in this case the polymer content also increases (1.5%). The optimal diene–dienophile ratio is equal to 1.5:1, at which the product yield is maximal at the lower consumption of hexachlorocyclopentadiene.

Thus, the reactivity of allyl aryl ethers in the diene condensation with hexachlorocyclopentadiene depends on the nature of the substituent in the benzene ring, on the temperature, reaction time and the diene–dienophile molar ratio.

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