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Abstract

Full Text

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Vinyl Compounds in the Diene Synthesis

Stereospecific Direction of the Diene Synthesis of Vinyl Aryl Ethers with Cyclopentadiene as a Function of Temperature

(Presented by Academician B. A. Kazanskii, February 24, 1960)

In previous communications, the possibility was shown of the participation in the diene-synthesis reaction with cyclopentadiene and hexachlorocyclopentadiene of simple vinyl and thiovinyl ethers ([1–3]). It turned out that the double bond in vinyl aryl and thiovinyl ethers possesses the greatest dienophilic activity. For a more complete characterization of the adducts obtained, it was necessary to study their stereochemistry, as well as the stereospecific direction of the reaction as a function of temperature.

Investigation of the stereochemistry of the reaction of cyclic dienes with dienophiles containing groups with multiple bonds or unshared electron pairs led to Alder' s rule ([4]) of the "accumulation of unsaturation," according to which an adduct with the endo configuration is formed preferentially. The preferential formation of the endo isomer is due to favorable kinetic factors, although the exo isomer is thermodynamically more advantageous. Upon raising the temperature to such an extent that a reaction with a higher activation energy becomes possible, or under equilibrium conditions, accumulation of the exo form and consumption of the endo form of the adduct are observed ([5]).

Recently published works by Alder ([6]), Mikhail ([7]), and Tate ([8]) contain interesting data on the influence of substituents in the dienophile on the ratio of the isomeric adducts formed, which in a number of cases leads to predominance of the exo isomer.

In view of the fact that the diene synthesis of simple vinyl ethers proceeds at a temperature not below 170–175°, the rule concerning predominance of the endo form in the adduct is complicated in the present case, and condensation of vinyl aryl ethers with cyclopentadiene leads to the formation of an adduct that is a mixture of two isomeric endo and exo forms.

$$\text{cyclopentadiene} + \mathrm{CH_2{=}CH{-}OAr} \longrightarrow \text{norbornene adduct} \longrightarrow \text{endo-(A)} + \text{exo-(B)}$$

Fig. 1. Spectra of endo-(IA) and exo-adducts (IB)

Figure 1: Fig. 1. Spectra of endo-(IA) and exo-adducts (IB)

Fig. 2. Spectra of endo-(IIA) and exo-adducts (IIB)

Figure 2: Fig. 2. Spectra of endo-(IIA) and exo-adducts (IIB)

$$\mathrm{Ar} = \mathrm{C_6H_5}\ (\mathrm{I}),\quad p\text{-tert.-}\mathrm{C_4H_9C_6H_4}\ (\mathrm{II}),\quad \mathrm{C_{10}H_7}\ (\beta)\ (\mathrm{III})$$

On examination of the literature data ([9,10]), it was noted that the endo and exo isomers, having similar boiling points, differ in other physical properties: the endo isomer has a higher melting point and lower solubility. On this basis, the adducts (IA) and (IIA), which are crystalline at room temperature, and the higher-melting adduct (IIIA), apparently have the endo configuration, whereas (IB) and (IIB), liquid at room temperature, and the low-melting adduct (IIIB) have the exo configuration. Using the difficulty of crystallization of endo-2-phenoxybicyclo-$(2, 2, 1)$-heptene-5 (IA), we determined its refractive index and specif-

ular weight. It turned out that the numerical values of these constants for the endo adduct are higher than for the adduct with the exo configuration.

A spectroscopic study of the two isomeric forms of adducts (I) and (II) showed that, in the IR spectra of both forms, the frequencies of the principal absorption bands coincide, but each form also has a number of its own absorption bands.

Fig. 1. Spectra of endo-(IA) and exo-adducts (IB)

For example, the exo adduct (IB) has bands at 1754, 1431, 1381, 1095, 982, 923, and 804 $\mathrm{cm^{-1}}$, which are absent from the spectrum of the endo isomer (IA); the endo adduct (IIA) has its own bands at 1402, 1095, 923, and 807 $\mathrm{cm^{-1}}$ (see Figs. 1 and 2). For analysis of the adducts obtained at increasing temperatures, for the content of endo and exo isomers, we used data obtained from IR spectra. The characteristic absorption bands of the two isomeric forms proved unsuitable for these purposes because of their low intensity.

Fig. 2. Spectra of endo-(IIA) and exo-adducts (IIB)

In the study of the IR spectra, a sharp difference was observed in the intensities of absorption bands present in the spectra of both forms. This

This property was used for analytical purposes in the case of phenoxybicycloheptene (I). In the case of adduct (II), this difference is less pronounced; therefore, only semiquantitative measurements can be made here.

Table 1

Graph for determining the content of the exo form in the first adduct

Figure 3: Graph for determining the content of the exo form in the first adduct

Reaction temperature, °C	x_{eff}	Content of isomers in the adduct, %: exo form	Content of isomers in the adduct, %: endo form
170	3.10	65	35
180	3.15	67	23
200	3.32	74	26
220	3.44	80	20

In determining the composition of the mixture of the two configurations in adduct (I), the calibration-curve method was used. In the analysis, the absorption band at 685 cm^{-1} was selected, the intensity of which differs most among the isomers. Since only the effective intensity at the maximum of the absorption band was measured, the calibration curve had a course that differed considerably from a straight line. To construct the calibration curve (see Fig. 3), artificially prepared mixtures containing 0, 50, 67, 83, and 100% of the exo form were used. On the ordinate axis the effective intensity (x_{eff}) was plotted, and on the abscissa axis—the content of the exo isomer in percent. The accuracy of determination was ±3-4% at an exo-isomer concentration in the mixture of more than 50%; at a lower concentration its accuracy of determination should be lower. The results of the analysis are given in Table 1.

Fig. 3. Graph for determining the content of the exo form in the 1st adduct.

Thus, it has been established that the adducts of the diene synthesis of vinyl aryl ethers with cyclopentadiene are mixtures of two isomeric forms having endo and exo configurations. Conditions for separating these isomers have been found and their IR spectra have been recorded, which made it possible to determine the content of the isomers in the mixture. With the aid of spectral analysis it was shown that, as the reaction temperature is raised, the content of the lower-melting isomer (exo form) increases. The observations made make it possible to carry out stereodirected diene synthesis of vinyl aryl ethers with cyclopentadiene.

Experimental Part

Isolation of the endo- and exo-isomers of 2-phenoxybicyclo-(2,2,1)-heptene-5 (I). 2-Phenoxybicyclo-(2,2,1)-heptene-5 was obtained by condensation of vinyl phenyl ether with cyclopentadiene at temperatures of 165–170°; 180–182°; 197–200°; 217–220°, according to the procedure described by us earlier (1), and had b.p. 87-88°/1.5 mm; n_D^{20} 1.5500; d_4^{20} 1.0720. Literature data

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(1): b.p. 114-114.5°/5 mm; n_D^{20} 1.5500; d_4^{20} 1.0732. 18.2 g of the adduct obtained was left with seed crystals* at +10-12° for 15-20 h. The crystals that separated were filtered off and recrystallized from methanol to constant melting temperature. This gave 5.4 g of the higher-melting isomer (endo form) with m.p. 39.5-40° (from methanol), b.p. 100.5-101°/2.5 mm; n_D^{20} 1.5531; d_4^{20} 1.0732.

Found, %: C 84.34; 84.44; H 7.60; 7.72
$C_{13}H_{14}O$. Calculated, %: C 84.36; H 7.58

* The seed was obtained as follows: 3 g of the adduct was dissolved in 12 ml of dry ether and kept at −20-30° until a crystalline precipitate no longer formed. The crystals (0.12 g) were quickly separated from the solution while cold.

For the spectrum of the endo isomer, see Fig. 1. To isolate the exo isomer, 15.5 g of the resulting adduct with seed crystals was left overnight at 0-2°. Separation of the low-melting isomer was carried out on a filter with cooling at +4 to +5°. The remaining filtrate was subjected to fractional freezing 4-5 times and then reprecipitated from methanol to a constant melting point. The isomer with the exo configuration (1.2 g) had mp 3.5-4°; bp 106-106.5°/3 mm; n_D^{20} 1.5483; d_4^{20} 1.0652.

Found, %: C 84.50; 84.46; H 7.72; 7.78
$C_{13}H_{14}O$. Calculated, %: C 84.36; H 7.58

Isolation of the endo and exo isomers of 2-*p*-tert-butylphenoxybicyclo-(2,2,1)-heptene-5 (II). By condensation of cyclopentadiene and vinyl-*p*-tert-butylphenyl ether according to the procedure described by us earlier (^{3}), 2-*p*-tert-butylphenoxybicyclo-(2,2,1)-heptene-5 was obtained, bp 137.5-139°/2 mm. Literature data (^{3}): bp 135-135.5°/1.5 mm. Most of the adduct obtained crystallized during 2 days of standing at room temperature. The crystalline adduct, to which the endo structure (IIA) was assigned, had mp 35-36° (from methanol); bp 135-135.5°/1.5 mm; n_D^{20} 1.5332.

Found, %: C 84.29; 84.58; H 9.25; 8.88
$C_{17}H_{22}O$. Calculated, %: C 84.24; H 9.15

The part of the adduct that did not crystallize at room temperature (exo isomer (IIB)) had mp 15.5-16.5° from methanol; bp 134-135°/1 mm; n_D^{20} 1.5327; d_4^{22} 1.0152; MR_D found 74.08; $C_{17}H_{22}O$ calculated MR_D 73.88.

Found, %: C 84.27; 83.98; H 9.17; 9.25
$C_{17}H_{22}O$. Calculated, %: C 84.24; H 9.15

Isolation of the endo and exo isomers of 2-β-naphthoxybicyclo-(2,2,1)-heptene-5 (III). The 2-β-naphthoxybicyclo-(2,2,1)-heptene-5 obtained by the procedure described by us earlier (^{3}), mp 65.5-67°, was subjected to fractional crystallization from methanol. Two products were obtained. The endo isomer (IIIA) had mp 72.5-73°.

Found, %: C 86.60; 86.52; H 6.98; 7.14
$C_{17}H_{16}O$. Calculated, %: C 86.40; H 6.83

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The exo isomer (IIIB) had mp 64–65.5°.

Found, %: C 86.32; 86.28; H 6.95; 6.96
$C_{17}H_{16}O$. Calculated, %: C 86.40; H 6.83

Infrared spectra were obtained on an IKS-14 double-beam IR spectrophotometer. The spectra were obtained for solutions of the substances in chloroform at a concentration of about 10-15 wt. %. The thickness of the absorbing layer during measurement was 0.01 cm. The accuracy of measurement of absorption-band frequencies was $±$5 cm^{-1}. The accuracy of measuring the percentage transmittance was $±$1%. The spectra were obtained with automatic opening of the instrument slits according to the law of constant energy. The spectral width was 5-11 cm^{-1}.

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