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Abstract

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MONODEUTEROCYCLOPENTADIENE

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The present communication is devoted to proving the existence, in substituted cyclopentadienes, of a hindered thermodynamic equilibrium between isomers differing in their intracyclic double bonds. As was shown by Hückel calculations (^{1}), cyclopentadiene can form the cyclopentadienyl anion, which possesses the classical sextet of electrons and constitutes a fairly stable aromatic system. The formation of such an anion was used by Kursanov and Parnes (^{2}) to explain the unusual ease of exchange of all six hydrogen atoms of cyclopentadiene for deuterium in an alkaline medium; in neutral media no such exchange was observed. Appreciable amounts of cyclopentadiene in the form of an anion with completely delocalized electrons in a neutral medium apparently are absent, since they could have been detected by the NMR method (^{3}). In the equilibrium discussed here between cyclopentadienes isomeric with respect to intracyclic double bonds, the correspondingly substituted cyclopentadienyl anion is regarded by us as the most probable transition state.

To prove the existence of the indicated equilibrium, we undertook a study of monodeuterocyclopentadiene, guided by the following considerations. The presence in the cyclopentadienyl anion of any substituent differing from hydrogen in electronic character (for example, an alkyl group) will lead to a distortion of the symmetry of the electron cloud of this anion. The latter may lead to a certain selectivity in the process of proton addition during regeneration of the usual form of cyclopentadiene. In addition, the concentrations of the components in equilibrium mixtures are determined only by thermodynamic factors, in other words, by the energetic favorability of the limiting equilibrium states. In limiting cases, in the equilibrium state the concentration of one of the components may approach 100%, as was observed, for example, by Mironov, Mavrov, and Elizarova for 1,3-dimethylcyclopentadiene (unpublished). The difference in energetic favorability of isomeric monodeuterocyclopentadienes may be neglected, and, if equilibrium is present, their concentrations in the mixture should be practically identical.

Monodeuterocyclopentadiene was obtained by treating cyclopentadienylmagnesium bromide with deuterium oxide; the processes occurring in this case may reaction scheme: cyclopentadienylmagnesium bromide treated with D_2O gives cyclopentadienyl anion/deuterated intermediates, leading through structures (I)–(VI)

Figure 1: reaction scheme: cyclopentadienylmagnesium bromide treated with D_2O gives cyclopentadienyl anion/deuterated intermediates, leading through structures (I)–(VI)

be described by the following scheme:

The initial product of the reaction can only be 5-deuterocyclopentadiene (III), since it will be formed upon addition of a deuteron to any of the C atoms of anion II. Isomer III can already form two anions—II and IV. Addition of a proton to anion IV can lead to all three isomers: 1-(V)-, 2-(VI)- and 5-(III)-deuterocyclopent-

tadienes. In the sample of monodeuterocyclopentadiene isolated by us, according to the IR and NMR spectra, the ratio of isomers III, V, and VI corresponds to the equilibrium one, i.e., is $1 : 1 : 1$ within the accuracy of the measurements.

Carrying out the synthesis and isolation of monodeuterocyclopentadiene at temperatures not exceeding —5° made it possible to isolate the initial reaction product, i.e., to retard the establishment of equilibrium. Under these conditions a sample of monodeuterocyclopentadiene enriched to 90–95% in isomer III was obtained. Heating this sample at 60° rapidly (within an hour) converts it into an equilibrium mixture of isomers ($\text{III} : \text{V} : \text{VI} = 1 : 1 : 1$). Further heating of this mixture does not lead to a change in the concentrations of its components.

The establishment of equal concentrations of the isomers in a mixture of practically homogeneous diene (III) is not accompanied by an increase in the concentration of ordinary cyclopentadiene and, correspondingly, by the formation of di- and polydeuterocyclopentadienes. This fact makes it possible to exclude the formation of isomers V and VI through redistribution of deuterium in hydrogen exchange between molecules. In addition, this makes it possible to suppose that in the transition state the deuteron and, in all probability, the proton are not removed (or do not have time to be removed) from each given molecule. In the absence of hydrogen exchange between molecules of monodeuterocyclopentadiene, the conversion of diene III into a mixture of equal amounts of isomers III, V, and VI can be explained only by the establishment of thermodynamic equilibrium among these isomers.

The possibility of isolating a nonequilibrium sample III shows that the process of establishing equilibrium among the monodeuterocyclopentadienes is retarded; in other words, the potential barrier for the interconversion of the isomers is relatively high.

The equilibrium discussed in the present communication is characteristic not only of monodeuterocyclopentadiene; the presence of a similar equilibrium has been shown for isomers of methyl- and tetramethylcyclopentadienes. Apparently, this phenomenon is of a general nature. Questions concerning the kinetics and mechanism of the process of establishing the indicated equilibrium are the subject of further investigations.

The presence in substituted cyclopentadienes of thermodynamic equilibrium among isomers with respect to the intracyclic double bonds makes it possible to explain numerous examples of the isolation of substituted cyclopentadienes with a different arrangement of the double bonds in the ring than would have been expected from the methods of their preparation (e.g., (4–6)). The preparation in some cases of mixtures of isomeric cyclopentadienes and the isomerization of initially formed forms of substituted cyclopentadienes into more stable forms are evidently connected with the establishment of the indicated equilibrium.

Experimental Part

The starting cyclopentadiene was obtained by depolymerization of crystalline dicyclopentadiene and purified by distillation on a column (32 theoretical plates). The product had b.p. 39.4° (748 mm), n_D^{20} 1.4469, d_4^{20} 0.8116.

Monodeuterocyclopentadiene. To a solution of 0.65 mole of ethylmagnesium bromide (from 17.4 g of magnesium and 70.9 g of ethyl bromide) in 200 ml of di-*n*-butyl ether, 30 g (0.455 mole) of cyclopentadiene was added dropwise at 50°. After the addition was completed, the reaction mixture was kept for 1 hour at the same temperature and for 3 hours at 80–85°. The resulting solution of cyclopentadienylmagnesium bromide, cooled to −15 to −20°, was treated with 17.3 g of deuterium oxide. Isolation of monodeuterocyclopentadiene from the reaction mixture was carried out by two methods:

1. The reaction product was distilled off at atmospheric pressure; 17.6 g of a fraction with b.p. 38–50° was collected. Purification of the substance was carried out by distillation

on the column (32 theoretical plates); 6.8 g of monodeuterocyclopentadiene was isolated, with b.p. 39.2° (751 mm), n_D^{20} 1.4458, d_4^{20} 0.8133. The large losses during distillation are apparently associated with the rather rapid dimerization of the diene.

According to the IR and Raman spectra, the product proved to be a mixture of dienes III, V, and VI in a ratio of 1 : 1 : 1; about 7% of material not containing deuterium was detected in the mixture

Fig. 1. IR spectrum of an equilibrium mixture of monodeuterocyclopentadienes. *a* —lines assigned to 5-deuterocyclopentadiene, *b* —to 1- and 2-deuterocyclopentadienes, *c* —to dimers.

of cyclopentadiene (664 and 803 cm^{-1} in the IR spectrum); possibly the latter is explained by hydrogen exchange of deuterocyclopentadiene with di-*n*-butyl ether at a relatively high temperature in an alkaline medium. The ratio of the

Fig. 1. IR spectrum of an equilibrium mixture of monodeuterocyclopentadienes. *a* —lines assigned to 5-deuterocyclopentadiene, *b* —to 1- and 2-deuterocyclopentadienes, *c* —to dimers.

Figure 2: Fig. 1. IR spectrum of an equilibrium mixture of monodeuterocyclopentadienes. *a* —lines assigned to 5-deuterocyclopentadiene, *b* —to 1- and 2-deuterocyclopentadienes, *c* —to dimers.

components of the mixture does not change during its storage and heating at 60° for one hour.

2. The reaction product was distilled off at a residual pressure of 30 mm, the temperature of the reaction mixture not exceeding −5°; condensation of the substance was carried out in a trap cooled to −72°. The condensate (16.1 g) was charged into an apparatus for molecular distillation at a residual pressure of 0.4 mm; distillation was carried out at a temperature of $-5 \div -10°$ into a receiver cooled with liquid nitrogen. As a result of the fractionation, 11.8 g of III of 90–95% purity was isolated; according to IR and Raman spectra, the sample contained small amounts of isomers, about 3% di-*n*-butyl ether, and was practically free from cyclopentadiene impurity.

On heating the sample for one hour at 60°, an equilibrium mixture of isomers identical with that described above was obtained; in this process no formation of appreciable amounts of cyclopentadiene was observed.

The structures of dienes III, V, and VI and the composition of their mixtures were determined from consideration of the Raman and IR spectra (see Figs. 1 and 2)*; the regions of the stretching vibrations of C—D and C—H and the region of the stretching vibrations of the double bonds of the ring were used as analytical regions. The frequencies of the stretching vibrations of the $-\mathrm{CH}_2$ —group and of the C—H stretching vibrations at double bonds in cyclopentadiene lie in the regions 2900 and 3100 cm^{-1}, respectively. When one of the hydrogen atoms is replaced by deuterium in position 5 (diene III), the intensity of the methylene-group band should decrease; in addition, a C—D stretching-vibration line should appear in the region of 2100 cm^{-1} (found 2156 cm^{-1}). Replacement of a hydrogen atom by deuterium in positions 1 and 2 (dienes V and VI) should analogously lead to some decrease in the intensity of the C —H stretching-vibration lines at double bonds and to the appearance of C—D stretching-vibration lines in the region of 2300 cm^{-1} (found 2302 and 2332 cm^{-1}).

Replacement of hydrogen by deuterium in the methylene group should not substantially affect the frequency of the symmetric stretching vibration of the double bonds (1500 cm^{-1} in cyclopentadiene), since in a similar case[7] replacement of hydrogen by deuterium in the imino group of pyrrole leads to a lowering of the frequency of the corresponding vibration by only 2 cm^{-1} (found 1499 cm^{-1}).

Fig. 2. IR spectrum of 5-deuterocyclopentadiene. The designations of the lines are the same as in Fig. 1

Figure 3: Fig. 2. IR spectrum of 5-deuterocyclopentadiene. The designations of the lines are the same as in Fig. 1

At the same time, the presence of deuterium atoms in the 1 and 2 positions should lead

* The spectral part of the work will be described in more detail in another communication.

to an appreciable change in the frequency of this band by an amount of the order of 10–20 cm^{-1} (1486 cm^{-1} was found). This permits analysis for the ratio of diene III and the sum of dienes V and VI from comparison of the integrated intensities of the lines $\Delta\nu$ 1499 and 1485 cm^{-1} in the Raman spectrum. In doing so it is assumed that the intensity of the line corresponding to this mode of vibration changes little when a hydrogen atom is replaced by deuterium; indeed,

$$I_\infty(\Delta\nu\,1500\ \text{cm}^{-1})$$

for cyclopentadiene

$$= I_\infty(\Delta\nu\,1499\ \text{cm}^{-1}) + I_\infty(\Delta\nu\,1485\ \text{cm}^{-1})$$

for the equilibrium mixture. The ratio of forms V and VI, 1 : 1, was found with sufficient accuracy from comparison of the concentrations of the dimers formed from them (determined from the intensity ratio of the lines of the stretching vibrations of the double bonds).

Fig. 2. IR spectrum of 5-deuterocyclopentadiene. The designations of the lines are the same as in Fig. 1.

The IR absorption spectra of samples of monodeuterocyclopentadiene were obtained on a "Leitz" spectrometer (NaCl prism); to exclude bands of the rapidly forming dimer, spectra of the same sample were recorded consecutively in time. The combination-scattering spectra of the indicated samples were obtained photographically on an ISP-51 spectrograph; the procedure for obtaining and measuring the spectra has been described previously (8). In order to remove dimer impurities, the samples were distilled directly before photography into the working part of the cuvette; the exposure time did not exceed 10–20 min. The IR spectra of the samples of monodeuterocyclopentadienes isolated by us are shown in Figs. 1 and 2.

Raman spectra (designations: —broad, —sharp, —background).

1. Equilibrium mixture of monodeuterocyclopentadienes (intensities at the maxima of the lines are given on the cyclohexane scale $I(\Delta\nu\,802) = 250$).

$\Delta\nu$ (cm^{-1}) : 312 (5), 348 (3), 438 (4), 475 (5), 509 (12), 544 (3),
706 (2), 762 (5), 796 (6), 814 (3), 832 (9), 850 (5), 872 (5), 888 (4),
912 (38), 930 (40), 952 (8), 968 (6), 984 (40), 1014 (5), 1033 (47),
1095 (70), 1105 (175), 1228 (16), 1252 (7), 1353 (50), 1372 (88),
1485 (400), 1499 (250), 1528 (4), 1568 (12), 2134 (6), 2156 (52), 2190
(2), 2280 (3), 2302 (30), 2332 (14), 2853 (6), 2886 (310), 2902 (135),
2934 (15), 3075 (200), 3089 (230), 3127 (36), 3148 (25).

2. 5-Deuterocyclopentadiene (intensities are given on a visual ten-point scale).[1]

$\Delta\nu$ (cm^{-1}) : 314 (1–2), 376(0), 441 (0–1), 763(0), 790 (1–2), 809(1),
829 (1), 850 (2), 875 (0–1), 895(0), 913 (4–5), 927 (2), 961 (0–1),
993 (2), 1008 (1), 1029 (1–2), 1052 (2), 1075 (0–1), 1091 (2),
1105 (8), 1125(1), 1144(0), 1200(0), 1227 (3–4), 1244(0), 1260 (0–1),
1278 (0–1), 1297 (0–1), 1318 (1–2), 1348(0), 1363(0), 1374 (4–5),
1425(1), 1461 (0–1), 1485(3), 1498 (10), 1516(1), 2136(2), 2156 (6–7),
2192 (0–1), 2228(0), 2892 (6), 3074 (4), 3094 (8), 3148(2).

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