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Abstract

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Methylcyclopentadiene as an Equilibrium Mixture of Isomers

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We have shown ([1], [2]) that substituted cyclopentadienes are characterized by a retarded thermodynamic equilibrium between isomers with respect to the intracyclic double bonds. The pseudoaromatic cyclopentadienyl anion was considered as the probable transition state in the interconversion of isomeric cyclopentadienes.

The present communication is devoted to the study of this equilibrium between 1-(I)-, 2-(II)-, and 5-(III)-methylcyclopentadienes, which differ in the position of the system of double bonds. The preparation of individual isomers of methylcyclopentadiene has been reported in the literature ([3]-[5]), as has the preparation of a mixture of them, which was separated by gas-liquid chromatography ([6]) or through adducts with N-phenylmaleimide ([7]). Interconversion of isomers (I), (II), and (III) had not previously been observed.

For the synthesis of methylcyclopentadiene we used alkylation of cyclopentadienylmagnesium bromide with dimethyl sulfate in di-*n*-butyl ether solution. The synthesis and isolation of methylcyclopentadiene were carried out at a temperature not above −10°. The reaction product was distilled from the reaction mixture in vacuo; the distillate contained di-*n*-butyl ether, methyl bromide, which is a by-product of the reaction, and ~30% methylcyclopentadiene. The latter proved to be practically pure 5-methylcyclopentadiene (III), containing no noticeable amounts of isomers (I) and (II), nor of the starting cyclopentadiene. This fact indicates that the primary products in the alkylation of organometallic derivatives of cyclopentadiene are 5-alkyl derivatives.*

Storage of the obtained sample of 5-methylcyclopentadiene (III) at 25-28° causes its rapid conversion into 1-methylcyclopentadiene (I). Under our conditions this process was practically complete within 3 hr; at the same time only small amounts (less than 5%) of 2-methylcyclopentadiene (II) were formed. Upon further standing of the sample of diene (I) at 25-26° for two days, its continuous conversion into a mixture of dienes (I) and (II) was observed.

In the gas phase at 25-28° the conversion of the dienes also took place: (III) → (I) → (I) + (II), but at a somewhat lower rate; the same result was obtained upon distillation of dienes (I) and (III) at atmospheric pressure. In any of the cases described, an equilibrium mixture of approximately equal amounts of dienes (I) and (II) was always obtained, containing only traces of diene (III); further storage or heating of this mixture did not change its composition. When samples of dienes (I) and (III) were stored in dry ice, their isomerization was not observed.

Identification of isomers (I), (II), and (III) and analysis of their mixtures were carried out on the basis of Raman spectra and infrared absorption spectra.** In doing so we were guided by the following considerations:

* It has previously been described in the literature that, upon alkylation of organometallic derivatives of cyclopentadiene, mixtures of 1- and 2-substituted cyclopentadienes are formed ([8], [9]), and under milder conditions relatively homogeneous 1-isomers ([9], [10]).

** The spectral results will be discussed in more detail in a special communication.

1. The frequency of the symmetric vibration of the double bonds of the cyclopentadiene ring (1500 cm^{-1} for cyclopentadiene) should increase when a methyl group is introduced into the 1- and 2-positions (found: 1526-1529 cm^{-1}); substitution in position 5 should have a less substantial effect* (found: 1507 cm^{-1}).
2. By analogy with open diene chains (piperylene–isoprene), it should be expected that in the IR spectra dienes (I) and (II) will differ in the intensity ratio of the symmetric and antisymmetric vibrations of the double bonds; upon substitution of cyclopentadiene in the 1-position (diene I), an increase in the intensity of the band of the symmetric vibration should be observed (violation of the alternation of Raman and IR spectra); for diene (II) this alternation should, in the main, be retained.

A significant difference in the IR spectra of dienes (I), (II), and (III) in the region 500-900 cm^{-1} made it possible to determine the composition of mixtures of these dienes at various stages of the transformations: ν (cm^{-1}) –I: 672 (10), 810 (4), 887 (8); II: 561 (8), 670 (10), 734 (8), 900 (10); III: 536 (2), 598 (7), 696 (10), 768 (10), 801 (3), 861 (5).** The presence of CH_3Br in the mixture was recorded from the intense lines 598 and 2959 cm^{-1} (Raman), $(n\text{-}C_4H_9)_2O$ –1123 cm^{-1} (IR).

Proof of the structure of the dienes was also carried out on the basis of the structure of their adducts with maleic anhydride. Thus, individual adducts (IV) and (VI) were obtained from samples of dienes (I) and (III); the equilibrium mixture of methylcyclopentadienes was characterized by a mixture of adducts containing approximately equal amounts of anhydrides (IV) and (V).

The structure of anhydrides (IV), (V), and (VI) was determined unambiguously from consideration of their Raman and NMR spectra. The principal criteria were the degree of substitution of the double bond in the bicyclo-(2,2,1)-heptene ring (Raman spectrum–region 1550-1650 cm^{-1}, NMR spectrum***–CH_3 at the structural formulas of adducts (IV), (V), and (VI)

Figure 1: structural formulas of adducts (IV), (V), and (VI)

double bond—region τ 8.3–8.2 ppm) and the presence of a methyl group in the 7-position of the bicyclo-(2,2,1)-heptene ring (NMR spectrum—doublet in the region $\tau \sim 9.2$ ppm). The formation at low temperature of anhydrides (IV) and (VI) from the corresponding dienes shows that the rate of interaction of methylcyclopentadienes with an active dienophile considerably exceeds the rate of establishment of equilibrium.

The data obtained indicate with complete certainty the presence of a hindered thermodynamic equilibrium among the isomeric methylcyclopentadienes (I), (II), and (III). At the same time, the potential barriers of mutual transformations are sufficiently large that the individual isomers can be isolated at relatively low temperatures. The conversion of diene (III) into the equilibrium mixture has a stepwise character, since it proceeds through the intermediate stage of formation of diene (I), from which diene (II) is then formed. This phenomenon is evidently connected with the different probabilities of proton addition to positions 1 and 2 after heterolytic cleavage of the C—H bond in position 5 (with formation of a transition-state system: aromatic anion—proton), and may be explained by the following factors****:

1. By distortion of the symmetric configuration of the electron cloud of the anion (under the influence of the substituent); the transition states of the mutual transformations of the methylcyclopentadienes in this case are assumed to be identical and to have a relatively long lifetime.
2. By a difference in the paths of proton migration from position 5 to positions 1 and 2, with a relatively short lifetime of the transition states. In this case the transition states for the transformations of the isomers into one another will differ in the position of the proton and, consequently, in the polarization of the electron cloud of the anion. In other words, the transition $III \rightleftarrows II$ will be unlikely, and the transitions in the equilibrium state can be represented by the scheme:

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* A general regularity for conjugated diene systems and, in particular, five-membered unsaturated rings.

** The numbers in parentheses are proportional to absorption in percent.

*** The NMR spectra were obtained by A. U. Stepanyants (Institute of Chemical Physics, Academy of Sciences of the USSR); they will be published in a separate communication.

**** The explanation of the mutual conversions of dienes (I), (II), and (III) by migration of double bonds of the allylic-rearrangement type should be excluded, since in that case diene (II), not (I), should have been obtained in the first stage.

reaction scheme: methylcyclopentadiene isomers I, II, III interconverting through protonated anion transition states; the direct transitions $III \rightleftarrows II$ are crossed out

Figure 2: reaction scheme: methylcyclopentadiene isomers I, II, III interconverting through protonated anion transition states; the direct transitions $III \rightleftarrows II$ are crossed out

The action of the second factor must be of a general nature for all derivatives of cyclopentadiene. The second variant of the interpretation appears to us the more probable.

The comparatively low values of the activation energies for the transitions of methylcyclopentadienes into one another may be connected with aromatic stabilization of the transition state. The isolation of a practically homogeneous diene (I) at an intermediate stage of the transformation is evidently possible because the potential barrier for the transition $I \rightarrow II$ is higher than that for $III \rightarrow I$. Apparently, the isomeric transitions of substituted cyclopentadienes are a first-order reaction. This is supported by the practically constant rate of conversion of diene III into diene I at different stages of the transformation, and by the comparable rates of the transitions in the liquid and gas phases.

Thus, we have for the first time shown the direction of alkylation of cyclopentadienylmagnesium bromide, proved the existence of thermodynamic equilibrium between methylcyclopentadienes isomeric with respect to the intracyclic double bonds, and established the stepwise character of the transformation of these isomers into one another. The kinetics and mechanism of the process by which the above equilibrium is established will be the subject of our further investigation.

Experimental Part

5-Methylcyclopentadiene. To a solution of ∼ 1 mole of cyclopentadienylmagnesium bromide in 0.5 l of $(n\text{-}C_4H_9)_2O\hat{}1$ at −15°, 278 g of dimethyl sulfate was added dropwise; the reaction mixture was stirred for 2.5 hours at the same temperature. The reaction product was distilled off at 2 mm (in a condenser at ∼ −70°); the temperature of the mixture did not exceed −10°. The condensate (88 g), according to spectral data*, was a solution of diene (III) (∼ 30%) in $(n\text{-}C_4H_9)_2O$ and CH_3Br; appreciable amounts of dienes (I) and (II) were absent in the sample obtained.

IR spectrum**–$\Delta\nu$ (cm^{-1}): 176 (3sh), 301 (1), 703 (1-2sh), 811 (0-1), 837 (1sh), 863 (2), 927 (2sh), 957 (0-1), 985 (2sh), 1011 (0), 1035 (0-1), 1063 (4sh), 1098 (3sh), 1123 (4p), 1237 (1), 1257 (1), 1299 (4sh?), 1323 (0-1), 1361 (1), 1381 (3), 1435 (1), 1453 (4sh), 1507 (10p), 2853 (3sh), 2872 (4sh), 2906 (3ph), 2934 (2-3ph), 3067 (2), 3085 (4).

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* The Raman spectra were obtained on an ISP-51 instrument; the method of obtaining and processing the spectra was described previously (11). The IR spectra were obtained on a "Leitz" instrument (NaCl) and an IKS-15 (LiF and KBr).

** Intensities here and below are given on a visual ten-point scale; impurity lines are excluded. Designations: sh—broad, p—sharp, ph—background.

The IR spectrum of the sample coincides (after exclusion of impurity bands) with that described earlier [6]. Adduct with maleic anhydride (VI)*: m.p. 145.5-146°; Raman: $\Delta\nu$ 1574 cm^{-1}.

Found, %: C 67.60; 67.43; H 5.58; 5.90
$C_{10}H_{10}O_3$. Calculated, %: C 67.40; H 5.66.

1-Methylcyclopentadiene (I). The sample of diene (III) (see above), on storage, is continuously converted into diene (I); at 25-28° in the liquid phase the substance isomerizes by half every 20-25 min., and in the gas phase (in the gas cell of the IKS-15 spectrometer)—every 30-40 min. The process is practically complete, respectively, in 3 and 4 hours; no formation of appreciable amounts of diene (II) is observed. By fivefold molecular distillation (10-15°), diene (I) of 85-90% purity was isolated (the remainder is mainly CH_3Br; $(n\text{-}C_4H_9)_2O$ is absent).

Raman spectrum—$\Delta\nu$ (cm^{-1}): 239 (10 sh), 327 (2-3 sh), 618 (1-2?), 811 (2 sh), 829 (1-2 sh), 870 (3), 943 (2-3), 981 (2-3), 1007 (3), 1026 (0-1), 1103 (7-8 p), 1114 (1-2 f), 1198 (0-1 sh), 1240 (3 sh), 1297 (4 sh), 1359 (3 p?), 1380 (6 sh), 1450 (4), 1529 (10 p), 1609 (4 p), 2736 (0-1 sh), 2861 (2), 2882 (8), 2902 (3 f), 2916 (6 f), 3070 (4 sh), 3093 (5).

The IR spectrum of the sample was in good agreement with that described earlier [6]; UV: $\lambda_{\max}$ 249.5 mμ. Adduct with maleic anhydride (IV): m.p. 88.5-89°; Raman: $\Delta\nu$ 1574 cm^{-1}. Found, %: C 67.26; 67.17; H 5.53; 5.63.

Equilibrium mixture of methylcyclopentadienes.
a) On storing diene (I) at 25-28°, establishment of equilibrium is completed in the liquid phase in 2-3 days. According to IR and Raman spectra, the resulting sample is a mixture of approximately equal amounts of dienes (I) and (II) and contains only traces of diene (III). b) Distillation of diene (I) at atmospheric pressure gives a mixture of methylcyclopentadienes identical with that described above: b.p. 72.5-73° (747 mm), n_D^{20} 1.4512, d_4^{20} 0.8098, $\lambda_{\max}$ (in heptane) 247 mμ, ε 3410**.

Found, %: C 89.80; 89.87; H 10.10; 10.10
C_6H_8. Calculated, %: C 89.94; H 10.06.

Raman spectrum—$\Delta\nu$ (cm^{-1}): 238 (2-3 sh), 327 (3 sh), 368 (1 sh), 509 (0-1), 594 (0-1 f), 615 (5), 704 (0), 736 (0 sh), 811 (2-3 sh), 827 (1-2), 870 (3-4), 899 (4), 916 (0-1 f), 923 (5-6), 942 (1-2 f), 965 (0-1), 981 (1-2), 1005 (4-5), 1026 (1), 1083 (4-5), 1103 (8 p), 1109 (3 f), 1193 (4 p), 1238 (3-4), 1296 (2-3 sh), 1358 (7-8 p), 1380 (7 sh), 1449 (5 sh), 1526 (10), 1609 (5), 1619 (2 f), 2735 (1-2), 2862 (3 f), 2882 (8-9), 2900 (3 f), 2917 (6-7 f), 2940 (2-3 f), 2968 (4 sh), 3065 (4-5 sh), 3093 (8).

Mixture of adducts with maleic anhydride (IV) and (V) from the equilibrium mixture of methylcyclopentadienes: b.p. 122-123° (3 mm), m.p. 47-49°, Raman: $\Delta\nu$ 1575 (4) and 1630 (4-5) cm^{-1}. Found, %: C 67.35; 67.62; H 5.73; 5.70.

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1. V. A. Mironov, E. V. Sobolev, A. N. Elizarova, DAN, **143**, 1112 (1962).
2. V. A. Mironov, T. M. Fadeeva, E. V. Sobolev, A. N. Elizarova, ZhOKh, in press.
3. I. N. Nazarov, N. V. Kuznetsov, DAN, **111**, 358 (1956).
4. N. I. Shuikin, T. I. Naryshkina, I. P. Egorov, Bull. Soc. Chim., 406 (1957).
5. T. I. Naryshkina, N. I. Shuikin, ZhOKh, **30**, 3205 (1960).
6. S. M. Csicsery, J. Org. Chem., **25**, 518 (1960).
7. M. J. Craven, Diss. Abstr., **15**, 2408 (1955).
8. K. Alder, H. Holzrichter, Ann., **524**, 145 (1936).
9. R. Riemschneider, E. Reisch, E. B. Grabitz, Monatsh., **91**, 805 (1960).
10. R. Riemschneider, E. Reichelt, E. B. Grabitz, Monatsh., **91**, 812 (1960).
11. V. T. Aleksanyan, Kh. E. Sterin, Optics and Spectroscopy, **3**, 562 (1957).
12. J. S. Powell, K. C. Edson, Anal. Chem., **20**, 510 (1948).

13. K. C. Edson, J. S. Powell, E. L. Fisher, Ind. and Eng. Chem., **40**, 1526 (1948).

* Adducts of samples of methylcyclopentadienes with maleic anhydride were obtained under conditions analogous to those used for preparation of adducts of tetramethylcyclopentadienes [2]. Yield 70-85% (based on maleic anhydride).

** Constants of the sample cf. [12,13].

Note: Figure translations are in progress. See original paper for figures.

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