

## CYCLIC UNSATURATED COMPOUNDS

## COMMUNICATION 47. TRANSFORMATIONS OF CYCLOPENTADIENES

## IN PRESENCE OF ALUMINUM OXIDE

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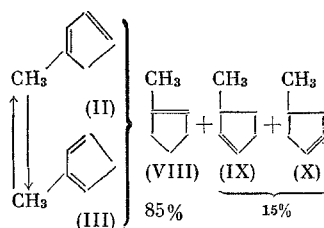
In previous communications [1-8], it was shown that at 200° the 5,5-disubstituted cyclopentadienes undergo irreversible isomerization to cyclopentadienes with a free methylene group. A reversible skeletal isomerization (change in the type of substitution) is realized in the latter dienes at a higher temperature (300-400°). An intramolecular 1,2(1,5)-shift of the alkyl group from the 5 position of the cyclopentadiene ring was regarded as being the mechanism of both transformations.

In the present paper, we studied the transformation of cyclopentadiene (I), of an equilibrium mixture of the 1- (II) and 2-methylcyclopentadienes (III), and also of the 1,5,5- (IV), 1,2,3- (V) and 1,2,4-trimethylcyclopentadienes (VI) in the presence of  $Al_2O_3$ .

In the absence of catalysts, the diene (I) molecule is thermally stable up to 500°. The catalytic action of  $Al_2O_3$  on (I) was studied in the range 330-500°. The irreversible conversion of (I) to cyclopentene (VII) occurs here. The degree of the conversion (I) → (VII) was determined by the GLC method (Table 1) and UV spectroscopy; within the limits of experimental error ( $\pm 5\%$ ), the UV spectroscopy data coincided with the data given in Table 1.

As can be seen from Table 1, at 350° and higher the reaction products contain (VII) in amounts that monotonically increase with increase in the temperature up to 62%. At a contact time of  $\sim 8$  sec the indicated degree of conversion is maximum; the formation of secondary reaction products failed to occur. In a preparative experiment (500°), where the catalyzate was treated with maleic anhydride and then subjected to molecular distillation, we isolated (VII) in 55% yield, which proved to be identical with an authentic sample.

The catalytic transformations of an equilibrium mixture of methylcyclopentadienes (II) and (III) [9, 10] were studied under analogous conditions (Table 2). As follows from Table 2, at temperatures above 380°, in the presence of  $Al_2O_3$ , the mixture of dienes (II) + (III) is converted to a mixture of methylcyclopentenes



In the given case the transformation proceeds at a much faster rate, and at  $\geq 490^\circ$  and a contact time of  $\sim 8$  sec, it goes almost to completion (degree of conversion  $\geq 97\%$ ). In the preparative experiment (480°), as the result of removing small amounts of unreacted dienes (II) and (III) from the condensate by treatment with maleic anhydride, we isolated a mixture of methylcyclopentenes in 78% yield. The structure of the main component in the mixture (85%) was established by comparing the data of the GLC and the Raman spectra of the sample with those of an authentic of 1-methylcyclopentene (VIII). The peak on the chromatograms with a shorter retention time (15%) was assigned to the 3- (IX) and 4-methylcyclopentenes (X) in view of the presence of a frequency at  $1613\text{ cm}^{-1}$  in the Raman spectrum, which is characteristic for an unsubstituted double

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TABLE 1. Composition of Transformation Products of Cyclopentadiene in the Presence of  $\text{Al}_2\text{O}_3$

T., °C	Diene (I), %	Cyclopentene (VII), %	T., °C	Diene (I), %	Cyclopentene (VII), %
330	100	0	430	47	53
350	91	9	440	45	55
370	81	19	450	39	61
385	77	23	475	37	63
400	69	31	500	36	62
445	59	41			

TABLE 2. Composition of Transformation Products of Equilibrium Mixture of Methylcyclopentadienes in Presence of  $\text{Al}_2\text{O}_3$

T., °C	Dienes (II) + (III), %	Methylcyclopentenes, %	T., °C	Dienes (II) + (III), %	Methylcyclopentenes, %
350	100	0	450	60	40
360	98	2	460	45	55
380	96	4	470	33	67
400	91	9	480	20	80
420	80	20	490	3	97
430	72	28	500	2	98
440	69	31			

TABLE 3. Composition of Transformation Products of 1,5,5-Trimethylcyclopentadiene (IV) in the Presence of  $\text{Al}_2\text{O}_3$

T., °C	Diene (IV), %	Trimethylcyclopentenes, %	T., °C	Diene (IV), %	Trimethylcyclopentenes, %
200	100	0	290	30	70
210	85	5	300	22	78
230	86	14	315	12	88
245	77	23	330	8	92
260	66	34	350	2	98
270	50	50	375	1	99
280	38	62	400	0	100

isomerization (V)  $\rightleftharpoons$  (VI) [1-3]. In the case of diene (IV), the irreversible skeletal isomerization (IV)  $\rightarrow$  (V) [6] is apparently realized prior to establishing the mentioned equilibrium. From a comparison of the temperatures at which the mentioned transformations proceed in the presence of  $\text{Al}_2\text{O}_3$  and under thermal isomerization conditions [3, 6], it is possible to assume that  $\text{Al}_2\text{O}_3$  catalyzes the migration of alkyl groups both in the 5,5-disubstituted derivatives and in the thermodynamically stable substituted cyclopentadienes.

The mixture of substances that is formed as the result of the catalytic transformations of the trimethylcyclopentadienes contains, when based on the GLC data, six components,† Based on the data of the UV and

\*Equilibrium mixtures of the isomers that differ in the position of the intracyclic double bonds, in which the given diene predominates [3].

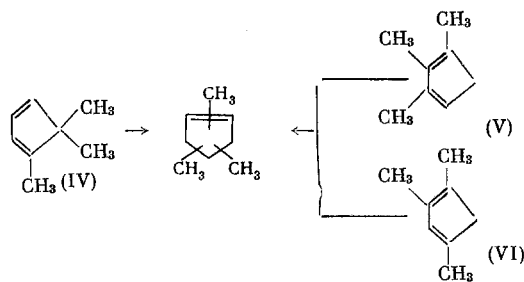
†Corresponds to the number of possible isomers of the 1,2,3- and 1,2,4-substituted trimethylcyclopentenes.

bond in a cyclopentene nucleus. The absence of noticeable amounts of methylcyclopentane in the given sample is corroborated by the data of the IR and Raman spectra (absence of lines and bands in the 1655-1660 and 3065-3085  $\text{cm}^{-1}$  regions).

It should be mentioned that, within the limits of experimental error, the ratio of olefins (VII) and (IX) + (X) remains constant over the entire studied temperature interval, with the conversion ranging from 0 to 100%. The latter can testify to the absence of isomeric transformations of methylcyclopentenes (VIII), (IX), and (X) under the experimental conditions.

The transformations of the three skeletal isomers of trimethylcyclopentadiene, namely dienes (IV) [6], (V)\* and (VI)\* were studied under analogous conditions, in the range 200-450°. The results of the GLC analysis of the reaction products are given in Tables 3 and 4.

From the presented data it can be seen that the trimethylcyclopentadienes (IV) - (VI) are converted to a mixture of trimethylcyclopentenes under the experimental conditions



The conversion of dienes (V) and (VI) to olefins proceeds at approximately the same speed, in this connection noticeably exceeding the rate of the analogous transformation of the methylcyclopentadienes: even at 300° the reaction products contain ~20% of olefins; under the given conditions the transformation is practically completed even at 450°. The conversion of diene (IV) to a mixture of olefins proceeds at an even faster rate.

In the preparative experiments a mixture of the formed olefins can always be isolated in a yield of 84-88%. It is characteristic that at 400° and higher, any of the starting trimethylcyclopentadienes leads to the same mixture of olefins. The identity of the formed mixtures of olefins in a wide temperature range indicates that a mutual isomerization of the trimethylcyclopentenes is improbable under the experimental conditions. From this it is possible to assume that in the presence of  $\text{Al}_2\text{O}_3$  the formation of the olefins is preceded by the establishment of a thermodynamic equilibrium between the 1,2,3- and 1,2,4-trimethylcyclopentadienes as the result of the reversible skeletal

TABLE 4. Composition of Transformation Products of 1,2,3-Trimethylcyclopentadiene (V) and 1,2,4-Trimethylcyclopentadiene (VI) in the Presence of  $\text{Al}_2\text{O}_3$

T., °C	Starting diene (V)		Starting diene (VI)	
	diene (V), %	trimethylcyclopentenes, %	diene (VI), %	trimethylcyclopentenes, %
280	97	3	100	0
300	79	21	84	16
315	58	42	67	33
330	40	60	50	50
340	26	74	36	64
350	21	79	29	71
365	10	90	23	77
385	8	92	15	85
400	5	95	12	88
425	4	96	8	92
450	2	98	4	96

vibrational spectra, it was unequivocally established that compounds of the aromatic series (in particular, xylenes) are absent in this mixture, while the Raman spectra of the mixture are also devoid of the lines and bands that are characteristic for methylenecyclopentanes. At the same time, a set of the characteristic vibrations of the  $\nu_{\text{C}=\text{C}}$  in a cyclopentene ring ( $1630\text{ cm}^{-1}$  for the monosubstituted, and  $1648\text{ cm}^{-1}$  for the disubstituted) is present in the vibrational spectra of the mixture. The ratio of the intensities of the mentioned lines in the IR and Raman spectra shows that the mixture contains comparatively small amounts of the isomers with two and one methyl groups attached to the double bond (the latter predominate), while the isomers with an unsubstituted double bond are practically absent.

As a result, in the presence of  $\text{Al}_2\text{O}_3$  the irreversible conversion of cyclopentadienes to cyclopentenes occurs at  $300\text{--}500^\circ$ . The rate of the given conversion increases sub-

stantially with increase in the number of methyl groups. It is characteristic that aromatic compounds were not detected in the reaction products in all of the investigated cases. From this, it is possible to assume that under the experimental conditions the redistribution of hydrogen occurs between the cyclopentadiene molecule and the high-molecular condensation products.

The data discussed in the present communication makes it possible to state that the migration of the alkyl groups in the 5,5-disubstituted and thermodynamically stable cyclopentadienes is catalyzed by  $\text{Al}_2\text{O}_3$ .

#### EXPERIMENTAL METHOD

The experiments on the catalytic isomerization were run by passing the cyclopentadienes through a  $200 \times 10\text{ mm}$  quartz tube (heated section), which was filled with  $\text{Al}_2\text{O}_3$  granules (2-3 mm in size). The air was displaced from the system in advance with nitrogen, while the vapors were condensed in a trap cooled to  $-70^\circ$ . We began to take samples not sooner than 15 min after the start of passage.

Analysis of the mixture by UV spectroscopy was based on determining the extinction coefficient at 240 nm for (I), and at 247 nm for (II) + (III) (in heptane). In the calculations we took  $\epsilon(240) = 3260$  for (I), and  $\epsilon(247) = 3320$  for (II) + (III) (average of three parallel determinations). The GLC analysis was run on a "Khrom-2" chromatograph at  $50^\circ$  and a nitrogen flow rate of 120 ml/min. We used a  $4 \times 6000\text{ mm}$  column that was filled with triethylene glycol butyrate (5%) deposited on Chromosorb G (30-60 mesh). The chromatograms of the products of the catalytic transformations of dienes (III), (V), and (VI) were obtained under the previously described [3] conditions.

The IR spectra were obtained on a UR-10 spectrometer, the Raman spectra were obtained on an ISP-51 spectrograph by the photographic method, and the UV spectra were obtained on an SF-4A spectrophotometer.

Transformation of Cyclopentadiene (I) in the Presence of  $\text{Al}_2\text{O}_3$ . a) At a given temperature ( $\pm 2^\circ$ ), 0.5 ml of (I) was added to the contact tube in 5 min. The mixtures of the reaction products were analyzed by GLC and UV spectroscopy; the results of the measurements are given in Table 1.

b) Under the indicated conditions, 10 g of cyclopentadiene (I) was passed through the contact tube in 110 min at  $500^\circ$ . The condensate was treated at  $0\text{--}10^\circ$  with 6 g of maleic anhydride. As the result of molecular distillation ( $0\text{--}3^\circ$ , 25 mm) we isolated 5.65 g (55%) of (VII), bp  $43.5^\circ$  (753 mm),  $n_D^{20}$  1.4312, the constants and IR spectrum of which were identical with the values characteristic for the authentic standard.\*

Transformation of Equilibrium Mixture of Methylcyclopentadienes in Presence of  $\text{Al}_2\text{O}_3$ . a) Samples of the mixed dienes (II) + (III) [6] (0.5 ml) were passed through the contact tube under the above described conditions. The degree of conversion of dienes (II) + (III) to a mixture of methylcyclopentenes (VIII), (IX), and (X) as a function of temperature is given in Table 2.

\*The standard for comparison was obtained in 72% yield by the dehydration of commercial cyclopentanol (cp) with phthalic anhydride under the conditions described in [11].

b) Under the same conditions, 6 g of the equilibrium mixture of methylcyclopentadienes was passed through the contact tube in 65 min at 480°. The condensate was treated with 2 g of maleic anhydride at 0-10°. Molecular distillation of the reaction mixture (0-3°, 15 mm) gave 4.7 g (78%) of mixed methylcyclopentenes, bp 74-74.5° (742 mm),  $n_D^{20}$  1.4295, a maximum is absent in the UV spectrum. Based on the GLC data, the mixture contained 85% of 1-methylcyclopentene (VIII), and 15% of the 3- (IX) and 4-methylcyclopentenes (X). The principal component was identified by comparison of the Raman spectra of the mixture and authentic methylcyclopentene (VIII).\* The presence of a band at 1613  $\text{cm}^{-1}$  in the Raman spectrum corroborates the presence of (IX) and (X) in the mixture. Based on the matching data of GLC, and IR, Raman and UV spectroscopy, the discussed mixture is not contaminated with benzene.

Transformation of 1,5,5- (IV), 1,2,3- (V) and 1,2,4-Trimethylcyclopentadiene (VI) in Presence of  $\text{Al}_2\text{O}_3$ .

a) Under the above described conditions, 0.5 ml samples of diene (IV) [6], (V) [3] or (VI) [3] were passed through the contact tube. The GLC analysis results for the mixtures of reaction products are summarized in Tables 3 and 4.

b) Diene (IV) (5 g) was passed through the contact tube in 50 min at 400°. Molecular distillation of the condensate (10-15°, 3 mm) gave 4.4 g (88%) of mixed trimethylcyclopentenes, bp 137-141° (751 mm);  $n_D^{20}$  1.4357. The mixture fails to show an absorption maximum in the UV spectrum. Raman spectrum ( $\Delta\nu$ ,  $\text{cm}^{-1}$ ): 1359 (5), 1451 (10br), 1629 (1), 1649 (2), 1683 (2). Infrared spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 1611 (sh), 1629 (m), 1647 (m), and 3033 (br. m).

c) Diene (V) (7 g) was passed through the contact tube in 70 min at 450°. Distillation of the condensate gave 6.01 g (86%) of mixed hydrocarbons, the constants (bp 137.5-141° (758 mm),  $n_D^{20}$  1.4356), chromatogram, and spectral characteristics of which agreed well with the above given data for the mixture of hydrocarbons that was obtained under the same conditions from diene (IV).

d) Under the same conditions, from 5 g of diene (VI) at 450° was obtained 4.21 g (84%) of a mixture of trimethylcyclopentenes, bp 137-141° (748 mm),  $n_D^{20}$  1.4357, which was identical with the above described samples.

## CONCLUSIONS

1. On the examples of cyclopentadiene, an equilibrium mixture of the 1- and 2-methylcyclopentadienes, and also the 1,5,5-, 1,2,3-, and 1,2,4-trimethylcyclopentadienes, it was shown that when passed over  $\text{Al}_2\text{O}_3$  at 300-500° the substituted cyclopentadienes undergo irreversible conversion to the corresponding cyclopentenes. The reaction is not accompanied by the formation of aromatic compounds.

2. The transformation of each of the trimethylcyclopentadienes in the presence of  $\text{Al}_2\text{O}_3$  leads to an identical mixture of trimethylcyclopentenes.

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\*Hydrocarbon (VIII) was obtained from 1-methyl-1-cyclopentanol under the conditions used to synthesize (VII), bp 76-76.5° (764 mm);  $n_D^{20}$  1.4298.