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SOME GENERAL CHARACTERISTIC PROPERTIES OF SUBSTITUTED CYCLOPENTADIENES[1]

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Abstract—A number of substituted cyclopentadienes display characteristic properties which are representate of all members in the series: (a) the endocyclic double bond isomers are in thermodynamic equilibrium; the process of establishing the equilibrium being retarded; (b) the transformation of isomeric cyclopentadienes proceeds by steps, i.e. a proton from the methylene group (5th position) passes mainly to the adjacent C-atom (1st position). The proton-cyclopentadienyl anions are probably transitional states in the transformation of isomers. It is assumed that this transformation is a first order reaction. As a result of this investigation it has been shown that the structure of the substituted cyclopentadiene (or the composition of the isomer mixtures) depends mainly on the character of the substituent and not on the method of synthesis.[2]

A NUMBER of anomalies observed during the syntheses of substituted cyclopentadienes have been reported. Thus decarboxylation of 2,4-diphenylcyclopentadiene-1-carboxylic acid gives 1,4-diphenylcyclopentadiene instead of the expected 1,3-compound.[3] On reduction of 2,3,4 trimethylcyclopent-2-en-1-one with lithium aluminum hydride 1,2,3-trimethylcyclopentadiene is isolated instead of the 1,2,5-compound.[4] Finally, the interaction of cyclopent-2-en-1-one and phenylmagnesium bromide leads to 1-phenyl- instead of 2-phenylcyclopentadiene.[5] All these facts have been explained by irreversible isomerization of one of the isomers into that form energetically more favourable. No general character has been ascribed to this phenomenon and its cause has not been elucidated.

Earlier we described[6] seven methods for dimethylcyclopentadiene formation, which, if considered from the formal point of view, should lead to 1,4-(I)- or 2,5-(II)-dimethylcyclopentadienes, but, in every case only 1,3-dimethylcyclopentadiene (III) or a mixture with 3-methylene-5-methylcyclopentene is obtained; the structures of the products were definitely established.[6a] Thus, the formation of a substituted cyclopentadiene in which the double bonds are arranged differently from the expected pattern is well known.

The main purpose of the present investigation is to elucidate the cause of this phenomenon. It is assumed that the thermodynamic equilibrium between the

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* The Laboratory of Chemistry of Corticoid Compounds.

[1] The present article is the 13th report in series *Substituted Cyclopentadienes and Related Compounds*.

[2] If a temperature above 50–60° is employed during synthesis.

[3] N. L. Drake and J. R. Adams, *J. Amer. Chem. Soc.* **61**, 1326 (1939).

[4] K. Alder and R. Muders, *Chem. Ber.* **91**, 1083 (1958).

[5] R. Riemschneider and R. Nerin, *Monatsh.* **91**, 829 (1960).

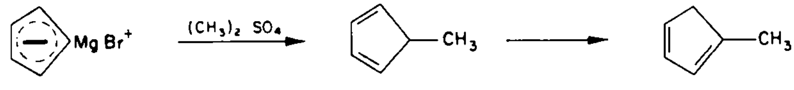
[6a] V. A. Mironov, M. V. Mavrov and A. N. Elizarova, *Zhur. Obshch. Khim.* **32**, 2723 (1962).

[6b] V. A. Mironov and A. N. Elizarova, *ibid*, **32**, 2731 (1962).

endocyclic double bond isomers is characteristic of substituted cyclopentadienes.[7] The validity of this assumption is demonstrated by the following examples:

Methylcyclopentadiene. It is well known that methylcyclopentadiene prepared by depolymerization of its dimer is a mixture of approximately equal amounts of 1-(IV)- and 2-(V)-methylcyclopentadienes.[11] The separation of the methylcyclopentadienes[11a] by gas chromatography,[12] as well as by their adducts with N-phenylmaleimide,[11b] has been described. The syntheses of homogeneous methylcyclopentadienes with structure (IV)[13] or (V)[14] have been described, but, the Raman spectra given for these compounds show that both are mixtures of dienes (IV) and (V) in an equal proportion (~1 : 1).

The methylation of cyclopentadienylmagnesium bromide usually leads to a mixture of 1- and 2-substituted cyclopentadienes[15,16] but under mild conditions the 1-isomer is predominantly formed.[16,17] The formation of mixtures of 1- and 2-substituted products is not attributed to isomerization of the isomer originally formed. Examination of the reaction scheme shows that substitution (for example, by a methyl group) at any of the C-atoms of the anion (VI) should lead to a 5-substituted cyclopentadiene. It may therefore be assumed that this diene is the initial product of the reaction.



VI VII IV

In fact, alkylation of cyclopentadienylmagnesium bromide with dimethylsulfate in di-n-butyl ether at −10 to −15° and separation of the reaction products at the same temperature yields a ~30 per cent solution of 5-methylcyclopentadiene (VII) in di-n-butyl ether and methyl bromide (as the by-product). The product contains negligible amounts of isomeric dienes and is practically free from the starting cyclopentadiene. Diene VII in the 30 per cent solution on storage at 25–30° undergoes a rapid change into diene (IV). Under these conditions this transformation is practically complete in 3 hours and less than 5 per cent of diene V is produced.

Further transformations proceed more slowly. If a sample of diene IV (85–90% purity, main impurity—methyl bromide) is stored at 25–26° for 2 days gradual isomerization into diene V takes place. Distillation of dienes IV or VII at atmospheric pressure also leads to the formation of a mixture of dienes (IV and V). In the gaseous phase at 25–28° the transformation of methylcyclopentadienes (VII) → (IV) → (IV) +

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[7] Such an assumption was made earlier by Peters[8] and Neureiter;[9] however this assumption has not been demonstrated and the generality of this phenomenon has not been recognized. In subsequent reports[10] Peters no longer used thermodinamic equilibrium an explanation for these anomalies observed by him in a series of substituted cyclopentadienes.

[8] D. Peters, *J. Chem. Soc.* 1761 (1959).

[9] N. P. Neureiter, *J. Org. Chem.* **24**, 2044 (1959).

[10] D. Peters, *J. Chem. Soc.* 1832 (1960); 1037, 1042 (1961).

[11a] S. M. Csicsery, *J. Org. Chem.* **25**, 518 (1960);

[11b] W. J. Craven, *Diss. Abstr.* **15**, 2408 (1955).

[12] By this method ~3% diene (VII) was also discovered in the mixture.

[13] T. I. Narychkina and N. I. Choukin, *Zhur. Obschei Khim.* **30**, 3205 (1960).

[14] N. I. Choukin, T. I. Narychkina and Y. P. Egorov, *Bull. Soc. chim. Fr.* 406 (1957).

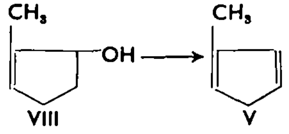
[15] K. Alder and H. Holzricher, *Liebigs Ann.* **524**, 145 (1936).

[16] R. Riemschneinder, A. Reisch and H. Horak, *Monatsch.* **91**, 805 (1960).

[17] R. Riemschneider, E. Reichelt and E. B. Grabitz, *Monatsch.* **91**, 812 (1960).

(V) takes place at a somewhat slower rate. In all these cases an identical mixture of about equal amounts of dienes IV and V, containing traces of diene VII, is formed.

The preparation of 2-methylcyclopentadiene (V; containing no more than 5 per cent of isomer IV) may be achieved by dehydration of 2-methylcyclopent-2-en-1-ol (VIII) at 25–30° in the presence of catalytic amounts of *p*-toluenesulfonic acid, provided the products are continuously removed from the reaction by distillation. Further distillation of diene V at atmospheric pressure again yields a mixture of dienes IV and V as the above.



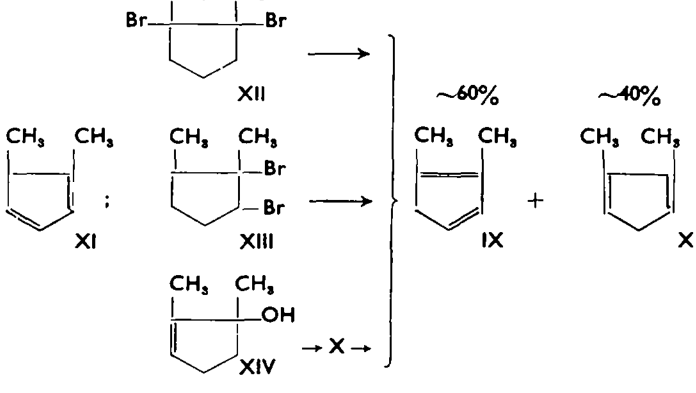
The ease with which isomeric methylcyclopentadienes undergo transformation and their tendency to form mixtures of constant composition, which subsequently does not change, can be explained only by the existence of a thermodynamic equilibrium between these isomers. This equilibrium is not readily established since it is possible to separate and preserve, at relatively low temperatures, the methylcyclopentadienes homogeneous in isomeric composition (non-equilibrated samples). These results explain the anomalies formerly observed by many authors during alkylation of metallo-organic derivatives of cyclopentadiene: 5-substituted cyclopentadienes are the initial products of the reaction; and during the establishment of equilibrium they change first into 1-isomers and then into a mixture of 1- and 2-isomers.

The formation of practically pure diene IV as an intermediate during the transformation of diene VII into an equilibrium mixture of methylcyclopentadienes shows that the isomeric dienes are transformed into each other by stages, and may be outlined as follow:

$$\mathrm{VII} \rightleftarrows \mathrm{IV} \rightleftarrows \mathrm{V}$$

The separation of a practically pure diene IV during an intermediate stage of transformation is apparently possible because of the much higher potential barrier of transition from IV to V than from VII to IV.

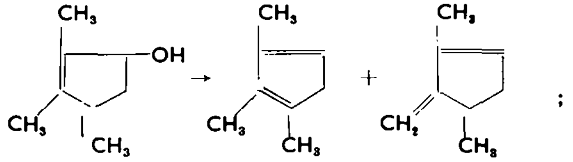
1,2-*Dimethylcyclopentadiene.* Dimethylcyclopentadiene (1,2-substituted) exists as three endocyclic double bond isomers: 1,2-(IX)-, 2,3-(X)- and 1,5-(XI)-dimethylcyclopentadienes. A mixture of these hydrocarbons (not described in literature) may be synthesized by three routes outlined in the following scheme:



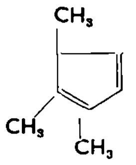
The dehydrobromation of both 1,2-dibromo-1,2-dimethylcyclopentane (XII) and 1,2-dibromo-2,3-dimethylcyclopentane (XIII) yields the same ratio of isomeric dimethylcyclopentadienes (IX:X $\simeq$ 3.2).[18]

Dehydration of 1,2-dimethylcyclopent-2-en-1-ol (XIV) under mild conditions (similar to those described for the alcohol, VIII) yields at least 90 per cent pure diene (X). Distillation of this sample in a column at a temperature of about 60° gives an 80 per cent yield of a mixture of isomers (IX and X) in the same proportion i.e. 3:2. Further storage or heating of this mixture does not lead to any change in its composition. From this evidence it is apparent that double bond isomeric 1,2-dimethylcyclopentadienes, like the methylcyclopentadienes, are in thermodynamic equilibrium.

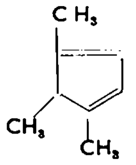
1,2,3-*Trimethylcyclopentadiene.* Depending on the position of the endocyclic double bonds, there are three isomeric forms, i.e. 1,2,3-(XV)-, 1,2,5-(XVI)- and 1,4,5-(XVII)-trimethylcyclopentadienes. Trimethylcyclopentadiene was first produced[4] by dehydration of 2,3,4-trimethylcyclopent-2-en-1-ol (XVIII); the product being described as a homogeneous hydrocarbon (XV). Actually, it has been shown that the product prepared by dehydration of the alcohol (XVIII) in a neutral acid, and alkaline media is a mixture of the diene (XV) and 3-methylene-2,4-dimethylcyclopentene (XIX) in a ~7:3 ratio. The components of this mixture were separated by distillation in a column. The trimethylcyclopentadiene obtained is the isomer XV with traces of dienes XVI and XVII. As this is the equilibrium state it was displaced towards the component with greater volatility by its continuous removal from the system by distillation in a column. Conditions were found under which the distillate is a mixture of dienes XVI and XVII with only negligible amounts of the diene XV which is predominant in the initial mixture. The diene composition of the distillation residue was a mixture with the components in unchanged proportion. It was not possible to shift the equilibrium further, i.e., to obtain pure diene XVI or XVII because of the closeness of the boiling points of these isomers; but under the experimental conditions observed, these two dienes considerably differ from the boiling point of diene XV by about 10°.



XVIII XV XIX



XVI



XVII

If the mixture of the dienes XVI and XVII is heated for 3 hours at 85° the original equilibrium mixture is formed. This confirms that the equilibrium discussed is also

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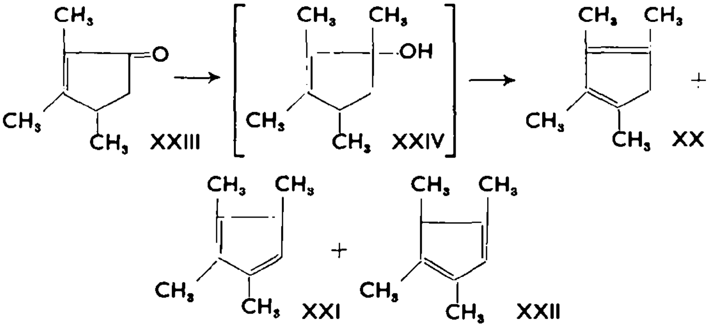
[18] The mixture may contain small amounts of diene XI. For details see ref. 19.

[19] V. A. Mironov, S. N. Kostina and A. N. Elizarova, *Izv. Akad. Nauk, SSSR, Otdel Khim. Nauk* Paper XII, of this series (1963, in press).

valid in this case. The sequence of the isomeric transformations before equilibrium is established was studied by means of vibrational spectra and shows that isomerization proceeds by steps.

Tetramethylcyclopentadiene. Theoretically tetramethylcyclopentadiene can exist in one of the three isomeric forms: 1,2,3,4-(XX)-, 1,2,3,5-(XXI)- and 1,2,4,5-(XXII)-tetramethylcyclopentadienes. Tetramethylcyclopentadiene was synthesized for the first time according to the following scheme:

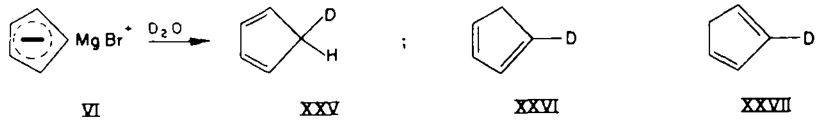


The alcohol (XXIV) appears to be unstable; according to spectral data the product is a mixture consisting of ~10% (XXII), ~20% (XXI) and ~70% (XX).

Distillation of this mixture in a column (~100 t.p. and under suitable conditions) results in an 80 per cent yield of 1,2,4,5-tetramethylcyclopentadiene (XXII) with less than 5 per cent of diene XX, which predominated in the starting mixture. In this case the relatively high concentration of diene XXII in the equilibrium mixture (~10%) and the considerable difference between the boiling point of this diene and that of the two other isomers is conducive to a smooth displacement of the equilibrium. The diene fraction of the distillation residue was a mixture of dienes XX, XXI and XXII in unchanged proportion when compared with the original mixture.

If the distillate is heated for about ~3 hours at 60° or for ~30 minutes at 100° the original mixture of dienes XX, XXI and XXII results. Further storage or heating of the mixture fails to alter the concentration of its components. At the same time storage of a sample of diene XXII for several days at room temperature shows no visible change in its composition. Thus, thermodynamic equilibrium is also characteristic of isomeric tetramethylcyclopentadienes.

Monodeuterocyclopentadiene. Monodeuterocyclopentadiene was prepared by treatment of cyclopentadienylmagnesium bromide with deuterium oxide at −15 to −10°. 5-Deuterocyclopentadiene (XXV) is the initial product of the reaction (according to the scheme) and contains practically no admixture of isomeric 1-(XXV)- and 2-(XXVII)-monodeuterocyclopentadienes or the starting cyclopentadiene.



Heating of the diene XXV for 1 hour at 60° leads to the formation of a mixture of 5-(XXV)-, 1-(XXVI)- and 2-(XXVII)-deuterocyclopentadienes in the proportion of ~1:1:1. The composition of the mixture produced is in good agreement with that expected for an equilibrium mixture of isomers XXV, XXVI and XXVII (see below). It must be emphasized that the process of establishing equilibrium concentrations of monodeuterocyclopentadienes from diene XXV does not involve formation of noticeable amounts of cyclopentadiene containing no deuterium and polydeuterocyclopentadienes. This shows beyond doubt that the "redistribution" of the deuterium in the molecule is not a result of hydrogen exchange but may be explained by migration of endocyclic double bonds. At the same time, in the transitional state the deuteron and obviously the proton do not lose their connection with the parent molecule.

A study of the sequence of isomeric transformations during the establishment of equilibrium shows that this may be represented by the following scheme:

$$\text{XXV} \rightleftarrows \text{XXVI} \rightleftarrows \text{XXVII}.$$

The rate of establishing the equilibrium depends in large measure on the substituent; however, in the cases investigated it is faster than the diene synthesis with a low-activity dienophil (dimerization of methylcyclopentadienes in solution,[20] formation of adducts of tetramethylcyclopentadienes with vinyl acetate[21]).

In contrast, the rate of the diene synthesis with an active dienophil (maleic anhydride) is much faster in all the cases investigated than the rate of equilibrium transformations. It is, therefore, possible to obtain adducts with maleic anhydride, corresponding in structure with the initial diene. For example, from the three non-equilibrium samples of methylcyclopentadienes (IV, V and VII) three crystalline adducts were synthesized (the structure was proved for the starting dienes as well as for their adducts). As the structure of the adducts of substituted cyclopentadienes with maleic anhydride confirms the structure of the initial diene; the ratio of the adducts produced confirms the quantitative composition of the mixtures of substituted cyclopentadienes.

Maleic anhydride adducts were obtained for the most of the dienes described in this paper. These adducts were saponified into their dicarboxylic or lactonic acids which were converted into corresponding di- and monomethyl ethers respectively.

The structure of the substituted cyclopentadienes and the composition of their mixtures was established by examining their electronic and vibrational spectra and the vibrational and N.M.R. spectra of individual adducts of the dienes with maleic anhydride.

The determination of the diene structures requires firstly, establishment of the configuration of the system of double bonds (*cis* or *trans*), and, secondly, establishment of the arrangement of the substituents in each isomer.

A hypsochromic shift of 15–20 mμ in the absorption maximum and about a 10,000 increase in the extinction coefficient were observed in the U.V.-spectra of dienes with fixed *trans*-configuration of the double bonds as compared with those of *cis*-cyclopentadienes.

A similar differentiation is possible by a study of the vibrational spectra. The intensities of depolarization ratios of the double bond lines in Raman spectra of the dienes with a *trans*-configuration are much higher than those of the dienes with two

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[20] V. A. Mironov, E. V. Sobolev and A. N. Elizarova, *Izv. Akad. Nauk, SSSR, Otd. Khim. Nauk*, 1607 (1963).

[21] A. N. Elizariva, V. A. Mironov and T. M. Fadeeva, *Zh. Obshch. Khim.* paper VII of this series (1963, in press).

endocyclic double bonds.[22] The I.R.-spectra of the dienes with an exocyclic double bond show characteristic frequencies of the terminal methylene group (for example, 3075, 1632 and 858 cm^{-1} in the spectrum of diene XIX).

As definite regularities in the behaviour of the frequencies ν(C=C) exist in either of the systems, depending on the type of substitution for the double bond, it is possible to solve the second problem. For example, *trans*-dienes with unsubstituted, mono- and disubstituted endocyclic double bonds are distinguished by a combination of two frequencies: in-phase (ν_s[C=C]) and out-of-phase (ν_{as}[C=C]) stretching modes (~1635 and 1575, ~1630 and 1620, ~1625 and 1655 cm^{-1} respectively).

Together with this increase in the degree of substitution of the endocyclic double bond a certain bathochromic shift of the absorption maximum in the U.V.-spectrum is observed.

The bands in the vibrational spectra of the dienes with two endocyclic double bonds are ascribed to certain isomers by a comparison with the spectra of other diene systems and five-membered unsaturated heterocycles of known structure and in particular the region of double bond frequencies was utilized.

Substitution of conjugated double bonds is associated with a tendency towards an increase of double bond stretching frequencies, the degree varying with the character of the substituent.

The values obtained of the in-phase (ν_s) and out-of-phase (ν_{as}) C=C frequencies are given in Table 1.

Substitution in position 5 only slightly affects the ν_s frequency. A single substituent in positions 1 and 2 causes a ν_s increase in 27 cm^{-1} as compared with cyclopentadiene. In their turn the 1- and 2-substituted cyclopentadienes differ in the ratio of the ν_s and ν_{as} band intensities in the I.R. and Raman-spectra; substitution in position 1 (diene IV) causes an increased intensity of the ν_s in the I.R.-spectrum and of the ν_{as} in Raman-spectrum as compared with the cyclopentadiene, i.e., a disturbed alternativity of Raman and I.R.-spectra; for diene V this alternativity is much more strictly retained.

Substitution at two double bonds leads to a considerable increase the ν_s frequency, whereas di-substitution of one double bond affects the value of this frequency far less (compared with the monosubstituted cyclopentadienes).

In order to demonstrate the structure of isomeric cyclopentadienes, the region of =C—H(=C—D) stretching vibrations and, in a number of cases, C=C and —C—H(—C—D) stretching frequencies of the dimers were investigated.

The details of the diene structures are given in a special report for each individual case, e.g. methyl-,[24] 1,2-dimethyl-,[19] 1.3-dimethyl-,[6a] 1,2,3-trimethyl-,[25] tetramethyl-,[26] monodeutero-[27] cyclopentadienes. The spectral aspect of the work will be published in greater detail in a special report.

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[22] Reference is made to in-phase stretching modes (ν_s) manifested in Raman spectra with greater intensity than the out-of-phase ones (ν_{as}).

[23] Predicted values.

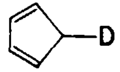
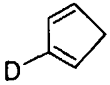
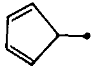
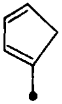
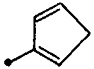
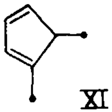
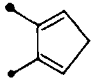
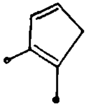
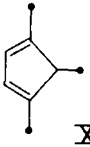
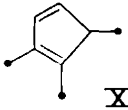
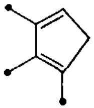
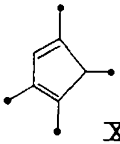
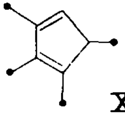
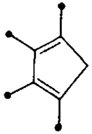
[24] V. A. Mironov, E. V. Sobolev and A. N. Elizarova, *Dokl. Akad. Nauk, SSSR*, **146**, 1098 (1962).

[25] V. A. Mironov, S. N. Kostina, E. V. Sobolev and A. N. Elizarova, *Izv. Akad. Nauk, SSSR, Otdel. Khim. Nauk* paper XI of this series (1963, in press).

[26] V. A. Mironov, T. M. Fadeeva, E. V. Sobolev and A. N. Elizarova, *Zh. Obshch. Khim.* **33**, 83 (1963).

[27] V. A. Mironov, E. V. Sobolev and A. N. Elizarova, *Dokl. Akad. Nauk, SSSR* **143**, 1112 (1962).

Table 1. Double bonds frequencies of substituted cyclopentadienes

Diene	$\nu_s(C{=}C)$	$\nu_{as}(C{=}C)$	Diene	$\nu_s(C{=}C)$	$\nu_{as}(C{=}C)$	Diene	$\nu_s(C{=}C)$	$\nu_{as}(C{=}C)$
	1500	1624						
 XXV	1498	1614	 XXVI	1485	~1600— —1615	 XXVII	1485	~1600— —1615
 VII	1507	1630	 IV	1529	1609	 V	1526	1619
 XI	~1530[23]	~1630[23]	 X	1562	1629	 IX	1533	1634
 XVII	1575	1625	 XVI	1542	1639	 XV	1583	1648
 XXII	1586	1648	 XXI	1595	1650	 XX	1613	1658

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[23] See foot of page 1945

The structures of the maleic anhydride adducts of substituted cyclopentadienes were in most cases, determined by the degree of substitution of the double bond in the bicyclo-(2,2,1)-heptane ring. Unsubstituted, mono- and disubstituted double bonds differ sharply in their frequencies ν(C=C) in Raman spectrum, being ν 1575, 1630 and 1660 cm^{-1} respectively. Only the monosubstituted double bond (1630 cm^{-1}) is manifested by a sufficiently intense band in the I.R.-spectra. The degree of substitution of the double bond in the ring can also be judged by the =C—H stretching frequencies region (I.R.: 3000–3080 cm^{-1}).

The structures of the adducts were confirmed by the N.M.R. spectra which also made it possible to record the presence of the substituent in the position 7 of bicyclo-(2,2,1)-heptane skeleton (doublet in the region of $\tau \sim 9{\cdot}2$ p.p.m.).

The application of these criteria made it possible to establish unambiguously the structure of the adduct in each case.

DISCUSSION

The experimental data is convincing evidence that thermodynamic equilibrium between endocyclic double bond isomers is characteristic of substituted cyclopentadienes. The process of establishing the equilibrium is retarded. This makes it possible to deal, within certain temperature limits, with mixtures of substituted cyclopentadienes (or relatively homogeneous dienes) which have not yet assumed an equilibrium state or have been artificially driven out of this state. But heating samples to a definite (relatively low) temperature for even a short time leads to the establishment of the aforesaid equilibrium.

As the example of monodeuterocyclopentadiene shows, the presence of the equilibrium under consideration does not depend on the character of substituent, i.e., the thermodynamic equilibrium between the isomers in their endocyclic double bonds is a general characteristic for the series of substituted cyclopentadienes.[28]

It is considered that the proton cyclopentadienyl anion, formed as a result of a heterolytic break of the C—H bond in the methylene group (position 5), is a possible transitional state during transformation of the isomers. The ease with which the interconversion of isomers takes place, in other words, the relatively low potential barriers of such transformations, attests to the aromatic stabilization in the transitional state. At the same time the potential barriers of the mutual transitions of isomers vary within rather wide limits, depending on the substituent.

For the methyl-, trimethyl- and monodeutercyclopentadienes a step character of isomer interconversion was observed, i.e. migration of the proton from position 5 preferably to the adjacent C-atom (into position 1). The different probability of proton migration from position 5 to positions 1 and 2 may be explained by the following factors.[30]

1. Distortion of the symmetrical configuration of the electron cloud of the anion under the influence of the substituents. In this case the transitional states existing

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[28] It may be anticipated, that the 5,5-disubstituted cyclopentadienes (involving the spiro-structures) will undergo isomerization (but at higher temperature) with a migration of one of the substituents from 5-position to 1-position, as a result of the structures containing a proton in position 5 (see for example[4,29]).

[29] B. F. Hallam, P. L. Pauson, *J. Chem. Soc.* 646 (1958).

[30] Migration of one double bond in the manner of allyl rearrangement is excluded because in this case diene (V) rather than diene (IV) would initially form from diene (VII).

TABLE 2. COMPOSITION OF EQUILIBRIUM MIXTURES OF SUBSTITUTED CYCLOPENTADIENES[32]

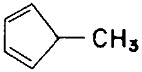
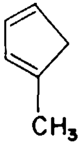
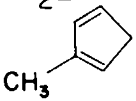
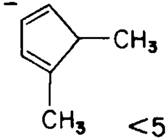
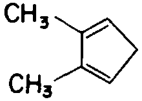
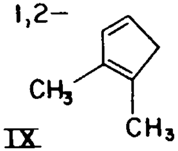
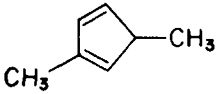
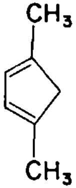
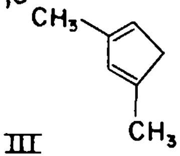
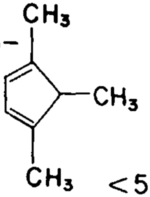
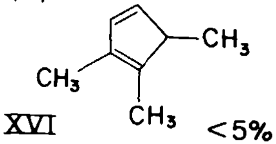
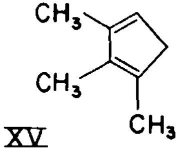
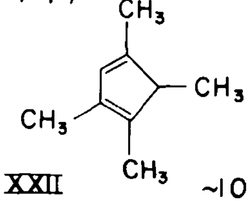
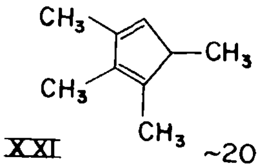
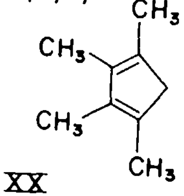
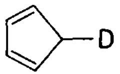
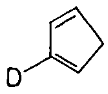
Methylcyclopentadiene	5-  VII <5%	1-  IV ~50%	2-  V ~50%
1,2-Dimethylcyclopentadiene	1,5-  XI <5%	2,3-  X ~40%	1,2-  IX ~60%
1,3-Dimethylcyclopentadiene	2,5-  II <5%	1,4-  I <5%	1,3-  III >90%

TABLE 2 (*cont'd*)

1,2,3-Trimethyl-cyclopentadiene	1,4,5-  XVII <5%	1,2,5-  XVI <5%	1,2,3-  XV >90%
1,2,3,4-Tetramethyl-cyclopentadiene	1,2,4,5-  XXII ~10%	1,2,3,5-  XXI ~20%	1,2,3,4-  XX ~70%
Monodeuterocyclo-pentadiene	5-  XXV ~33%	1-  XXVI ~33%	2-  XXVII ~33%

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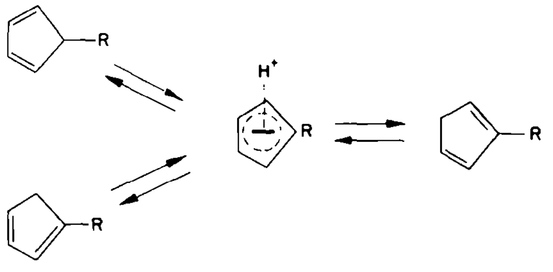
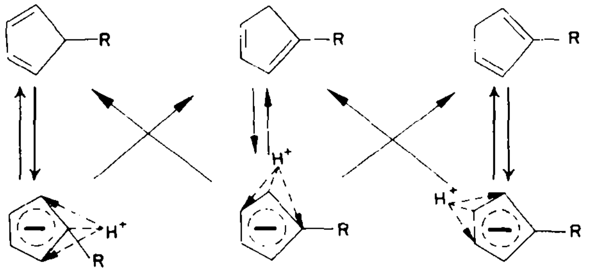
[32] The figures in the upper part of the graphs show the position of the substituents, in the lower part—the isomer content in the mixture.

during the diene transformations are assumed to be identical and have a relatively longer life.



2. Different ways of migration of the proton from position 5 to positions 1 and 2 with a relatively short life of the transitional states. In this case the transitional states during transformation of isomers into each other will differ in the position of the proton and, consequently, the polarization of the electron cloud of the anion in the field of this proton.



The investigation of the monodeuterocyclopentadiene allows to exclude affect substituent on the symmetrical configuration of the electron cloud of the anion in the transitional state. The presence of steps in the mutual transformation of isomeric monodeuterocyclopentadienes indicates that the second of the above mentioned mechanisms is correct. The fact that the isomeric transformations take place independently of the substituent present shows that the step character of equilibrium transformations must be a general characteristic of all substituted cyclopentadienes.

The transformation of isomeric cyclopentadienes into each other is apparently a first order reaction and is substantiated by the following:

(1) The absence of hydrogen exchange during the establishment of equilibrium;

(2) decrease in the concentration of the initial substance by half within equal periods of time (during the whole process of establishing of equilibrium);[31]

(3) comparable rate of transformations during the liquid and gaseous phases.

The concentration of isomeric dienes in equilibrium mixtures primarily depends on the character of the substituent. For the cases investigated the compositions of the equilibrium mixtures are shown in Table 2.

The concentration of components in equilibrium mixtures is determined by thermodynamic factors and two extreme compositions of equilibrium mixtures are possible.

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[31] For substance practically absent in the equilibrium mixture, i.e., in the case in which transformation can be approximately considered as an irreversible reaction (for example, |VII| → |IV|).

1. In cases in which the difference in the thermodynamic stability of the isomers can be ignored their concentrations in the mixture prove practically equal; as was observed for isomeric monodeuterocyclopentadienes (XXV : XXVI : XXVII $\simeq$ 1 : 1 : 1).
2. The concentration of one of the components in the equilibrium mixture may approximate to 100 per cent (for example, dienes III and XV).

In most cases the composition of the equilibrium mixture is intermediate between these two extreme states.

Examination of Table 2 reveals that from an energy point of view the isomers containing the methyl group in position 5 are considerably less favourable than the isomers containing a free methylene group. At the same time the isomers substituted in positions 1- and 2- are found, as a rule, in equilibrium mixtures in equal concentrations.

The existence of a thermodynamic equilibrium between endocyclic double bond isomers of cyclopentadienes warrants the conclusion that the structure of the substituted cyclopentadiene (or the composition of the mixture of isomers) does not depend on the method of synthesis, if the method of production or isolation of the substance requires a temperature exceeding 50–60°.

The data on the composition of equilibrium mixtures of methyl-substituted cyclopentadienes, contained in this work, make it possible to predict the isomeric composition of mixtures not yet synthesized and to reconsider critically the data given in the literature for cyclopentadienes containing alkyl groups and substituents closely related in electronic character.

With rare exceptions, the structure of substituted cyclopentadienes has not been proved; an arrangement of endo-cyclic double bonds, based on a formal examination of the reaction scheme, was usually accepted to be the case. A few instances are quoted.

Cyclopentadienes labelled C^{14} in position 2 have been described;[33] in these samples the double bonds can apparently be in any position, i.e., C^{14} will be in position 2, as well as positions 1 and 5.

As was shown by Riemschneider *et al.* (for example[34]) alkylcyclopentadienes (up to C_4) are mixtures of 1- and 2-isomers. It is to be expected that this composition of equilibrium mixtures should be retained for all substituents closely related to alkyls in electronic character. Thus, the samples of 1- and 2-alkylcyclopentadienes described as pure compounds (for example[13,14]) are undoubtedly equilibrium mixtures containing different impurities (for example, dienes with a fixed *trans*-system of double bonds). Analogously, the formerly described[35] 5-cyclopentyl- and 5-cyclohexyl cyclopentadienes (λ_{max} 247 mμ) are apparently mixtures of 1- and 2-isomers. The same may also apply to β-glucopyranosylcyclopentadiene[36] and a number of other cyclopentadiene derivatives. The substances described in the literature as 1-ethyl-3-methyl-[37] and 1-methyl-3-ethylcyclopentadienes[38] must constitute a similar mixture of these two isomers. The cyclopentadienes with two different substituents[39] in positions 1 and 2,

[33] G. T. Brooks, *Chem. & Ind.*, 194 (1958); G. Pajaro, L. Baldi, *Ann. di Chim.* **49**, 1830 (1959).

[34] R. Riemschneider and E. B. Grabitz, *Monatsch* **91**, 23 (1960).

[35] W. Kirnise, L. Korner and H. Hoffman, *Liebigs Ann.* **614**, 19 (1958).

[36] A. N. de Belder, E. I. Bourne and J. B. Pridham, *Chem. & Ind.*, **14**, 432 (1961).

[37] D. A. H. Taylor, *J. Chem. Soc.* 4779 (1958).

[38] P. Duden and R. Freyday, *Ber. Dtsch. Chem. Bes.* **36**, 944 (1903).

[39] P. K. Dutta, *Sci. and Cult.* **15**, 237 (1949); *J. Indian Chem. Soc.* **26**, 545 (1949).

described as homogeneous, must be mixtures of at least 3 and possibly 5 isomers.

It is well known that cyclopentadienes substituted by such groups as phenyl,[5] carboxyl[40] and carboxymethyl[8] are practically homogeneous 1-isomers. These isomers apparently sharply predominate in equilibrium mixtures because of the greater advantage of a longer conjugation chain.

The kinetics and mechanism of the intertransformations of isomeric cyclopentadienes will be the subject of a further investigation.

EXPERIMENTAL

I.R. spectra were obtained on "Leitz" (NaCl) and IKS-15(LiF and KBr) double beam spectrometers; Raman spectra were obtained on the ISP-51 three-prism glass spectrograph by the photographic method; U.V. spectra were obtained on a SF-4 spectrometer.

Starting materials. The 2,3,4-trimethylcyclopent-2-en-1-one (XXIII) was prepared by the method of Nazarov and Zaretskaya;[41] 2-methylcyclopent-2-en-1-one was obtained by the procedure of Rinkes;[42] in the method of preparation a solution of cyclopentadienylmagnesium bromide in di-*n*-butyl ether was discribed earlier.[27]

5-*Methylcyclopentadiene* (VII)

At −15° 278 g dimethylsulphate was added dropwise to a ~1 mole cyclopentadienylmagnesium bromide solution in 0·5 l. di-*n*-butyl ether; the reaction mixture was stirred for 2·5 hr at the same temp. The product of the reaction was distilled *in vacuo* (2 mm; ~ −70°), the temp of the mixture not exceeding −10°. The condensate (88 g) was, according to spectral data, a solution of diene VII (~30%) in di-*n*-butyl ether and methyl bromide (by-product of the reaction); appreciable amounts of dienes (IV and V) and starting cyclopentadiene were absent and after exclusion of the impurity bands, the I.R.-spectrum of diene (VII) coincided with the one obtained before[11a]; Raman spectrum see.[24]

1-*Methylcyclopentadiene* (IV)

In the foregoing sample VII is continuously transformed into IV; at 25–28° in the liquid phase VII isomerizes by half every 20–25 min; in the gaseous phase (in a gas cuvette of the IKS-15 spectrometer) at the same temp—every 30–40 min. The process is practically completed in 3 to 4 hr respectively. At the same time the formation of only negligible amounts of V (less than 5%) is observed.

After fivefold molecular distillation of the sample, IV in 85–90% purity was obtained (the rest was essentially methyl bromide; di-*n*-butyl ether was absent). The I.R. spectrum of the substance coincided very well with the well-known[11a]; λ_{max} 249·5 mμ (in heptane); Raman spectrum see ref. 24.

2-*Methylcyclopentadiene* (V)

(a) 2-Methylcyclopent-2-en-1-ol (VIII) was obtained in 82% yield on reduction of 2-methylcyclopent-2-en-1-one with lithium aluminum hydride in an ether solution; b.p. 56° (11 mm), n_D^{20} 1·4784, d_4^{20} 0·9565. (Found: C, 73·3; H, 10·3. $C_6H_{10}O$ requires: C, 73·4; H, 10·3%).

(b) To 150 mg *p*-toluenesulfonic acid in a distillation flask in a vacuum (14 mm) 12·7 g alcohol (VIII) was added dropwise; the products of the reaction were continuously distilled off (in a receiver at ~ −70°); the temp of the reaction mixture did not exceed 25–30°. The diene (V) was separated from water and purified by molecular distillation; yield: 4·5 g (43%). According to spectral data the sample was V of more than 90% purity (the rest was IV). The I.R.-spectrum of the sample coincided with the well-known[11a]; Raman spectrum see ref. 20; n_D^{20} 1·4541, d_4^{20} 0·8085, λ_{max} 243·5 mμ, ε 3050 (in hexane). (Found: C, 89·9; H, 10·0. C_6H_8 requires: C, 89·9; H, 10·1%).

[40] K. Alder, F. H. Flock, A. Hausweiler and R. Reeber, *Chem. Ber.* **87**, 1752 (1954).

[41] I. N. Nazarov and I. I. Zaretskaya, *Izv. Akad. Nauk, SSSR, Otdel. Khim. Nauk*, 529 (1946).

[42] J. Rinkes, *Rec. trav. chim.*, **57**, 176 (1938).

Equilibrium mixture of methylcyclopentadienes

An identical equilibrium mixture of methylcyclopentadienes is formed during distillation at atm. press. of each of the foregoing samples of dienes (IV, V and VII). The same result was achieved by keeping a ~30% solution of IV in di-*n*-butyl ether and methyl bromide (see above) for 2–3 days at 25–28°. In the gaseous phase the process of establishing equilibrium is complete in 2 weeks.

According to spectral data the mixture of methylcyclopentadienes is a mixture of about equal amounts of IV and V containing only traces of VII; Raman spectrum see[24]; b.p. 72·5–73° (747 mm), n_D^{20} 1·4512, d_4^{20} 0·8098, λ_{max} 247 mμ, ε 3410 (in heptane).[43] (Found: C, 89·9; H, 10·1. C_6H_8 requires: C, 89·9; H, 10·1%).

2,3-*Dimethylcyclopentadiene* (X)

(a) Interaction of 2-methylcyclopent-2-en-1-one with methylmagnesium iodide under standard conditions produced 45% of an extremely unstable 1,2-dimethylcyclopent-2-en-1-ol (XIV); b.p. 57–58° (60 mm); n_D^{20} 1·4719 (Found: C, 74·7; H, 10·8. $C_7H_{12}O$ requires: C, 74·9; H, 10·8%).

(b) Dehydration of alcohol (XIV) under conditions analogous to those described above for VIII gave X in 41% yield; according to spectral data the product contained more than 90% X and only negligible amounts of IX and 3-methylene-2-methylcyclopentene; Raman and I.R. spectra see[19]; n_D^{20} 1·4693, d_4^{20} 0·8179, λ_{max} 240·5 mμ, ε 4050 (in hexane). (Found: C, 89·2; H, 10·6. C_7H_{10} requires: C, 89·3; H, 10·7%).

Equilibrium mixture of 1,2-*dimethylcyclopentadienes*

Practically homogeneous X (8·6 g) was distilled in a column (32 t.p.) in a vacuum (147·5 mm) with *o*-xylene as a cushion, with a reflux ratio 35–37. One main fraction (6·9 g, 80%), according to spectral data a mixture of IX and X in a ~3:2 ratio, was separated; Raman and I.R. spectra see[19]; b.p. 55·75–55·9° (147·5 mm), n_D^{20} 1·4623, d_4^{20} 0·8150, λ_{max} 248 mμ, ε 3100 (in hexane). (Found: C, 89·3; H, 10·7. C_7H_{10} requires: C, 89·3; H, 10·7%).

Equilibrium mixture of 1,2,3-*trimethylcyclopentadienes*

(a) Reduction of ketone (XXIII) by lithium aluminum hydride in an ether solution under standard conditions led to 2,3,4-*trimethylcyclopent*-2-*en*-1-*ol* (XVIII)[45] in 79% yield; b.p. 46·5° (2·5 mm), n_D^{20} 1·4736, d_4^{20} 0·9257. (Found: C, 75·9; H, 11·1. $C_8H_{14}O$ requires: C, 76·2; H, 11·1%).

(b) Alcohol (XVIII) was dehydrated under the following conditions: distillation at atm. press. (yield: 66%); distillation at atm. press. over potassium carbonate (yield: 54%); under conditions analogous to those described above for VIII (but at 3 mm, yield: 52%). It was found that the product of all 3 methods was essentially the same mixture of dienes. According to spectral data it consisted of ~30% XIX and ~70% equilibrium mixture of 1,2,3-trimethylcyclopentadienes; b.p. 63–67° (70 mm), n_D^{20} 1·4709–1·4712, λ_{max} 238 mμ, ε 6800–6950 (in heptane).

The components of this mixture were separated by vacuum distillation on a column (100 t.p.) with reflux ratio 50–60. Tetraline was used as a cushion. The distillation yielded:

(1) 3-methylene-2,4-dimethylcyclopentene (XIX) containing ~7% XVI and XVII (in sum); Raman and I.R. spectra see[25]; b.p. 47·4° (51 mm), n_D^{20} 1·4734, d_4^{20} 0·8138, λ_{max} 236·5 mμ, ε 14050 (in hexane). (Found: C, 88·9; H, 11·0. C_8H_{12} requires: C, 88·8; H, 11·2%).

(2) Equilibrium mixture of trimethylcyclopentadienes (pure from XIX). According to spectral data this mixture is practically a homogeneous 1,2,3-trimethylcyclopentadiene (XV), containing but traces of XVI and XVII; Raman and I.R. spectra see[25]; b.p. 55·9–56·0° (51 mm), n_D^{20} 1·4690, d_4^{20} 0·8290, λ_{max} 253 mμ, ε 3030 (in hexane). (Found: C, 89·1; H, 11·0. C_8H_{12} requires: C, 88·8; H, 11·2%).

Mixture of 1,2,4-(XVI)- *and* 1,4,5-(XVII)-*trimethylcyclopentadienes*

Distillation of 42.0 g of an equilibrium mixture of trimethylcyclopentadienes in a column (~100 t.p.) *in vacuo* (55 mm) at reflux ratio of about 2000–2500 produced 8·2 g of a fraction containing

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[43] The closely agreement of these constants with those given for the sample prepared from the dimer of methylcyclopentadiene[44] shows that the latter is also an equilibrium mixture of isomers.

[44] J. S. Powell and K. S. Edson, *Anal. Chem.* **20**, 510 (1948).

[45] The work of Alder and Muders (Ref. 4) contains no description of this compound.

according to spectral data XVI and XVII in a ~1:1 ratio; XV, predominating in the equilibrium mixture, was absent from this fraction; Raman and I.R. spectra see[26]; b.p. 47·1–47·4° (55 mm), n_D^{20} 1·4617, d_4^{20} 0·8117, λ_{max} 262·5 mμ, ε 3000 (in hexane). (Found: C, 88·8; H, 11·2. C_8H_{12} requires: C, 88·8; H, 11·2%).

The packing and glass cotton in the pot of the column were thoroughly washed with ether; the ether removed and the residue vacuum distilled to yield 29·8 g of a diene fraction, which was identical with the starting equilibrium mixture. The yield of a non-equilibrium sample was 20 and 67% respectively with regard to the starting and reacted equilibrium mixture.

Equilibrium mixture of trimethylcyclopentadienes from a mixture of 1,2,5-(XVI)- *and* 1,4,5-(XVII)-*trimethylcyclopentadienes*

(a) 4·32 g of a mixture of XVI and XVII (~1:1) were sealed into tube at a residual pressure of ~2 mm (cooling with liquid nitrogen); in the process of pumping out, the air dissolved in the sample was removed during repeated crystallizations and melting of the substance. The sealed tube was kept for ~3 hr at 85°. Distillation yielded 3·57 g (83%) of an equilibrium mixture of trimethylcyclopentadienes (more than 95% XV).

(b) The sequence of trimethylcyclopentadiene transformations was observed by means of I.R. and Raman spectra of non-equilibrium samples during transformation into an equilibrium mixture. The I.R. bands (XV): 728 and 861 cm^{-1}, (XVI): 717 cm^{-1}, and (XVIII): 774 and 824 cm^{-1} were analysed and in the Raman spectra the C=C stretching frequencies region were examined. The I.R. and Raman spectra revealed the following features:

1. There is a considerable change in the ratio of the band intensity of isomers (XVI and XVII) during the initial stages of transformation until a certain definite ratio is reached. At the same time the intensity of the bands of XVI diminishes much faster.
2. Uniform weakening of the bands of XVI and XVII during the subsequent stages of transformation until they almost disappear.
3. Continuous regular growth of the bands corresponding to XV which predominates in the equilibrium mixture.

The characteristic features indicate the stepwise character of the transitions of XV, XVI and XVII and the transformations may have the following scheme:

$$(\text{XVII}) \underset{v_2}{\overset{v_1}{\rightleftarrows}} (\text{XVI}) \underset{v_4}{\overset{v_3}{\rightleftarrows}} (\text{XV})$$

providing $v_3 > v_1 \gg v_4$ with comparable values of v_2 and v_3 (v shows the rates of the corresponding transitions).

Equilibrium mixture of tetramethylcyclopentadienes

To a solution of methylmegnesium iodide (83·5 g methyl iodide and 13·5 g magnesium) in 300 ml ether a solution of 48·6 g 2,3,4-trimethylcyclopent-2-en-1-one (XXIII) in 150 ml ether was added dropwise at a rate ensuring uniform boiling of the ether. When the addition was complete, the mixture was stirred for 30 min and poured into a mixture of 44 ml conc hydrochloric acid, 200 ml water and ~100 g ice. The ether layer was separated, the water layer extracted with ether (3 × 50 ml); the combined extracts dried ($MgSO_4$) and distilled *in vacuo*, to yield 31·7 g (66%) of an equilibrium mixture of tetramethylcyclopentadienes. According to the I.R. and Raman spectra the mixture contains XX, XXI and XXII in a ~7:2:1 ratio respectively; Raman and I.R. spectra see[26]; b.p. 31–32° (5 mm), m.p. 1–3°, n_D^{20} 1·4723, d_4^{20} 0·8342, λ_{max} 262·5 mμ, ε 3360 (in *i*-octane). (Found: C, 88·6; H, 11·1. C_9H_{14} requires: C, 88·5; H, 11·5%).

1,2,4,5-*Tetramethylcyclopentadiene* (XXII)

An equilibrium mixture of tetramethylcyclopentadienes (183·7 g) was distilled in a vacuum in a column (~100 t.p.) with a reflux ratio ~60. 143·5 g of a homogeneous fraction containing more than 90% of diene (XXII) was separated; Raman and I.R. spectra see[26]; b.p. 40·3–40·7° (14 mm) n_D^{20} 1·4639, d_4^{20} 0·8200, λ_{max} 262 mμ, ε 3480 (in *i*-octane). (Found: C, 88·5; H, 11·5. C_9H_{14} requires: C, 88·5; H, 11·5%).

The diene fraction (30·6 g) of the pot residue (obtained analogously to that described above) proved identical with the starting equilibrium mixture of tetramethylcyclopentadienes. The yield of isomerization product (XXII) was 78 and 94% respectively with regard to the starting and reacted equilibrium mixture.

Equilibrium tetramethylcyclopentadiene mixture from 1,2,4,5-*tetramethylcyclopentadiene* (XXII)

(a) Diene (XXII; 7 g) was sealed into an evacuated tube under conditions described above; after heating for 3 hr at 60°, 6·3 g (90%) of an equilibrium mixture of tetramethylcyclopentadienes was obtained.

(b) A similar result was obtained by heating 7 g of diene sealed under the same conditions, for ~30 min at 100°; the product was 6·1 g (87%) of an equilibrium mixture of tetramethylcyclopentadienes.

5-*Deuterocyclopentadiene* (XXV)

To a solution of ~0·45 mole cyclopentadienylmagnesium bromide in 200 ml di-*n*-butyl ether at -15 to $-20°$ 17·3 h deuterium oxide was added. The product of the reaction was distilled *in vacuo* (30 mm); the distillate being collected at ~ $-70°$; the temp of the reaction mixture did not exceed $-5°$. From the distillate (16·1 g) by molecular distillation *in vacuo* (0·4 mm) was obtained 11·8 g XXV; the temp during distillation was -5 to $-10°$. According to the I.R. and Raman spectra, XXV contained 90–95% of the basic substance, about 3% of di-*n*-butyl ether, traces of other monodeuterocyclopentadienes, and was practically free from the impurity of the parent cyclopentadiene. Raman and I.R. spectra see[27].

Equilibrium monodeuterocyclopentadiene mixture

(a) On heating for 1 hr at 60° a sample of XXV yielded a mixture of (XXV, XXVI and XXVII) in which, according to I.R. and Raman spectra,[27] the ratio of the concentrations of the components was ~1 : 1 : 1, i.e., was equal to that predicted theoretically. Further storage or heating of the resultant mixture does not lead to any change in this ratio.

The process of establishing equilibrium concentrations of (XXV, XXVI and XXVII) from a practically homogeneous XXV does not involve formation of appreciable amounts of deuterium non-containing cyclopentadiene, whose presence can be easily recorded on the I.R. spectrum (664 and 803 cm^{-1}).

(b) The step character of transformation of the isomeric monodeuterocyclopentadienes was recorded by I.R. spectra of a sample of XXV at different stages of its transformation into an equilibrium mixture of monodeuterocyclopentadienes. An analysis of the I.R. spectra revealed that:

(1) the intensity of the bands of the XXV diminishes continuously during the transformation until a certain minimum characteristic of the equilibrium mixture is reached;

(2) the bands attributed to XXVI and XXVII can be divided into two groups, the intensity of the bands of the first group growing during the initial stages of transformation and soon reaching a maximum value, while the intensity of the bands of the second group continues to grow until the equilibrium is reached.

It seems that under these conditions the ratio of the intensity of the bands inside the spectra of an individual isomer must not change; the character of the change in the intensity thus indicates successive transformations of the type:

$$(XXV) \rightleftarrows (XXVI) \rightleftarrows (XXVII)$$

Adducts of substituted cyclopentadienes with maleic anhydride

Most cyclopentadienes mentioned in this report were characterized by their adducts with maleic anhydride. The yields, m.p. and results of the elementary analyses of the individual adducts are shown in Table 3.

The adducts were synthesized by the following standard procedure: A solution of the diene in a mixture of dry benzene and ether (1 : 1) was added dropwise to a suspension of an equimolar amount of maleic anhydride in the same mixture of solvents at a temp of -10 to $-15°$. In the course of 30 min the temp of the reaction mixture was brought up to room temp. The residue after removal of solvents was purified by a series of crystallizations from benzene–hexane (in a 1:3–1:5 ratio respectively).

Anhydrides (XXVIII, XXIX, XXX, XXXI and XXVI) were obtained from practically homogeneous non-equilibrium samples of dienes. For the dienes (IV and VII) obtained only in the form of

TABLE 3. INDIVIDUAL ADDUCTS OF SUBSTITUTION CYCLOPENTADIENES WITH MALEIC ANHYDRIDE AND THEIR DERIVATIVES. The graphs show: yield in %, melting point (uncorrected) and the results of the clementary analyses.

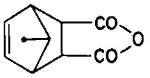
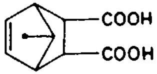
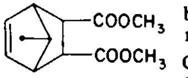
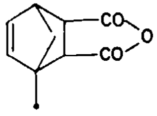
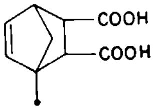
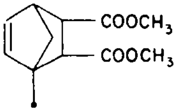
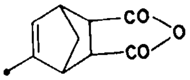
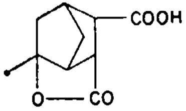
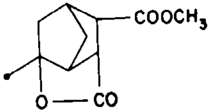
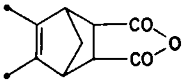
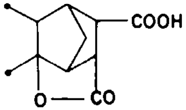
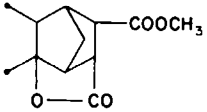
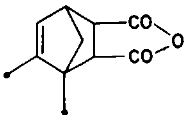
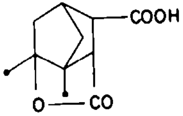
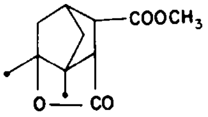
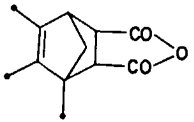
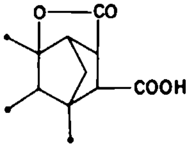
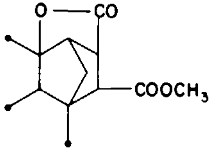
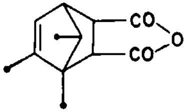
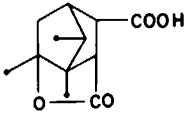
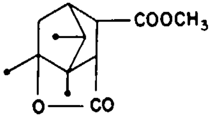
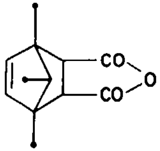
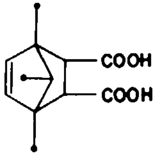
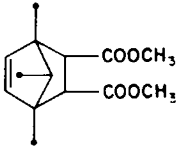
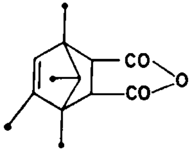
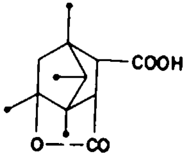
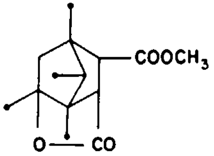
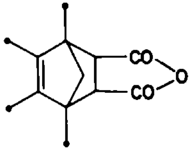
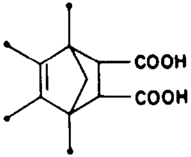
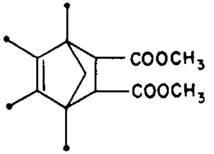
Diene	Adduct		Acid		Ether	
VII	 XXVIII	67 %^{xx} 145, 5–146° C, 67·4; H, 5·6. $C_{10}H_{10}O_3$.C, 67·4; H, 5·7%	 XXXVIII	88 % 178–179° C, 61·0; H, 6·2. $C_{10}H_{12}O_4$.C, 61·2; H, 6·2%	 XLVIII	~100 %^{xxx} b.p. 75, 5–76°(0, 7 mm) n_D^{20} 1, 4828; d_4^{20} 1, 152 C, 64·2; H, 7·3. $C_{12}H_{16}O_4$. 64·3; H 7·2%
IV	 XXIX	73 %^{xx} 88, 5–89° C, 67·3; H, 5·6. $C_{10}H_{10}O_3$.C, 67·4; H, 5·7%	 XXXIX	64 % 118, 5–119, 5° C, 61·2; H, 6·2. $C_{10}H_{12}O_4$.C, 61·2; H, 6·2%	 XLIX	~100 % b.p. 85°(0, 7) mm n_D^{20} 1·4826; d_4^{20} 1,151 C, 64·3; H, 7·2. $C_{12}H_{16}O_4$.C, 64·3; H, 7·2%
V	 XXX	85 % 66–66, 5° C, 67·4; H, 5·6. $C_{10}H_{10}O_3$.C, 67·4; H, 5·7%	 XL	90 % 200–201, 5° C, 61·2; H, 6·2. $C_{10}H_{12}H_4$.C, 61·2; H, 6·2%	 L	~100 % 71–71·5° C, 62·8; H, 6·7 $C_{11}H_{14}O_4$.C, 62·8; H 6·7%.
X	 XXXI	78 %^{xx} 69, 5–70, 5° C, 68·8; H, 6·3. $C_{11}H_{12}O_3$.C, 68·7; H, 6·3%	 XLI	81 % 187–189, 5° C, 62·9; H, 6·7. $C_{11}H_{14}O_4$.C, 62·8; H, 6·7%	 LI	~100 % 75, 5–76, 5° C, 64·3; H, 7·1. $C_{12}H_{16}O_4$.C, 64·3; H, 7·2%.
IX	 XXXII	47 %^{x} 84, 5–85, 5° C, 63·7; H, 6·3. $C_{11}H_{12}O_3$.C. 68·7; H, 6·3%	 XLII	83 % 215–217° (decomp) C, 63·0; H, 6·7 $C_{11}H_{14}O_4$.C, 62·8; H, 6·7%	 LII	~100 % 87–87, 5° C, 64·3; H, 7·3. $C_{12}H_{16}O_4$.C, 64·3; H, 7·2 %

TABLE 3 (*cont'd*)

XV	 XXXIII 82% 95, 5–96, 5° C, 69·9; H, 6·8. $C_{13}H_{14}O_3$,C, 69·9; H, 6·8%.	 XLIII 66% 161–162° C, 64·0; H, 7·1. $C_{12}H_{16}O_4$.C, 64·3; H, 7·2%	 LIII ~100% 110, 5–111, 5° C, 65·6; H, 7·6. $C_{13}H_{18}O_4$.C, 65·5; H, 7·6%.
XVI	 XXXIV mixture with XXXV	 XLIV — 191, 5–192, 5° C, 64·3; H, 7·2. $C_{12}H_{16}O_4$.C, 64·3; H, 7·2%	 LIV ~100% 88–89° C, 65·5; H, 7·5 $C_{13}H_{18}O_4$.C, 65·5; H, 7·6%.
XVII	 XXXV mixture with XXXIV	 XLV mixture with XLIV	 LV — 78–79° C, 66·6; H, 8·1. $C_{14}H_{20}O_4$.C, 66·6; H, 8·0%.
XXII	 XXXVI 76% 81, 5–82, 5° C, 70·9; H, 7·3 $C_{13}H_{16}O_3$.C, 70·9; H, 7·3%	 XLVI 92% 193–194, 5° C, 65·4; H, 7·6. $C_{13}H_{18}O_4$.C, 65·5; H, 7·6%	 LVI ~100% 129, 5–130, 5° C, 66·6; H, 8·0. $C_{14}H_{20}O_4$.C, 66·6; H, 8·0%
XX	 XXXVII 68%[x] 108–109° C, 71·1; H, 7·4. $C_{13}H_{16}O_3$.C, 70·9; H, 7·3%	 XLVII 83% 168–169° C, 65·7; H, 7·7. $C_{13}H_{18}O_4$.C, 65·5; H, 7·6%	 LVII ~100% 45, 5–46° C, 67·7; H, 8·3. $C_{15}H_{22}O_4$.C, 67·6; H, 8·3%.

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[x] Obtained from equilibrium mixture

[xx] Yield with regard to maleic anhydride

[xxx] Crystallizes on standing; m.p. 33–34·5°

concentrated solutions, the reaction was performed with a slight shortage of maleic anhydride (5–10%). Anhydrides (XXXIII and XXXVII) were obtained directly from equilibrium mixtures of the corresponding dienes in which XV and XX predominate. Anhydride (XXXII) was produced by crystallization of a mixture of anhydrides (XXXI and XXXII) obtained from an equilibrium mixture of 1,2-dimethylcyclopentadienes.

Derivatives from the adducts of substituted cyclopentadienes with maleic anhydride

(a) All individual adducts of dienes with maleic anhydride were saponified by boiling the anhydride (1–3 g) with water (used in amounts sufficient to dissolve the acid formed) for 8 hr. The water was evaporated, the crystalline residue dried and purified by crystallization from acetone (XXXVIII) or from a mixture with benzene in 1:2–1:5 ratios.

During saponification under these conditions the anhydrides with unsubstituted double bonds (XXVIII, XXIX and XXXV), as well as XXXVII, formed substitution bicyclo-(2,2,1)-hept-2-ene-5,6-dicarboxylic acids. During saponification of anhydrides with substituted double bonds (all the rest) spontaneous lactonization was observed. The presence or absence of γ-lactone grouping in the resultant acids was determined by their I.R. spectrum (the 1770 cm^{-1} band, in nujol). The yields, m.p. and results of elementary analyses of the acids obtained are shown in Table 3.

(b) All dicarboxylic and lactonic acids obtained were characterized by their di- and monomethyl ethers. The ethers were prepared in almost quantitative yield by treating the acids with the superfluous ether solution of diazomethane at 0–+3°. The substances were purified by chromatography (in benzol) on aluminium oxide (which was preliminarily boiled with ethyl acetate) and then distilled or crystallized with a mixture of chloroform and hexane (1:4–1:5). The properties of the individual ethers are given in Table 3.

Mixtures of adducts of substituted cyclopentadienes with a maleic anhydride and their separation

The compositions of the mixtures of substituted cyclopentadienes determined by spectroscopic methods were confirmed on diene condensation with maleic anhydride and isolation of individual derivatives of each of the major components of the mixtures at the stage of anhydrides, acids or ethers.

(a) A mixture of XXIX and XXX was obtained from an equilibrium mixture of methylcyclopentadienes. By the intensity of the C=C lines of these anhydrides in Raman spectrum (1574 and 1629 cm^{-1}) it was found that the ratio of the components of this mixture was close to 1:1; i.e., it coincided with the established ratio of the dienes in the equilibrium mixture. From the mixture of acids (XXXIX and XL) obtained on saponification of the mixture of these adducts it was possible during crystallization to separate an individual lactonic acid (XL) which was found to be identical with the acid produced by saponification of an individual anhydride (XXX).

The mixture of acids (XXXIX and XL) was transformed into a mixture of ethers (XLIX and L); both being isolated in pure form by means of preparative thin layer chromatography on aluminium oxide preliminarily boiled with ethyl acetate (in a 1:2 hexane–benzol mixture, $R_f = 0{\cdot}31$ and 0·05) respectively).

(b) A similar investigation was conducted for a non-equilibrium sample of trimethylcyclopentadiene—from a mixture of XVI and XVII, a mixture of adducts (XXXIV and XXXV) was prepared; by means of Raman spectrum it was shown that the ratio of the components in this mixture corresponds to the ratio of the dienes in the parent mixture; by crystallization of the mixture of acids (XLIV and XLV) obtained by saponification of the mixture of anhydrides an individual lactonic acid (XLIV) was produced (see Table 3); both the individual ethers (LIV and LV) corresponding to dienes (XVI and XVII) were separated by the preparative chromatography under the afore-described conditions ($R_f = 0{\cdot}065$ and 0·41 respectively).

(c) An individual anhydride (XXXII) was isolated from the mixture of XXXI and XXXII obtained from the equilibrium mixture of 1,2-dimethylcyclopentadienes during crystallization. The residue from the separation of the anhydride (XXXII) was saponified, and from the mixture of acids obtained an individual lactonic acid (XLI) was isolated by crystallization. This acid was found to be identical with the sample obtained by saponification of the pure anhydride (XXXI).

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