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CYCLIC UNSATURATED COMPOUNDS. XX. ON THE QUESTION OF THE MECHANISM OF ENDO-EXO-ISOMERIZATION OF CYCLOPENTADIENE-MALEIC ANHYDRIDE ADDUCTS (BICYCLO-/2,2,1/-HEPT-2-ENE-5,6-DICARBONIC ACIDS ANHYDRIDES) [1]

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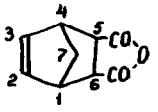
The question of the thermic isomerization of endo-adducts of cyclopentadiene (which as a rule are the major products of Diels-Alder reaction[2]) to more thermodynamically stable exo-isomers is an object of a large number of the investigations [3,4]. This problem is of interest because the data on the mechanism of such a conversion is important to a more complete understanding of diene additions processes. The mechanism of the interconversion of endo- to exo-adducts has been represented as 1) a retrogression of the parent adduct to the addends which than recombine to give the other stereoisomer (or "external" pathway) [3] and 2) a direct conversion, not involving dissociation into kinetically free fragments (or "internal" pathway) [4]. The grait majority of works on the mechanism of endo-exo-isomerization were done on the simplest example that is transformation of endo-cyclopentadiene - maleic anhydride adduct (Ia) to the corresponding exo-isomer (Ib) (2e; 3d,e; 4a-d).

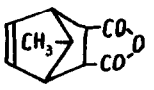
The present investigation includes new data, demonstrating

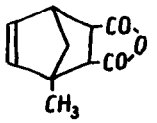
that (Ia) ⟶ (Ib) thermic isomerization occurs by a simple "external" dissociation-recombination mechanism. The mechanism of this process was reported previously to be "internal" [4a,b]. In the other cases it was supposed that the endo-exo-conversion occurs both by an "internal" and "external" pathways [4c,d].

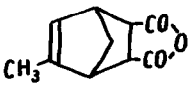
Recently we found that under relatively mild conditions it takes place the migration of endocyclic double bonds system in cyclopentadienes as a result of intramolecular 1,2-shift of hydrogene [5]. Thus on unprolonged heating at about 60-80°C each of 1-, 2- or 5-methylcyclopentadienes produces the equilibrium mixture, consisting of about equal amounts of 1- and 2-methylcyclopentadienes and containing less then 5 per cent of 5-methylcyclopentadiene [6]. The facility of interconversion of methylcyclopentadienes was used now for establishment of the mechanism of endo-exo-isomerization of their adducts.

The termic isomerization of three isomeric methylcyclopentadienes - maleic anhydride endo-adducts - 7-(IIa)-, 1-(IIIa)- and 2-(IVa)-methylbicyclo-/2,2,1/-hept-2-ene-5,6-dicarbonic acids anhydrides has been investigated. The anhydrides (IIa)-(IVa) have been described by authors previously [5,6]. The endo-configuration of the adducts (IIa)-(IVa) has been proved.[1,7]









Ia-endo	IIa-endo	IIIa-endo	IVa-endo
IIb-exo	IIb-exo	IIIb-exo	IVb-exo

It was found that on heating under conditions of endo-exo-isomerization (20 min in boiling tetraline) each of isomers (IIa)-(IVa) gave the same equilibrium mixture of products. In this

mixture by NMR-technique the structural isomer (III) and (IV) ratio was found to be approximately 1:2 respectively. The mixture contained probably small amounts (less than 5 per cent) of the anhydrides (II). Thus under experimental conditions there is not only endo-exo-conversion but the structural isomerization.

The reaction (IIa) ⟶ (III) + (IV) may be considered as an irreversible one owing to the essentially completely conversion the adduct (IIa) under the experimental conditions. The kinetics of this reaction has been studied over the 180-207°C temperature range. Consentrations of the structural isomers were determined by comparison of CH_3-grupps protons signal intensivity in NMR spectra [7]. The chemical shifts of protons in analytic region were: δ 0.78 p.p.m. (dublet from C.7-CH_3, compound II), δ 1.49 p.p.m. (singlet from C.1-CH_3, compound III), δ 1.61 p.p.m.(singlet from C.2-CH_3, compound IV).

A kinetic study of the rearrangement (IIa) ⟶ (III) + (IV) led to first-order rate constants for the conversion: $K \cdot 10^4 (sec^{-1}) = 5 \cdot 1 \pm 0.2$ (at 180°C), $19 \cdot 4 \pm 1.9$ (at 193°C), $68 \cdot 2 \pm 4.2$ (at 207°C). Calculation gave Arrhenius activation energies and pre-exponential factors: $E = 41 \cdot 3 \pm 1.5$ kcal.mole^{-1}, $Z = (5.4 \pm 0.3) \cdot 10^{16}$ sec^{-1}. The (III) and (IV) concentrations ratio was found to equal 0.46 ± 0.01 and to be constant at all stages of the conversion over the ~100 to ~0% range of isomers (II) concentration. This ratio was not affected markedly by the temperature change over the studied temperature range.

It is noticeable that the composition of the equilibrium mixture of the adducts is in general agreement with that observed for the methylcyclopentadienes (see avobe). This indicates clearly

that formation of kinetically free dienic components of adducts takes place in the course of the endo-exo-conversion. Forming methylcyclopentadienes undergo typical of them double bonds isomerization. In view of an "internal" mechanism it is difficult to explain the composition of structural isomers mixture.

The observed constant ratio of the adducts (III) and (IV) in the course of the isomerization cannot be explained in view of an "internal" pathway. Such an pathway postulates breaking only one of diene-dienofil bonds. Admitted "internal" mechanisms [4] include C.1-C.6 bond cleavage followed by C.2-C.6 bond formation. Hence on isomerization the adduct (IIa) production of the adducts (III) should be accomplished only as a result of subsequent reactions (II) → (IV) → (III). Therefore, if the "internal" mechanism is correct, some prevalence of isomer (IV) should take place during the initial stages of transformation of adduct (IIa) into the equilibrium mixture. This is in contrast with the mentioned above experimental data.

An assumption that the structural and endo-exo-conversions occur by different mechanisms (the former by an "external", the latter by an "internal") is incorrect because every act of endo- to exo-transformation by an "internal" mechanism must be accompanied by structural isomerization which should occur by the subsequent reaction (II) → (IV) → (III) (see above).

On these evidences it is apparent that the endo-exo-isomerization of cyclopentadiene - maleic anhydride adducts occurs by "external" mechanism involving dissociation a parent adduct into kinetically free addends, which then recombine to give another stereoisomer. The same conclusion was made simultaneously with us

by Ganter, Scheidegger and Roberts (cf.[2e] and [3e]) on the ground of reexamination of Berson's data [4b,c,h] which erlier are considered to prove an "internal" mechanism for the (Ia) —⇌ (Ib) conversion.

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