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# CYCLIC UNSATURATED COMPOUNDS.XXXVI.THE REVERSIBLE SKELETAL ISOMERIZATION OF 1,2,3- AND 1,2,4-TRIMETHYLCYCLOPENTADIENES.

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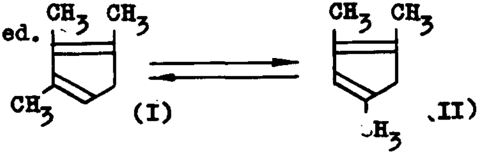
Earlier we have found[1] that in substituted cyclopentadienes (CPD) intramolecular thermal 1,5-shift of hydrogen[2] occurs under relatively mild conditions. We have noted [1c] the general tendency to lower thermodynamic stability of 5-alkyl-CPDs in comparison with the double bond isomers having a free methylene group. Accordingly, 5,5-disubstituted CPDs are unstable and undergo skeletal isomerization into CPDs with a free methylene group as a result of 1,5--shift of an alkyl group accompanied by 1,5-shift of hydrogen[3]. It must be emphasized that this isomerization is irreversible.

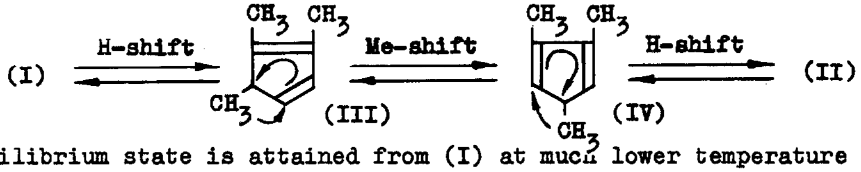
We present here the data demonstrating that in thermodynamically stable CPDs (with a free methylene group) intramolecular thermal 1,5-shift of alkyl group also takes place. The thermal transformations of 1,2,3-(I)-[1d,4] and 1,2,4-(II)-[4-6] trimethyl-CPDs have been investigated[7]. It was found that on passing of (I) or (II) at 375-500° through a quartz tube packed with crushed quartz (I)$\rightleftarrows$(II) reversible skeletal isomerization takes place. Under the conditions mentioned at a contact time ~8sec the equilibrium state (I:II ratio is 1.25:1 by GLC) is attained at 435° from (I) and at 490° from (II). The fact that thermal isomerization of (I) or (II) leads to essentially the same mixture is supported by IR and Raman spectra data[6] and by results obtained by a direct chemical method: the product of pyrolysis of (I) (of (II) in another experiment) was treated by maleic anhydride; the adduct mixture obtained was hydrolyzed to yield the mixture of corresponding lacto-acids, from which the individual derivatives of (I)[1d] and (II)[6] were isolated.



(I)

(II)

The yield of by-products in the reaction (I)$\rightleftarrows$(II) was low ($<$ 5% below 460°) but rose markedly with increasing temperature (at 500°: ~13% from (I) and ~17% from (II)). Di- and tetramethyl-CPDs were not discovered in the products of pyrolysis. Hence, one may suppose that the (I)$\rightleftarrows$(II) interconversion is intramolecular. As to the mechanism of (I) (II) isomerization, it seems reasonable to invoke an intramolecular 1,5-shift of methyl group from 5-positiion of CPD, assuming 1,5-shift of hydrogen as initial and final steps of the reaction:



The equilibrium state is attained from (I) at much lower temperature than that from (II). This is in agreement with concentrations of dienes (III) and (IV) in the parent equilibrium mixtures of double bond isomers[6]. Thus, isomers (III) and (IV) may be considered to be responsible for the skeletal isomerization.

The fact that an alkyl group is able to migrate in thermodynamically stable CPDs shows that such an isomerization is a general phenomenon in CPD series. The same isomerization was observed in 1,2- and 1,3-dimethyl-CPDs and in 1-$C^{14}H_3$2,3,4-tetramethyl-CPD.

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7. The thermal behavior of (I) and (II) under other conditions has been studied earlier[3c] but the (I)$\rightleftarrows$(II) isomerization was not proved.