Tetrahedron Letters No.6, pp. 499-500, 1969. Pergamon Press. Printed in Great Britain.

CYCLIC UNSATURATED COMPOUNDS.XXXV.

INTRAMOLECULAR THERMAL 1,5-SHIFT OF HYDROGEN IN CYCLOHEPTA-1,3-DIENE SERIES.

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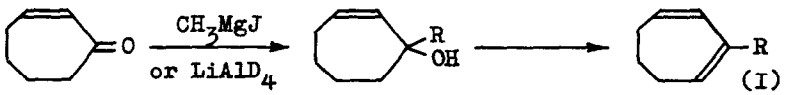
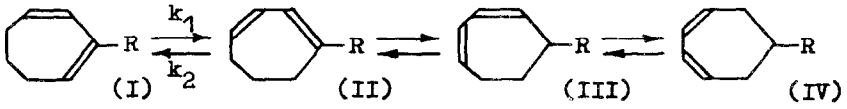
(Received in UK 21 December 1968; accepted for publication 6 January 1969)

It is known that cyclopentadienes[1], cycloheptatrienes[2] and certain penta-1,3-dienes (the latter at much higher temperatures)[3] undergo double bond isomerization as a result of intramolecular 1,5-shift of hydrogen. The reversible thermal transformations of these compounds lead to the establishment of thermodynamic equilibrium between double bond isomers. In the present paper we report on the thermal 1,5-shift of hydrogen in cyclohepta-1,3-diene (CHD) series. The thermal behavior of methyl- and monodeutero-CHDs has been investigated. 2-Methyl-CHD(Ia)[4] and 2-deutero-CHD(Ib)[5] were prepared by following routes:



(Ia) : R=CH_3
(Ib) : R=D

It was found that on heating at 120-160° (Ia) is converted into equilibrium mixture of methyl-CHDs consisting of 37.6% 2-(Ia)-, 57.7% 1-(IIa)- and 10.7% 3-(IIIa)- and 4-(IVa)-isomers according to GLC[6]. Further heating of this mixture does not lead to any change in its composition. At early stages of (Ia) isomerization the concentration of (IIa) increases to about equilibrium value, while less than 5% of (IIIa) and (IVa) is formed. Consequently, (IIa) is the initial product of (Ia) transformation and interconversion of CHDs occurs by 1,5-shift of hydrogen as shown in the scheme:



(Ia)-(IVa) : R=CH_3
(Ib)-(IVb) : R=D

The kinetics of (Ia) ⇄ (IIa) reaction has been studied over 140-160° tempe-

rature range at the first stage of (Ia) isomerization. Calculation based on the first-order rate constants obtained gave Arrhenius activation energies and pre-exponential factors: E_1=29.5±1.5 kcal/mole, lg Z_1=11.4±0.5 (for Ia → IIa) and E_2=28.6±1.5 kcal/mole, lg Z_2=10.8±0.5 (for IIa → Ia).

In 2-deutero-CHD(Ib) (>98% d_1 by mass spectrometry) according to IR and Raman spectra all D-atoms are located at the double bond (ν 2241cm^{-1}). It was found that on heating at 160° for 3 hours (Ib) is converted into equilibrium mixture of deutero-CHDs which consists of comparable amounts of (Ib)+(IIb) and (IIIb)+(IVb) (ν 2161 and 2241cm^{-1} with about equal intensities)[7]. The mass spectrum of this mixture is identical with that of the starting material. Thus the formation of d_2- and d_0-CHDs in d_1-CHDs interconversion does not take place. Hence, the redistribution of deuterium in the molecule is not a result of hydrogen exchange but may be explained by migration of double bonds. Absence of any hydrogen exchange in this case shows doubtlessly that interconversion of CHDs occurs by an intramolecular mechanism.

The evidence presented demonstrates that in cyclohepta-1,3-dienes above 120° double bond system migration takes place as a result of intramolecular 1,5-shift of hydrogen.

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146,1098(1962); Tetrahedron,19,1939(1963).

2. A.P.ter Borg, H.Kloosterziel, N.van Meurs, Proceed.,1962,359; Rec.Trav.Chim. 82,717(1963).
3. J.Wolinsky, B.Chollar, M.D.Baird, J.Amer.Chem.Soc.,84,2775(1962).
4. The dehydration of 1-methylcyclohept-2-en-1-ol produces the mixture of 71% (Ia) and 29% (IIa) owing to 1,4-elimination taking a part in dehydration of unsaturated cyclic alcohols, see V.A.Mironov, A.A.Akhrem, Izv.Acad.Nauk,SSSR Ser.Khim., in press. Diene (Ia) (>99.9% purity by GLC) was isolated from this mixture by ~100 t.p. column distillation: b.p.48.3–48.4°(25mm), n_D^{20} 1.4963, d_4^{20} 0.8554, $\lambda_{max}^{heptane}$ 252nm, ε 6700. Found: C 88.7, 88.8; H 11.3, 11.1. C_8H_{12} requires: C 88.8; H 11.2.
5. B.p.71–71.5°(153mm), n_D^{20} 1.5011, d_4^{20} 0.8684, $\lambda_{max}^{heptane}$ 246.5nm, ε 8430. It may believe[4] that dehydration of 1-deuterocyclohept-2-en-1-ol leads to a mixture of dienes (Ib) and (IIb).
6. B.p.57–59°(39.5mm), n_D^{20} 1.4980, d_4^{20} 0.8518, $\lambda_{max}^{heptane}$ 252nm(ε 7410), 257nm (ε 6830). Found: C 88.7, 88.8; H 11.0, 11.1. C_8H_{12} requires: C 88.8; H 11.2.
7. B.p.71.5–72.5°(155mm), n_D^{20} 1.5016, d_4^{20} 0.8724, $\lambda_{max}^{heptane}$ 246.5nm, ε 8310.