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A REGIOSPECIFIC DOUBLE BOND SHIFT INDUCED BY TITANOCENE CATALYSTS

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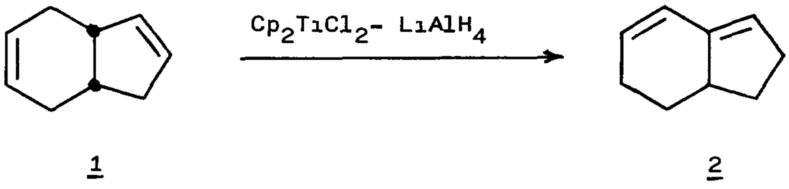
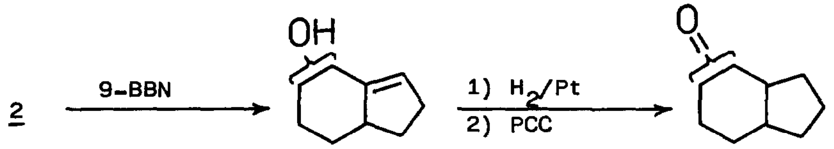
Summary: cis-Bicyclo(4.3.0)-3,7-nonadiene is isomerized by titanocene-derived catalysts to bicyclo(4.3.0)-2,9-nonadiene.

Titanocene catalysts are known to induce hydroalumination, hydrogenation and isomerization of olefins.[2] Recently, we have reported that 1,5,9-cyclododecatriene (CDT) was isomerized by the titanocene catalyst prepared in situ from Cp_2TiCl_2 and $LiAlH_4$.[3] In CDT the reaction starts by a convergent double bond shift of the 1,5-diene to 1,3-diene system, the latter being consumed in the intramolecular Diels-Alder reaction yielding mainly (80%) tricyclo-$(7.3.0.0^{2,6})$-7-dodecenes.[3] Since the convergent isomerization of readily available 1,5-dienes to 1,3-dienes is of synthetic interest, we applied our catalyst to isomerization of bicyclo(4.3.0)-3,7-nonadienes.

At 165°C the cis-annulated diene 1 is cleanly converted by the Cp_2TiCl_2 $LiAlH_4$ catalyst to the conjugated isomer - bicyclo(4.3.0)-2,9-nonadiene - 2 in nearly quantitative yield.



The optimum molar ratio - diene : Cp_2TiCl_2 : $LiAlH_4$ - was found to be 250 : 1 . 4. The structure of 2 was confirmed by mass spectra (m/z 120, 105, 92, 91 (base peak), 79, 77, 65), UV ($\lambda_{max.}$ = 237 nm), ^{1}H-NMR (δ,ppm): 0.88 - 1.71m, 2.21m, 9H; 5.46m, 1H, 5.73m, 1H, 6.27d (J = 9.8 Hz), 1H, ^{13}C-NMR· 26.4t, 30.1t, 31.5t, 32.0t, 43.4d, 123.1d, 123.8d, 130.1d, 142.8s, and chemical correlation :



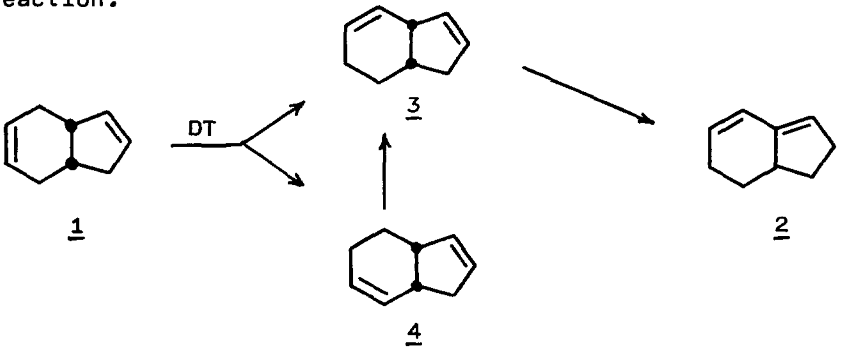
$\nu(C{=}O) = 1718\ cm^{-1}$

9-BBN: 9-borabicyclo(3.3.1)nonane[4], PCC: pyridinium chlorochromate[5]

As the isomerization using the Cp_2TiCl_2-$LiAlH_4$ system can be tedious or even unfeasible when handling very small quantities of dienes, an alternative, simple procedure was developped which makes use of μ-(η^5: η^5-fulvalene)-di-μ-hydrido-bis(cyclopentadienyltitanium) ("dimeric titanocene", DT) as the catalyst. DT can be prepared in quantitative yield by reducing Cp_2TiCl_2 with $LiAlH_4$ in high-boiling olefinic or aromatic solvents of which mesitylene is superior.[6] The following procedure is representative for the isomerization of 1 to 2 , when DT is employed:

An aliquot of the mesitylene solution of DT is transferred to the reaction bulb and the solvent is distilled off in vacuo. The diene 1 is distilled to the solid catalyst to achieve 0.01 $mol.L^{-1}$ concentration of the latter. The bulb is sealed off and heated to 180°C for 6 hours. The cooled bulb is then opened and the product 2 is distilled off in vacuo. Air and moisture should be strictly avoided and the starting diene should not contain reducible oxygen or halogen-containing impurities in an amount comparable to that of DT.

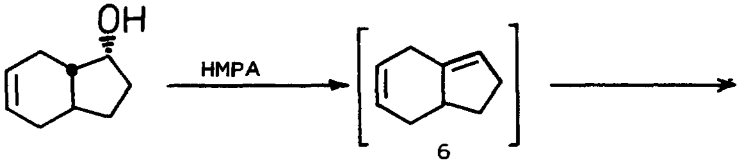
The DT-catalyzed isomerization of 1 starts slowly at 140°C and two intermediates 3 and 4 can be trapped simultaneously in the early stage of the reaction.[7]



The conjugated diene 2 is stable to DT up to 200°C. At higher temperatures, 2 is slowly isomerized to a mixture of other C_9H_{12} isomers and also the intermolecular hydrogen transfer takes place yielding indane and C_9H_{14}

hydrocarbons. Simultaneously, the amount of $(C_9H_{12})_n$ oligomers increases rapidly with rising temperature.

trans-Bicyclo(4.3 0)-3,7-nonadiene 5 [8] reacts sluggishly with DT. After 4h at 200°C the reaction mixture contained mainly the starting diene 5 (64%) together with 2 (22%), indane (7%) and a mixture of C_9H_{14} isomers (7%). At higher temperatures the formation of indane and C_9H_{14} olefins was more pronounced and a considerable amount of 5 was converted to oligomers. The much slower isomerization of 5 compared with 1 indicates that both double bonds of the 1,5-diene system must be available to the titanium catalyst. The favourable arrangement of double bonds is easily achieved only in 1 which has a flexible skeleton. However, the remarkable regiospecificity of isomerization of 1 is probably not due to any simultaneous shift of both double bonds as evidenced by the isolation of 3 and 4. An attempt to prepare the third possible intermediate 6 resulted in formation of 2.[8] Hence, 6 cannot be excluded as an intermediate of the isomerization of 1, but it is probably too unstable to be trapped.



6

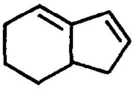
2

In order to compare the relative stabilities of the three possible heteroannular, conjugated dienes 2, 7 and 8, the total energies were calculated by the CNDO/2 method (full geometry optimalization).[9]

2

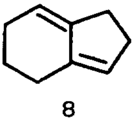
conformer 2a: $\Delta\Delta H_f = 12.5$ kcal.mol^{-1}

conformer 2b $\Delta\Delta H_f = 13.5$ kcal.mol^{-1}



$\Delta\Delta H_f = 13.4$ kcal.mol^{-1}

7



$\Delta\Delta H_f = 0$

8

The calculated data indicate that the isomerization of 1 is not controlled by the stability of the resulting olefin. Even if the most stable isomer 8 were unaccessible due to kinetic reasons, about 20% of 7 could be expected in the reaction mixture, contrary to our observation.

In both catalytic systems, the active species - Cp_2TiR - is formed by addition of the intermediate $(Cp_2TiH)_n$ to the olefin. The presence of Cp_2TiR is evidenced by the sharp ESR signal which appears at the beginning of the isomerization. With 1 the ESR signal at g = 1.991 started to grow at 140°C.

At 160°C it was replaced by another signal at g = 1.993.[10] With 2 and 5 , the latter signal appeared at 175°C increasing its intensity up to 240°C. Above 240°C a new signal was detected at g = 1.996.[11] The different temperatures of the appearance of Cp_2TiR species point at the active role of the olefin in the decomposition of DT. The decomposition must be commenced by insertion of the olefin double bond into the bridge Ti-H bond. This is probably followed by dissociation of fulvalene into two cyclopentadienyl ligands. The isomerization proceeds either by the displacement mechanism or by that involving intermediate formation titanium hydride species.

In concluding, both titanocene catalysts enable a one-step preparation of 2 which is otherwise unaccessible unless by a multistep synthesis. Further abilities of these catalysts, as well as the nature of the catalytically active species, are under investigation.

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8. Prepared by the HMPA dehydration of trans-8-hydroxybicyclo(4.3.0)-3-nonene (F. Tureček and A. Vystrčil, Coll. Czech. Chem. Commun. 41, 1571 (1976) R.S. Monson, Tetrahedron Lett. 567 (1971)).
9. The calculations were kindly performed by Dr. F. Strejček of the Department of Organic Chemistry, Institute of Chemical Technology, Prague.
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11. Other signals occurring irreproducibly at g = 1.987 and 1.975 are due to oxygen-containing impurities.

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