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RING CLOSURE IN 1,2-DIVINYLCYCLOHEXANES AND ISOMERIZATION TO 3-METHYL-3a,4,5,6,7,7a-HEXAHYDRO-1H-INDENES CATALYZED BY TITANOCENE HYDRIDE DERIVATIVES

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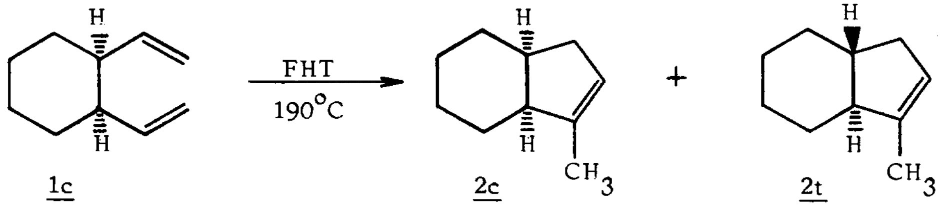
Summary: Titanocene hydride derivatives induce the cyclization of 1,2-divinylcyclohexanes to trans- and cis-1-methylene-octahydro-1H-indene and their isomerization to trans- and cis-3-methyl-3a,4,5,6,7,7a-hexahydro-1H-indene.

cis-1,2-Divinylcyclohexane 1c is easily accessible by the Cope rearrangement of (E,Z)-1,5-cyclodecadiene[2] - the product of nickel catalyzed co-oligomerization of 1,3-butadiene and ethylene[3]. Since it has been recently shown that μ-(η^5:η^5-fulvalene)-di-μ-hydrido-bis(cyclopentadienyltitanium) (FHT) catalyzes both the conversion of vinylcycloalkanes to ethylidenecycloalkanes[4] and the convergent double bond shift in 1,5-dienes to produce 2,4-dienes[4,5], we attempted preparation of 1,2-bis-(ethylidene)cyclohexane from 1c using FHT[6] and a bis(cyclopentadienyl)titanium(III)hydride complex[7]. Compound 1c containing FHT ($[Ti] = 2.10^{-3}$ mol.l^{-1}) was heated in sealed glass ampoules in vacuo to 135-190°C for 3 h. After cooling, the ampoules were opened and the volatile products were distilled off in vacuo giving a better than 98% recovery of C_{10}-hydrocarbons. The content of compounds bearing the terminal double bonds decreased considerably only after heating to 170-190°C. The two main products were separated by preparative GLC[8] and their composition $C_{10}H_{16}$ was determined through their mass spectra. According to ^{1}H- and ^{13}C-NMR spectra, both compounds exhibit similar structural features (one tri-substituted double bond with the attached methyl group, two sp^3-methines and five sp^3-methylenes, see Table 1), consistent with the structure of trans- and cis-3-methyl-3a,4,5,6,7,7a-hexahydro-1H-indene, 2t, and 2c. cis-Isomer 2c was readily identified by ^{13}C-NMR spectra, for its bridgehead carbons were more shielded than those of 2t, owing to the γ-gauche interactions[9]. As the reaction path to these compounds was not clear, the formation of intermediates was followed at lower reaction temperatures. At the lowest temperature at which FHT is still active (135°C), trans-1,2-divinylcyclohexane 1t was identified among main reaction products by GLC and infrared spectra. After heating to 150°C for 3 h the reaction mixture already contained 2t (22%) accompanied by a new compound 3t (66%). On heating to 190°C the following composition of products was obtained: 2t (45%), 2c (42%) and 3t (12%).



1c 2c 2t

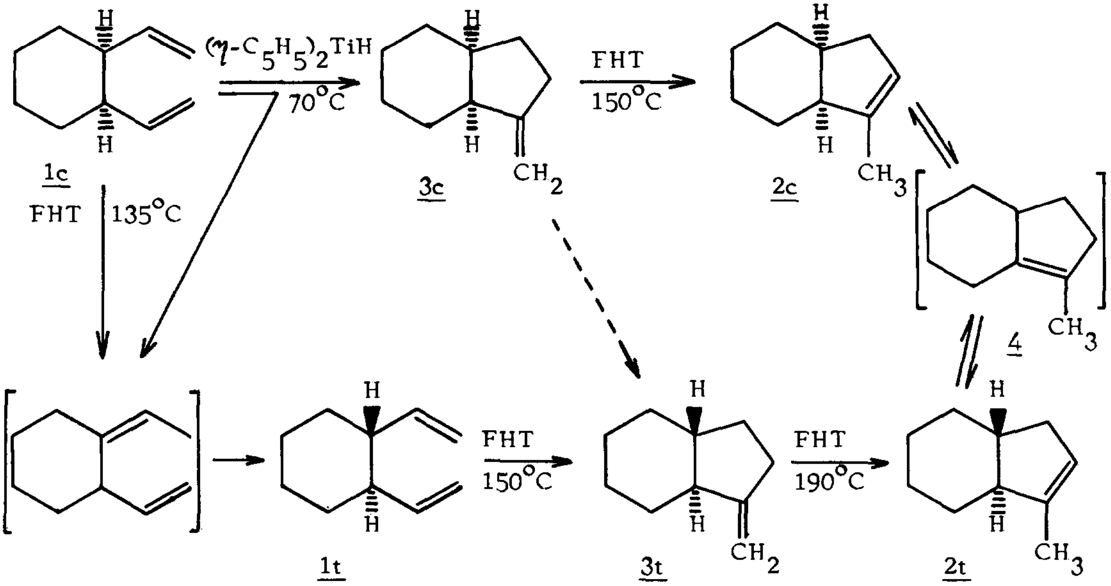
Since the double bond shift in 1c to give ethylidene derivatives might require milder conditions, we catalyzed the isomerization of 1c by a preformed complex containing $(\eta\text{-}C_5H_5)_2TiH$ bound to AlH_3[7]. After heating a solution of the complex in 1c ([Ti] = 5.10^{-2} mol.l^{-1}) to 70°C for 3 h, the product contained 1t (22%), 3t (30%) and 3c (30%). Compounds 3t and 3c were separated by preparative GLC and proved to be bicyclic $C_{10}H_{16}$ isomers containing one exomethylene group (NMR: one sp^2-methylene, one sp^2-quaternary carbon; IR: ν = 1654 cm^{-1}; see Table 1). The structure of cis-1-methylene-octahydro-1H-indene, 3c, was assigned by ^{13}C-NMR spectra to the compound in which the bridgehead methine carbon atoms appeared at a higher field[9]. cis-Isomer 3c could be trapped only in the $(\eta\text{-}C_5H_5)_2TiH$-catalyzed reaction (70°C) and its absence among the reaction products of the FHT-catalyzed reaction (135°C) points at its higher propensity to further isomerization to 3t and/or 2c. Isomerization of 1t with $(\eta\text{-}C_5H_5)_2TiH$ catalyst (80°C, 3 h) yielded the expected trans-isomers 3t (42%), and 2t (19%), together with unreacted 1t (16%). However, at 170°C FHT converted both 1c and 1t to the same mixture of products, i.e. 2t (58%), 2c (18%) and 3t (15%). If compared with the results obtained at 190°C, this shows that 2t and 2c are interconverted via another isomer, 9-methylbicyclo [4.3.0] non-1(9)-ene 4. Actually, 4 appeared to be more abundant when the isomerization was run above 200°C and it could be isolated from the reaction mixture.

The isomerization of 1c to 1t suggests a reversible addition of titanium hydride to the double bond yielding intermediate 1-vinyl-2-ethylidenecyclohexane and 1,2-bis(ethylidene)cyclohexane which have also been reported for nickel-catalyzed isomerization of 1c[10]. The simultaneous detection of a trace amount of 1,2-diethylbenzene which had to arise by intra- and intermolecular hydrogen transfer reactions confirms the probable

Table 1. Spectroscopic Data of Hydrocarbons 2t, 2c, 3t and 3c

2t	IR (cm^{-1}) :	3042 s, 2920 vs, 2850 vs, 2800 s, 1633 m, 1587 w, 1560 w, 1444 vs, 1376 s, 1260 m, 1173 m, 1073 m, 1006 s, 933 m, 924 m, 900 m, 797 vs, 562 m, 542 m, 457 m.
	^{1}H-NMR (δ, ppm):	1.0 - 2.4 (m, 12H), 1.67 (br s, 3H), 5.35 (m, 1H).
	^{13}C-NMR (δ, ppm):	14.3 q, 26.6 t, 26.7 t, 29.1 t, 30.6 t, 36.5 t, 50.3 d, 53.1 d, 123.8 d, 144.4 s.
2c	IR (cm^{-1}):	3042 s, 2920 vs, 2854 vs, 1650 m, 1602 w, 1582 w, 1444 vs, 1380 s, 1260 m, 1176 m, 1028 m, 1010 m, 926 m, 906 m, 858 m, 850 m, 806 s, 798 s, 620 w, 570 m, 530 w, 502w.
	^{1}H-NMR (δ, ppm):	1.38 br s, 1.68 (br s, 3H), 2.12 m, 2.29 m, 5.28 (m, 1H).
	^{13}C-NMR (δ, ppm):	14.9 q, 23.4 t, 23.6 t, 27.0 t, 28.3 t, 36.5 t, 38.5 d, 46.4 d, 123.5 d, 144.4 s.
3t	IR (cm^{-1}):	3073 s, 2987 s, 2927 vs, 2854 vs, 1760 w, 1654 s, 1458 s, 1446 s, 1432 s, 1212 m, 966 m, 906 m, 878 s, 858 m, 838 m, 568 m, 530 w, 418 m.
	^{1}H-NMR (δ, ppm):	1.1 - 2.2 (m, 12H), 2.29 (t, J=7.8 Hz, 2H), 4.71 (t, J=2.4 Hz, 2H).
	^{13}C-NMR (δ, ppm):	25.9 t, 26.3 t, 28.8 t, 30.3 t, 30.5 t, 32.2 t, 46.5 d, 50.5 d, 101.8 t, 145.7 s.
3c	IR (cm^{-1}):	3073 s, 2985 s, 2920 vs, 2850 vs, 1760 w, 1654 s, 1468 sh, 1458 sh, 1448 s, 1434 sh, 1032 m, 985 m, 910 m, 876 s, 863 sh, 850 m, 486 m.
	^{1}H-NMR (δ, ppm):	1.3 - 2.2 (m, 12H), 2.39 (t, J=7.6 Hz, 2H), 4.83 (m, 2H).
	^{13}C-NMR (δ, ppm):	22.3 t, 24.2 t, 26.4 t, 27.5 t, 28.6 t, 30.1 t, 39.6 d, 44.1 d, 104.0 t, 146.7 s.

participation of ethylidene isomers in conversion of 1c to 1t. The overall reaction scheme of isomerization of 1c under different reaction conditions is shown below.



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