INTERMOLECULAR HYDROGEN TRANSFER IN UNSATURATED HYDROCARBONS INDUCED BY DIMERIC TITANOCENE

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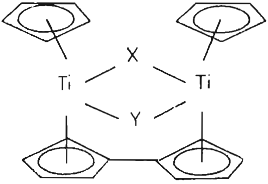
Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

μ-(η^5:η^5-Fulvalene)-di-μ-hydrido-bis(η^5-cyclopentadienyltitanium) and μ-(η^5:η^5-fulvalene)-μ-chloro-μ-hydrido-bis(cyclopentadienyltitanium) form a thermally stable complex which catalyzes the intermolecular hydrogen transfer in unsaturated hydrocarbons, in addition to isomerizations and cyclizations. Cyclic hydrocarbons disproportionate under catalysis to saturated and aromatic hydrocarbons, while linear olefins yield predominantly linear alkanes and high molecular weight tar. The catalyst enables the hydrocarbon system to approach the thermodynamic equilibrium through a series of substitution reactions between alkyl- and allyltitanocene-like species and olefins and dienes. The catalytic complex was characterized by UV and ESR spectra. About one half of overall titanium content could be converted to mononuclear η^3-allyltitanocene-like species, stable up to 400°C. This exceptional thermal stability is ascribed to a firmly bound allyl containing ligand.

The dimeric titanocene, μ-(η^5:η^5-fulvalene)-di-μ-hydrido-bis(η^5-cyclopentadienyltitanium(III)) (FHT), and the catalytic system Cp_2TiCl_2–$LiAlH_4$ have been shown to catalyze intramolecular double bond shifts in dienes and olefins to give the most stable isomers[1–4]. The advantage of FHT lies in its high thermal stability which is superior to other titanocene hydride species formed *in situ* in systems Cp_2TiCl_2–$LiAlH_4$ or $(Cp_2TiCl)_2$–$LiAlH_4$ in hydrocarbon media[4,5].

While the latter species reacts quantitatively with sterically unhindered dienes at room temperature to give η^3-allyltitanocene derivatives[4,5], FHT mostly starts to react with unsaturated hydrocarbons at 140°C only[1–3]. The reaction onset always coincides with the occurence of ESR single-line signals having g-values and the line half-widths ($g \sim 1{\cdot}993$, $\Delta H = 0{\cdot}3-0{\cdot}6$ mT) in the same region as allyltitanocene derivatives[1,4,6]. The corresponding paramagnetic species was therefore assumed to exhibit a catalytic activity, inducing low-activation energy reactions such as *E,Z*-isomerization, double bond shifts and intramolecular cyclizations. In some thermodynamically favored cases the above processes were accompanied by intermolecular hydrogen transfer reactions yielding *e.g.*, 5,6,7,8,9,10-hexahydrobenzocyclooctene from *Z,E,E*-1,5,9-cyclododecatriene[7], indan from bicyclo[4.3.0]nona-3,7-diene and ethylbenzene from 4-vinylcyclohex-1-ene at 240°C (see[8]).

In this communication we report on the application of FTH and its derivative, μ-(η^5:η^5-fulvalene)-μ-chloro-μ-hydrido-bis(η^5-cyclopentadienyltitanium (III)) (FCHT), to the catalysis of the intermolecular hydrogen transfer reactions at higher temperatures, whereby examples of both cyclic and linear unsaturated hydrocarbons have been investigated. The catalytic behavior of the systems is correlated with the nature and concentration of the paramagnetic species formed by the interaction of FHT or FCHT with unsaturated hydrocarbons.

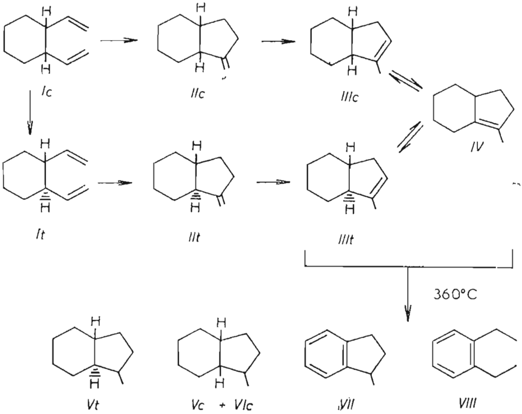


FHT (X = Y = H)
FCHT (X = Cl, Y = H)

Isomerizations and Intermolecular Hydrogen Transfer Reactions

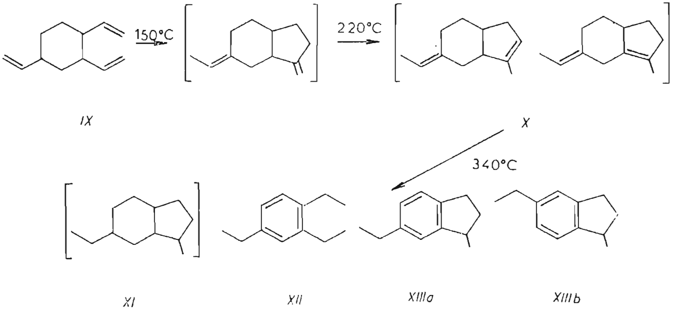
cis-1,2-*Divinylcyclohexane* (Ic). *cis*-1,2-Divinylcyclohexane (*Ic*) has recently been employed in an attempt to prepare 1,2-bis-(ethylidene)cyclohexane isomers; it was found, however, that the double bond shift participated only in the initial isomerization of *Ic* to *trans*-1,2-divinylcyclohexane (*It*) (Scheme 1) (ref.[2]). Both *Ic* and *It* then underwent a very easy cyclization to 7-methylene-*trans*-bicyclo[4.3.0]nonane (*IIt*) and 7-methylene-*cis*-bicyclo[4.3.0]nonane (*IIc*), followed by the shift of the exomethylene double bond into the cycle. This shift was completed at 220°C, the resulting equilibrium mixture containing 7-methyl-*cis*-bicyclo[4.3.0]non-7-ene (*IIIc*) 45%, 7-methyl-*trans*-bicyclo[4.3.0]non-7-ene (*IIIt*) 38% and 7-methylbicyclo[4.3.0]non-6-ene (*IV*) 10% in addition to minor amounts of unidentified hydrocarbons. The solution of FHT in this mixture was exposed to a further temperature increase with the aim to examine the activity of the catalyst in the hydrogen transfer reactions at high temperatures.

Above 220°C the content of *IIIc* and *IV* in the equilibrium mixture slowly increased at the expense of *IIIt*. At 280°C the latter isomer started to disproportionate to 7-methyl-*trans*-bicyclo[4·3·0]nonane (*Vt*) and 1-methylindan (*VII*). At temperatures 300 – 310°C *IIIt* was already consumed and the ratio *IV* : *IIIc* increased to one. At yet higher temperatures another two saturated hydrocarbons *Vc* and *VIc* were formed at the expense of both *IIIc* and *IV* (Scheme 1). The structure of *Vc* and *VIc* followed from the ^{13}C NMR and mass spectra of a mixture, although the configuration of the methyl group was not assigned. At the optimum temperature (360°C) a mixture of saturated hydrocarbons 61% (among them *Vt* 18%, (*Vc* + *VIc*) 19%) and *VII* 22% was obtained while the most stable olefin *IV* amounted to 8% only. The presence of *o*-diethylbenzene (*VIII*) 3% found already at 340°C gave evidence for the formation of intermediate 1,2-*bis*-(ethylidene)cyclohexanes under isomerisation conditions, although they were neither detected nor separated from the olefinic mixture because of their minor content. The complementary 1,2-diethylcyclohexane was detected by gas chromatography – mass spectrometry (*m*/*z* 120, 111, 69) in an amount lower by one order than that of *VIII*, which indicates that 1,2-*bis*(ethylidene)cyclohexanes are better hydrogen donors than *IIIc* and *IV*. An unidentified tar (7 weight %) arose probably from polymerization of intermediate cyclohexadienes and indenes. Identical results (throughout the reaction Scheme 1) were obtained when (*E*,*Z*)-1,5-cyclodecadiene was used as a starting compound instead of *Ic*, because the former was converted to *Ic* at 140°C *via* the Cope rearrangement[1].



1,2,4-*Trivinylcyclohexane* (IX). The isomerization of *IX* is very complicated because of a variety of geometrical isomers formed as intermediates which precludes a detailed study. However, the disappearance of the vinyl absorption band ν(C=C) at 1 643 cm^{-1} and the occurrence of another ν(C=C) band of the exomethylene group at 1 654 cm^{-1} showed that the cyclization of the vicinal vinyl groups was the main isomerization process at 150°C. The isolated vinyl group was simultaneously isomerized to the ethylidene group as shown previously for vinylcycloalkanes[3].

The increase of the isomerization temperature to 220°C led to the disappearance of the $\nu(C{=}C)$ absorption band of the exomethylene group and a mixture of *cis*- and *trans* annelated isomers of 3- and 4-ethylidene-7-methylbicyclo[4.3.0]non-7-enes and 3- and 4-ethylidene-7-methylbicyclo[4.3.0]non-6-enes (*X*) was obtained (Scheme 2). These intermediate components were identified only tentatively by gas chromatography – mass spectrometry. A further heating of this reaction mixture to 320°C afforded a mixture of saturated hydrocarbons (*XI*), 1,2,4-triethylbenzene (*XII*) (12%) and 1-methyl-6-ethylindan (*XIIIa*) and 1-methyl-5-ethylindan (*XIIIb*). The position of the alkyl groups in the latter two isomers was established by means of their proton-coupled ^{13}C NMR spectra. With *XIIIa* the signal of the sp^2 methine, oriented *meta* with respect to the ethyl group, appears as a triplet due to two equal ^3J couplings with the protons of the ring methylene group. With *XIIIb* the same signal appears as a singlet broadened by ^2J and ^3J interactions. In line with this assignment the signal of the quaternary sp^2 carbon in the vicinity of the methyl group appears at a lower field in *XIIIa* (148·7) than in *IIIb* (146·2) because of the *para*-effect of the ethyl group[9]. From completed formation of *XII* at 320°C it follows that the intramolecular hydrogen transfer is easier than the intermolecular one. The higher content of *XII* in comparison with that of *VIII* indicates that the isolated vinyl group influences the competitive cyclization and double bond shifts of vicinal vinyl groups in favor of the latter process. The nearly equimolar amounts of *XIIIa* and *XIIIb* increased with the temperature and time to give about 40% of the total amount of the recovered C_{12} hydrocarbons at 340°C after 15 h (Table I). The complementary saturated hydrocarbons *XI* amounted to 45%, while unidentified residues of olefinic hydrocarbons represented only 5% of all C_{12} products. The ratio of the saturated to aromatic hydrocarbons arising from the hydrogen transfer only is slightly higher than one. This disagreement with the theoretical stoichiometric ratio 1 : 2 is due to the



relatively high amount of undestillable tar (20 weight %) which is probably formed from styrene and indene derivatives.

1-*Alkenes.* 1-Decene isomerized at 180°C completely to a mixture of *trans*- and *cis*-decenes, the former isomers predominating. The intermolecular hydrogen transfer occured at 290°C, the yield of n-decane (10%) increasing with rising temperature to 41% of all C_{10} products at 360°C. The other C_{10} products consisted of different internal decenes, beside minute amounts (less than 1% each) of isopropyltoluene and butylbenzene as detected by gas chromatography – mass spectrometry. The tar formed in about 10 weight % of the original 1-decene is probably composed of highly unsaturated products.

1-Tetradecene behaved in all respects similarly as 1-decene giving n-tetradecane as the final product; the absence of skeletally isomerized branched tetradecanes was proved by NMR and mass spectral data. However, at 354°C the observable traces of products of C_{14} hydrocarbon cracking appeared, becoming more abundant at higher temperatures (Table II). A blank experiment, in which the hydrocarbon products isolated after heating with FHT to 310°C were heated further to 402°C in the absence of FHT showed that this thermal cracking was not affected by the catalyst except that more tetradecenes remained in the reaction mixture in this case.

Catalyst and Mechanism of Catalysis

Green solutions of FHT and FCHT in aromatic solvents are stable up to 250°C, while the solutions in the above mentioned unsaturated hydrocarbons turn to brown above 200°C and the colour deepens during heating to higher temperatures. The

TABLE I

The concentration of paramagnetic species and the composition of products in the isomerization of *IX* with FCHT[a] at 340°C

Duration h	Concentration, mol l^{-1} . 10^{-3}		Product composition, %				
	Cp'_2TiR	other species	*X*	*XI*	*XII*	*XIIIa*	*XIIIb*
1	1·9	5·5	48	23	12	9	8
3	2·8	5·9	25	34	15	15	14
6	3·0	6·9	16	40	12	17	15
12	3·0	7·1	44	5	12	21	18

[a] Initial concentration of FCHT was $8{\cdot}3 \, . \, 10^{-3}$M.

TABLE II

Concentrations of paramagnetic species and yields of *n*-tetradecane in systems FHT and FCHT — 1-tetradecene after heating to different temperatures[a]

Temperature °C	Catalyst	*g*-Values of ESR signals		Concentration (10^{-3}M)		*n*-Tetradecane, %[b]
		Cp'_2TiR	other species	Cp'_2TiR	others	
188	FHT	1·9937	1·9865 ≫ 1·980 ≫ 1·975	0·20	0·36	—
	FCHT	1·9937	1·9865 ≫ 1·980 ~ 1·975	0·20	0·34	—
216	FHT	1·9939	1·9865 ≫ 1·980 ≫ 1·975	0·22	0·27	—
	FCHT	1·9939	1·9865 [illegible] 1·980 ~ 1·975	0·22	0·28	—
254	FHT	1·9940	1·9865 negligible	0·51	0·61	—
	FCHT	1·9940	1·9865 [illegible] 1·9820	0·63	1·4	—
310	FHT	1·9944	1·9865	0·83	1·0	13
	FCHT	1·9942	1·9820	0·78	2·0	15
354	FHT	1·9944	—	2·2	0·7	33
	FCHT	1·9944	1·970 very broad	2·7	2·1	49
374	FHT	1·9944	—	2·7	0·5	42[c]
	FCHT	1·9944	1·970 very broad	3·9	2·1	56[c]
402	FHT	1·9945	—	4·4	0·6	74[c]
	FCHT	1·9945	1·970 very broad	4·3	3·1	68[c]

[a] Initial concentrations [FHT] = 4·6 . 10^{-3}M, [FCHT] = 4·9 . 10^{-3}M, heating period 3 h. [b] Related to C_{14} hydrocarbons (100%). [c] At 374°C about 15% and at 402°C about 43% of cracking products were formed independently of the catalyst type.

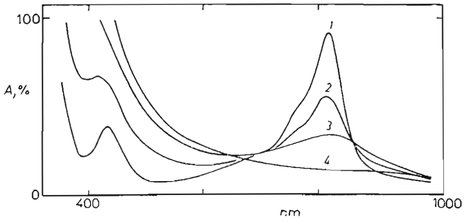


FIG. 1

The electronic absorption spectra of the system FHT–1-tetradecene: *1* initial solution, after heating to 188°C — *2*, 254°C — *3* and 310°C — *4* electronic absorption spectra showed that the complexes FHT (λ_{max} = 425 and 828 nm, Fig. 1) and FCHT (λ_{max} = 480 and 650 nm) disappeared, while a new continuous absorption covering the whole visible range intensified with rising temperature. The intensity of this absorption increased from about 1 000 nm to shorter wavelengths, obscuring the distinct absorption bands of residual FHT and FCHT and/or their intermediate thermolytic products which were formed at 254°C from both FHT and FCHT. The former decomposition product exhibits a broad absorption band at 800 nm (Fig. 1, 3), the latter forms a shoulder at 560 nm. At 310°C both intermediates were already absent while the edge of the complete absorption shifted to longer wavelengths (Fig. 1, 4).

The ESR spectra indicated the appearance of a paramagnetic species at 140°C, the temperature at which the first isomerization products were detected in all systems under study. Weak ESR single-line signals at g = 1·9937, 1·9865, 1·980 and 1·975 appeared after heating to 180°C, their intensity increasing on heating to 200°C. Of these, only the first signal grew steadily in intensity on further heating up to 400°C and its g-value moved to final 1·9945. In the temperature range 300 to 400°C the other signals disappeared nearly completely in systems containing FHR, but in systems containing FCHT another very broad signal at g = 1·970 appeared and its intensity became comparable with that of the signal at g = 1·9945. A quantitative evaluation of intensities of ESR signals in the tetradecene solutions of FHT and FCHT after heating is given in Table II. The yields of paramagnetic species obtained at particular temperatures were independent of preceding heating of the sample at any lower temperature. It was shown on the system FCHT-*IX* kept at 340°C for different time periods (Table I) that the heating longer than 3 h did not increase substantially the concentration of the paramagnetic species responsible for the ESR signal at 1·9944, though the hydrocarbon system required much longer time to approach the equilibrium composition. The results showed that this paramagnetic species was stable at 340°C and its stability at lower temperature was proved by repeated ESR measurements of the samples either immediately after heating or after 6 months standing at room temperature.

From the catalytic point of view only the ESR single-line signal at g = 1·9937 to 1·9945 is of direct interest because it occurs in the whole temperature range in which the catalytic activity is observed, too. Its g-value is nearly the same as the g-values of η^3-allyltitanocene derivatives (g = 1·9927 – 1·9938) (ref.[4,6,10]) which are the highest g-values observed for any Ti(III) compounds known so far. Related alkyltitanocene compounds display ESR signals at g-values ranging from 1·965 for tert-alkyltitanocenes to 1·983 for n-alkyltitanocenes[10]. ESR spectra of titanocene hydride complexes containing aluminium hydrides are observed at g = 1·988 – 1·991 (ref.[5]). The virtual coincidence of the g-values of the above paramagnetic species and those of η^3-allyltitanocene derivatives (Cp_2TiR) implies the similarity of the intimate surrounding of titanium atoms in both types of compounds. Moreover, the identity of isomerization products of 1,5-dienes and vinylcycloalkanes obtained both by the Cp_2TiCl_2–$LiAlH_4$ system producing Cp_2TiR and by the FHT catalyst[3] indicates the close similarity of catalytic particles.

The η^3-allyltitanocene-like compounds (Cp'TiR) obtained from FHT and FCHT are probably produced in an analogous way as the Cp_2TiR complexes which can be prepared from titanocene hydride complexes in systems Cp_2TiCl_2–$LiAlH_4$ and $(Cp_2TiCl)_2$–$LiAlH_4$ (ref.[4,5,10]). The latter hydrides react with dienes to give Cp_2TiR quantitatively, while their reaction with olefins gives rise to alkyltitanocenes which are unstable at ambient temperature and disproportionate to give Cp_2TiR, albeit in a low yield[10]. We suggest that above 140°C, FHT and FCHT react with olefins by addition of the bridging Ti–H group, giving thus an alkyltitanocene-like derivative which, at these temperatures, is transformed to a more stable η^3-allyl derivative Cp'_2TiR by the intermolecular hydrogen transfer to another olefin molecule.

The species Cp'_2TiR differ from Cp_2TiR by their exceptional thermal stability. The latter compounds are stable in the medium of appropriate diene up to 100°C but at higher temperature in the dienes or at lower temperatures in other hydrocarbon solvents they decompose to give diamagnetic products mostly insoluble in the hydrocarbons. On the other hand, the concentration of Cp'_2TiR species increased in all studied systems up to the optimum temperature of the intermolecular hydrogen transfer. In tetradecene the Cp'_2TiR concentration increased up to 400°C,

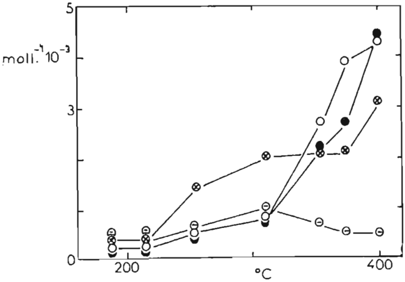


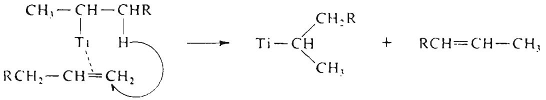
FIG. 2

Plots of concentrations of Cp'_2TiR and the sum of other paramagnetic particles in systems FHT and FCHT-1-tetradecene in dependence on the temperature of heating: ● — Cp'_2TiR — FHT, ⊖ — other particles — FHT, ○ — Cp'_2TiR — FCHT, ⊗ — other particles — FCHT the temperature at which the extensive thermal cracking of the hydrocarbons occurred. The radicals formed in the homolytic scission of an alkyl chain at 354°C and higher temperatures probably did not effect considerably the formation of Cp'_2TiR as evident from the plot of Cp'_2TiR concentrations against temperature (Fig. 2). The concentrations of Cp'_2TiR approach the initial molar concentrations of FHT and FCHT at 400°C. While in the case of FHT the species Cp'_2TiR gives the only observable distinct ESR signal, in the FCHT system, another signal of Ti(III) species is formed in an amount comparable to that of Cp'_2TiR. This indicates that in both systems Cp'_2TiR is probably a mononuclear titanium compound. The other product of the dissociation of FHT is diamagnetic, while that of FCHT gives at least partly a paramagnetic product. The g-value equal to 1·970 and the large line-width may indicate that the latter compound is structurally similar to the dimer of titanocene chloride (Cp_2TiCl_2) ($g = 1{\cdot}977$, $\Delta H = 9{\cdot}2$ mT) (ref.[4]).

The high stability of Cp'_2TiR has to be due to a strengthening of the Ti–η^3-allylic bond because the high stability of η^5-Cp–Ti bonds in a Cp_2Ti^+ ion is well known. η^n-Cycloalkenyl and alkadienyl structures ($n = 3, 5$) of the ligand can be excluded as η^3-allyltitanocene compounds derived from cyclic dienes having the number of ring carbon atoms less than ten are unstable[6] and also the third cyclopentadienyl group of tris(cyclopentadienyl)titanium is bonded by the weak σ-bond as a consequence of the sterical hindrance[11]. On the other hand, the conjugation of a double bond to the η^3-allylic group does not increase substantially the strength of the η^3-allyl–Ti bond[12]. We suggest that the high stability of Cp'_2TiR is probably achieved by bonding of the η^3-allylic group to the cyclopentadienyl ligand(s) which may occur simultaneously with the scission of the fulvalene ligand.

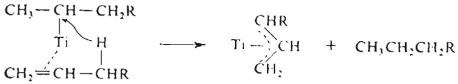
The isomerization of olefins probably proceeds through the addition and elimination of a titanocene hydride function according to Eq. (A) or through a displacement mechanism in which the β-hydrogen atom of the alkyl group to be displaced is transferred to the coordinating olefin in the transient complex (Eq. (B)).

$$RCH_2{-}CH{=}CH_2 + Ti{-}H \longrightarrow RCH_2{-}(CH{-}Ti){-}CH_3 \longrightarrow RCH{=}CH{-}CH_3 + Ti{-}H \qquad (A)$$



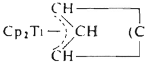
(B)

The intermolecular hydrogen transfer can be explained by a displacement mechanism in which the hydrogen is transferred from coordinating olefin to the leaving alkyl group (Eq. (C)).

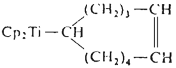

(C)

The formation of a great variety of products by the action of this type of catalyst is visualized by an example using the well defined η^3-allyltitanocene derivative. The isomerization of (*Z*,*E*)-1,5-cyclodecadiene catalyzed by 1,3-heptamethylene-η^3-allyltitanocene (*A*) at 100°C led to the equilibrium hydrocarbon mixture containing the most abundant (Z,Z)-1,6-cyclodecadiene (89)% and only minor amount of (Z,Z)-1,3-cyclodecadiene (8%) while (*A*) remained the only detectable alkenyltitanocene derivative during and after the isomerization[1]. It means that the main isomerization product had to be produced by a nondetectable amount of unstable cyclodec-5-ene-1-yltitanocene (*B*).

A



B



A very similar situation occurs in FHT and FCHT induced isomerization and intermolecular hydrogen transfer reactions. In this case the very stable Cp'_2TiR compound should be in equilibrium with probably negligible amounts of all possible alkyl, alkenyl and alkadienyl titanocene derivatives which all together bring the hydrocarbon system into equilibrium.

The present results may offer an alternative explanation for the conversion of ethylene to ethane and 1,3-butadiene which was reported to be catalyzed by FHT (ref.[13]). The maximum number of 22 turnovers for the formation of butadiene was obtained in THF solution at 100°C after 78 h. Instead of the postulated stereospecific addition of two ethylene molecules to the Ti–Ti frame followed by the formation of a dititanacyclohexane derivative eliminating butadiene, the whole process including the formation of observed by-products can be explained as follows. 1-Butene, formed in the oligomerization of ethylene under the described conditions, may react with ethylene by the FHT-catalyzed intermolecular hydrogen transfer reaction yielding ethane and 1,3-butadiene. The excess of ethane (3 to 30-times more than butadiene) can arise from the hydrogen transfer reaction with other formed oligomers. The relatively mild conditions of the hydrogen transfer reactions may be due to both the solvating effect of THF and high reactivity of ethylene. The brown colour of the catalytic solution reported for the ethylene converting reaction may indicate that the catalytic species was the same as that proposed to catalyze the intermolecular hydrogen transfer in higher olefinic hydrocarbons.

EXPERIMENTAL

Chemicals. Dimeric titanocene-μ-(η^5:η^5-fulvalene-di-μ-hydrido-bis(η^5-cyclopentadienyltitanium) (FHT) was prepared by the reaction of Cp_2TiCl_2 with $LiAlH_4$ (Metallgeselschaft, A.G., Frankfurt a.M.) in boiling mesitylene[14]. μ-(η^5:η^5-Fulvalene)-μ-chloro-μ-hydrido-bis(cyclopentadienyltitanium) (FCHT) was prepared by the same method as FHT but the reaction was stopped by cooling to room temperature soon after the yellow green colour of $(Cp_2TiCl)_2$ changed to the dark green colour of FCHT. The content of FHT in the product was decreased to 2% by the extraction of the solid product with n-hexane. The purity of FHT and FCHT as well as concentrations of their benzene solutions were determined by electronic absorption spectra using molar extinction coefficients of absorption bands: FHT — 828 nm, $\varepsilon = 1\,980$, FCHT — 650 nm, $\varepsilon = 1\,180$ l cm mol^{-1} (ref.[14]).

cis-1,2-Divinylcyclohexane, 1,2,4-trivinylcyclohexane, 1-decene (all Fluka) were distilled *in vacuo* onto FHT and the solutions were heated to 130°C for 3 h to remove all oxygenated impurities. The hydrocarbons were distilled *in vacuo* on a new portion of FHT and the process was repeated until the solution remained green after heating to 130°C. 1-Tetradecene (Koch Light) was distilled *in vacuo* on FHT or FCHT and appeared to be pure since the solutions remained green even at 130°C.

Isomerizations. Benzene solutions of FHT and FCHT were evaporated and the solid complexes dissolved in olefinic hydrocarbons to be isomerized. The green solutions of FHT and FCHT ($0{\cdot}5-1{\cdot}0 \,.\, 10^{-2}$M) were distributed (~0·5 ml) into ESR tubes (Simax glass, $d = 3{\cdot}0$ mm) and the tubes were sealed off. The ESR tubes were heated at the required temperature at least for 3 *h* and after the measurement of ESR spectra at room temperature they were opened to air and the products were distilled *in vacuo* to separate the hydrocarbons from tar and oxygenated rests of catalysts. About 5 ml of the solutions were isomerized in sealed tubes when the samples served for the gas chromatographic isolation of pure product components.

Methods. The ESR spectra were taken on an ERS-220 spectrometer (ZWG-DAW, Berlin, GDR) in the X-band at room temperature. Concentrations of paramagnetic particles were determined by comparison with the standard solution of DPPH using integrated records. The electronic absorption spectra were taken on a Varian Cary 17 D spectrometer using sealed quartz cuvettes. The gas chromatographic analyses and preparations were carried out on Perkin-Elmer F-21 preparative gas chromatograph using Carbowax M-20 (10% on Chromaton N-AW) and SE-30 (15% on Chromaton N-AW) columns (4 m ~ 10 mm). The mass spectra were recorded on a JEOL JMS D-100 spectrometer at 75 eV, using the gas chromatograph — mass spectrometer coupling. Infrared spectra were recorded in thin film on a UR-75 spectrometer (Zeiss, Jena) and a Fourier transform spectrometer Nicolet MX-1E. ^1H and ^{13}C NMR spectra were taken on a JEOL FX-60 spectrometer at 60 MHz and 15·897 MHz — FT-mode, respectively. (Chemical shifts in the δ (ppm) scale).

Products from Ic. The compounds were isolated by preparative gas chromatography from distillable products of *Ic* after heating with FHT to 290°C (*IV*) and 360°C (*Vt*, *Vc*, *VIc*, *VII* and *VIII*). 7-Methylbicyclo[4.3.0]non-6-ene (*IV*) — mass spectrum gives formula $C_{10}H_{16}$; ^1H NMR spectrum: 0·74—2·61 mt, 1·60 br s (3 H); ^{13}C NMR spectrum: 13·8 q, 26·1 t (2 C), 26·7 t, 29·4 t, 35·9 t, 37·0 t, 48·9 d, 127·8 s, 137·0 s; IR spectrum (cm^{-1}): 2 900—2 950 vs, b, 2 850 vs, 1 448 s, 1 383 m, 1 335 w, 1 303 vw, 1 261 w, 1 244 w, 1 217 vw, 1 166 vw, 1 146 vw, 1 120 vw, 1 103 vw, 1 061 w, 977 vw, 960 vw, 837 w. 7-Methyl-*trans*-bicyclo[4.3.0]nonane (*Vt*) — mass spectrum gives formula $C_{10}H_{18}$; ^1H NMR spectrum: 0·70—2·05 mt, 0·93 d ($J = 6{\cdot}4$ Hz, 3 H); ^{13}C NMR spectrum: 18·7 q, 26·4 t, 26·5 t, 30·0 t, 30·3 t, 31·6 d, 32·3 t, 39·2 t, 46·8 d, 53·7 d; IR spectrum: 2 910—2 953 vs, 2 852—2 870 vs, 1 450 s, 1 378 m, 1 313 w, 1 264 vw, 1 253 vw, 980 vw, 932 vw, 842 w. The position of the methyl group was not determined. 7-Methyl-*cis*-bicyclo[4.3.0]nonanes (*Vc* and *VIc*) differing probably in *syn*- and *anti*-position of the methyl group were not separated by gas chromatography. The evidence for the presence of two isomers (1:1) was obtained from ^{13}C NMR spectrum: 17·8 q (2C) 20·4 d, 22·4 d, 24·9 t, 26·2 t, 26·6 t, 26·8 t, 27·9 t, 29·0 t, 29·8 t, 31·4 t, 32·1 t, 32·7 t, 34·4 t, 34·5 t, 39·2 d, 42·0 d, 47·0 d, 49·4 d. Mass spectrum gives formula $C_{10}H_{18}$; ^{1}H NMR spectrum: 0·80–2·45 mt, 0·78 d (J = 6·8 Hz, 0·92 d (J = 6·4 Hz); IR spectrum: 2 960–2 900 vs, 2 866–2 853 vs, 1 462 sh, 1 449 s, 1 377 s, 980 vw, 955 vw, 851 vw, 841 vw, 800 vw. 1-Methylindan – mass spectrum and infrared spectrum agree with the literature data, ^{1}H NMR spectrum: 1·28 d (J = 6·7 Hz, 3 H), 1·39–3·49 mt (5 H), 7·18 br s (4 H); ^{13}C NMR spectrum: 19·9 q, 31·5 t, 34·8 t, 39·4 d, 123·1 d, 124·3 d, 126·1 d (2 C), 143·8 s. 1,2-Diethylbenzene (*VIII*) was identified by mass spectrum, ^{1}H and ^{13}C NMR and IR spectra; all agreed with the literature data.

Products from IX. The compounds were isolated by preparative gas chromatography from a hydrocarbon mixture distilled out after heating of *IX* with FHT to 320°C for 8 h. *Cis* and *trans* isomers of both 3-ethyl-7-methylbicyclo[4.3.0]nonane and 4-ethyl-7-methylbicyclo[4·3·0]nonane (all together *XI*) gave mass spectra fitting to formula $C_{12}H_{22}$. The absence of double bonds in this mixture of hydrocarbons was proved by ^{1}H and ^{13}C NMR spectra. 1,2,4-Triethylbenzene (*XII*) – mass spectrum, NMR and IR spectra were compatible with the structure. 1-Methyl-6-ethylindan (*XIIIa*) – mass spectrum gave formula $C_{12}H_{16}$; ^{1}H NMR spectrum: 1·22 t (J = 7·3 Hz, 3 H), 1·27 d (J = 7·3 Hz, 3 H), 1·53–3·33 mt (7 H), 7·02 mt (3 H); ^{13}C NMR spectrum: 16·0 q, 19·8 q, 28·9 t, 31·0 t, 35·0 t, 39·4 d, 122·7 d, 124·1 d, 125·8 d, 141·1 s, 142·3 s, 148·9 s; IR spectrum: 1 873 w, 1827 vw, 1 760 w, 1 614 m, 1 580 w, 1 490 s, 1 455 vs, 1 375 s, 1 333 m, 1 320 m, 1 296 w, 1 140 m, 1 062 m, 887 s, 825 s, 731 w, 706 w, 449 m. 1-Methyl-5-ethylidan (*XIIIb*) – mass spectrum gave formula $C_{12}H_{16}$; ^{1}H NMR spectrum: 1·20 t (J = 6·7 Hz, 3 H), 1·29 d (J = 7·3 Hz, 3 H), 1·58–3·33 mt (7 H), 7·04 mt (3 H); ^{13}C NMR spectrum: 16·0 w, 20·0 q, 28·9 t, 31·5 t, 35·1 t, 39·1 d, 123·1 d, 123·8 d, 125·8 d, 144·1 s. IR spectrum: 1 875 w, 1 827 vw, 1 753 w, 1 614 m, 1 580 w, 1 490 s, 1 455 vs, 1 375 s, 1 333 s, 1 210 w, 1 140 m, 1 078 m, 1 064 m, 882 s, 826 vs, 602 m, 581 m.

Products from 1-*decene*. After heating of 1-decene with FHT to 360°C for 3 h three fractions were separated by preparative gas chromatography, containing n-decane, a mixture of *trans*-decenes and mixture of *cis*-decenes. n-Decane – mass spectrum gives formula $C_{10}H_{22}$; ^{1}H NMR spectrum: 0·88 t (J = 6·1 Hz, 3 H), 1·25 br s (8 H); ^{13}C NMR spectrum: 14·2 q, 27·9 t, 29·6 t, 29·9 t, 32·1 t. NMR data are consistent with the structure of nonbranched linear hydrocarbon (ref.[15]). *trans*-(2–5)-Decenes were characterized by the infrared spectrum: 3 006 s, 2 850 to 2 950 vs, 1 464 s, 1 440 sh, 1 380 m, 970 s, 726 m, *cis*-(2–5)-Decenes gave IR spectrum: 3 013 s, 2 850–2 950 vs, 1 654 w, 1 461 s, 1 404 w, 1 380 m, 725 w, 702 m. The distribution of decene isomers differing by the position of the double bond was estimated from the products of potassium permanganate oxidation[16] which yielded generally pairs of carboxylic acids. Relative abundances of their methyl esters, determined by gas chromatography, showed unequivocally that 2- and 3-decenes were the most abundant isomers, though the complementary C-2 and C-3 esters were detected in unsatisfactorilly low yields, due to work-up losses.

Products from 1-*tetradecene*. Tetradecane was isolated by column chromatography (silica gel, n-hexane) form the reaction mixture obtained by heating 1-tetradecene with FHT to 310°C for 3 h. n-Tetradecane – mass spectrum fits to formula $C_{14}H_{30}$; IR spectrum: 2 850–2 950 vs. 1 466 s, 1 380 m, 1 306 w, 894 w, 725 m. Internal tetradecenes were predominantly *E*-isomers as evidenced by strong infrared band at 970 cm^{-1}.

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