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DIMERIZATION AND CODIMERIZATION OF HIGHER α -OLEFINS, CATALYZED

BY ZIRCONIUM COMPLEXES

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Information on the dimerization of α -olefins, containing five and more C atoms, in the presence of metal-complex catalysts is very scanty. Nickel complexes, which are the most active catalysts for the dimerization of the lower α -olefins, are inefficient in the dimerization of the higher α -olefins [1]. Thus, 1-pentene is dimerized by Ni catalysts to give a mixture of decenes in 40% yield, while the higher α -olefins are isomerized to olefins with an internal position of the C=C bonds [1]. The dimerization up to C₁₀ α -olefins on either TiCl₃-CH₃AlCl₂ or TiCl₄-Al₂Et₃Cl₂ complexes leads together with dimers, to trimers and tetramers, including those with isomerized double bonds [2-4].

In order to develop highly selective and active catalysts for the dimerization and codimerization of α -olefins we studied the complexes of zirconium with alkylaluminum halides, which are active in the dimerization of ethylene and 1,3-dienes of variable structure [5]. The most active catalytic system for the dimerization and codimerization of the higher α olefins was obtained by reducing $Zr(OC_4H_9)_4$ with diethylaluminum chloride. The reaction proceeds under mild conditions ($\sim 20^{\circ}$ C) and the yield of the dimers decreases substantially with increase in the number of C atoms in the olefin. Thus, 1-hexene on the catalyst $Zr(OC_4H_9)_4$ -(C_2H_5)_2AlCl (1:12) (Ct) in CH_2Cl_2 solution, at $\sim 20^{\circ}$ C, is converted with a high selectivity and in over 80% yield to 5-methyleneundecane (Ia). 1-Octene under analogous conditions gives 7-methyleneheptadecane (Ib) in $\sim 60\%$ yield. The unconverted 1-octene is partially isomerized with a shift of the C=C bond. Dimers are not obtained from 1-decene under these conditions. The structure of dimers (Ia, b) was confirmed by the IR, PMR, and mass spectra.

The yield of the dimers is increased by increasing the temperature of the process, but here the selectivity of the reaction drops. In particular, 1-hexene on Ct at 100° is converted to a mixture of 5-methylundecane (IIa), 5-methyl-cis-5-undecene (IIIa), 5-methyl-trans-5-undecene (IVa), and 5-methyltrans-7-undecene (Va) in a 30:20:28:22 ratio, with a yield of \geq 95%. From 1-octene under the same conditions were obtained 7-methyleneheptadecane (Ib), 7methylheptadecane (IIb), and 7-methyl-trans-7-heptadecane (IVb) in a 62:12:26 ratio, with an overall yield of 90%. 1-Decene under the same conditions is dimerized in 20% yield to 9methylenenonadecane (Ic). At 150° the decane is converted with a high selectivity to 9methylnonadecane (IIc) (\sim 70% yield):



 $R = C_3H_7$ (a), C_5H_{11} (b), C_7H_{15} (c).

As a result, when the temperature is raised there is observed, besides the dimerization of the higher α -olefins, also their subsequent hydrogenation, apparently under the influence of the hydride complexes of zirconium.

Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2320-2322, October, 1980. Original article submitted November 19, 1979. In contrast to the C_6-C_{10} α -olefins, trimethylvinylsilane, both at 25° and at higher temperature, is dimerized almost exclusively and in high yield (over 90%) to trans-1,4-(trimethylsilyl)-1-butene (VI).

In order to obtain methylenealkanes of variable structure we studied the codimerization of 1-hexene with propylene and 1-octene on Ct. 1-Hexene reacts with propylene and is converted to 2-methyleneoctane (VIIa) and 4-methyleneoctane (VIIIa) in a 3:1 ratio. The codimerization of equimolar amounts of 1-hexene with 1-octene leads to homodimers (Ia, b) and codimers (VIIb) and (VIIIb), the amount of which in the mixture of hydrocarbons is 50%. Unfortunately, we were unable to separate the hydrocarbon pairs (VIIb-VIIIb) and (VIIa-VIIIa) due to their close boiling points.

 $\begin{array}{c} 2 \ (\mathrm{CH}_3)_3 \mathrm{Si} \longrightarrow & (\mathrm{CH}_3)_3 \mathrm{Si} \longrightarrow & (\mathrm{Si}(\mathrm{CH}_3)_3 \ (\mathrm{VI}) \\ & & & & \\ \mathrm{R} \longrightarrow & \mathrm{R} \longrightarrow & \mathrm{R} \longrightarrow & \mathrm{R'} + \mathrm{R'} \longrightarrow & \mathrm{R'} \\ & & & & (\mathrm{VIIa}, \mathrm{b}) \end{array} \\ \mathrm{R} = \mathrm{H}, \ \mathrm{R'} = \mathrm{C}_3 \mathrm{H}_7, \ \mathrm{a}), \ \mathrm{R} = \mathrm{C}_3 \mathrm{H}_7, \ \mathrm{R'} = \mathrm{C}_5 \mathrm{H}_{\mathrm{II}} \ (\mathrm{b}). \end{array}$

The obtained results make it possible to conclude that the complexes of zirconium with alkylaluminum halides are efficient catalysts for the dimerization of the higher α -olefins. Here the yield of the dimers decreases with increase in the number of C atoms in the α -olefin and at the same time the degree of migration of the C=C bonds in them decreases.

EXPERIMENTAL

The employed olefins were at least 98% pure and prior to use were distilled over $i-Bu_3Al$. The PMR spectra were recorded on a Tesla 480-BS instrument (in CCl₄ solution, and using HMDS as the internal standard), the IR spectra were recorded on a UR-20 spectrophotometer (as a film), and the mass spectra were recorded on an MX-1306 instrument (energy of ionizing electrons = 70 eV).

The GLC analysis was run on a Chrom-41 instrument, which was equipped with a flame-ionization detector and two columns: 1) 4.7×3 mm, packed with 15% Carbowax-6000 deposited on Chromaton N-AW (for the hydrocarbons up to C₁₉), and 2) 4.7×3 mm, packed with 15% Carbowax-1500 deposited on Chromaton N-AW (for the C₁₇ hydrocarbons and higher). Helium was used as the carrier gas at a flow rate of 60 ml/min. The products were separated on a model LKhP-71 preparative chromatograph, equipped with a 5.04×18 mm column packed with 20% Carbowax-6000 deposited on Chromosorb A. The carrier gas was helium at a flow rate of 700 ml/min, and the volume of the samples was 200 µl.

Dimerization and Codimerization of Olefins. Into a 300-ml stainless-steel autoclave, in a dry argon stream, were charged a solution of 3.83 g (10 mmoles) of $Zr(OBu)_4$ in 20 ml of either toluene or CH_2Cl_2 , 14 g (120 mmoles) of $AlEt_2Cl$, and 1 mole of the α -olefin, and the mixture was kept for 3 h. Then the catalyst was decomposed with methanol, and the reaction mass was washed in succession with 5% HCl solution and water, and then dried over MgSO₄. After removal of the solvent the residue was vacuum-distilled. From 84 g of 1-hexene at 20° we obtained 67 g of 5-methyleneundecane (Ia) [6], bp 88-89° (14 mm), $n_D^{2°}$ 1.4333. Infrared spectrum (ν , cm⁻¹): 890, 3080 (CH₂C=). PMR spectrum (δ , ppm): 0.86 m (6H, CH₃), 1.25 m (12H, CH₂), 1.9 m (4H, CH₂=C), 4.55 s (2H, CH₂=C), m/e 168.

From 84 g of 1-hexene at 100° we obtained 76 g of mixed dimers with bp 80-85° (5 mm), from which by preparative GLC were isolated: 5-methylundecane (IIa), bp 84° (8 mm), $n_D^{2°}$ 1.4231 PMR spectrum (δ , ppm): 0.84 m (9H, CH₃), 1.05 m (1H, CH), 1.22 m (16H, CH₂), m/e 170; 5-methyl cis-5-undecene (IIIa), bp 75-67° (12 mm), $n_D^{2°}$ 1.4329. Infrared spectrum (ν , cm⁻¹): 830, 3020 (C=CH). PMR spectrum (δ , ppm): 0.85 m (6H, CH₃), 1.22 m (10H, CH₂), 5.0 m (1H, HC=C). m/e 168; 5-methyl-trans-5-undecene (IVa), bp 90-92° (15 mm), $n_D^{2°}$ 1.4368. Infrared spectrum (ν , cm⁻¹): 830-3020 (C=CH). PMR spectrum (δ , ppm); 0.83 m (6H, CH₃), 120 m (10H, CH₂), 1.48 s (3H, CH₃C=), 1.88 m (4H, CH₂C=), 5.0 m (1H, =CCH). m/e 168; 5-methyl-trans-7-undecene (Va), bp 85° (8 mm), $n_D^{2°}$ 1.4281. Infrared spectrum (ν , cm⁻¹): 975, 3030 (trans-CH=CH). PMR spectrum (δ , ppm): 0.83 m (9H, CH₃), 1.20 m (9H, CH₂), 1.91 m (4H, CH₂C=), 5.25 m (2H, CH=CH). m/e 168.

1-Octene at 20° gives 7-methyleneheptadecane (Ib) [7] in 60% yield, bp 110° (3 mm), n_D^{20} 1.4420. Infrared spectrum (v, cm⁻¹): 890, 3080 (CH₂=C). PMR spectrum (δ , ppm): 0.84 m (6H, CH₃), 1.25 m (2OH, CH₂), 1.87 m (4H, CH₂C=), 4.55 s (2H, CH₂=C). m/e 224.

From l-octene at 100° we obtained a mixture of hydrocarbons, composed of 7-methylheptadecane (IIb), bp 115° (4 mm), $n_D^{2°}$ 1.4350. m/e 226; 7-methyleneheptadecane (Ib) and 7-methyltrans-7-heptadecene (IVb), bp 135° (17 mm), $n_D^{2°}$ 1.4450. Infrared spectrum (v, cm⁻¹): 830, 3020 (C=CH). PMR spectrum (δ , ppm): 0.82 m (6H, CH₃), 1.21 m (18H, CH₂), 1.47 s (3H, CH₃C=), 1.88 m (4H, CH₂C=), 5.0 m (1H, HC=CH). m/e 224.

From 1-decene under analogous conditions we obtained 5-methylenenonadecane (Ic) [8] in 20% yield, bp 148-149° (1 mm), $n_D^{2^\circ}$ 1.4540. Infrared spectrum (v, cm⁻¹): 890, 3080 (CH₂=C). PMR spectrum (δ , ppm): 0.86 m (6H, CH₃), 1.24 m (28H, CH₃), 1.91 m (4H, CH₂C=), 4.55 s (2H, CH₂=C). m/e 280. From 1-decene at 150° we obtained 9-methylnonadecane (IIc) [8] in 70% yield, bp 151-152° (1 mm), $n_D^{2^\circ}$ 1.4510. m/e 282.

The codimerization of 42 g of 1-hexene with 21 g of propylene at 20° gives in 95% yield a mixture of hydrocarbons, composed of 30% of methyl-1-pentene [9], 20% of dimer (Ia), and 50% of a mixture of 3-methyleneoctane (VIIa) and 4-methyleneoctane (VIIIa) (3:1), bp 50° (20 mm), $n_D^{2\circ}$ 1.4200. Infrared spectrum (ν , cm⁻¹): 890, 3080 (CH₂=C). PMR spectrum (δ , ppm): 0.87 m (4H, CH₃), 1.27 m (7.5H, CH₂), 1.63 m (2H, CH₃), 1.95 m (2.5H, CH₂C=), 4.6 s (2H, CH₂=C). m/e 126.

The codimerization of 42 g of 1-hexene and 57 g of 1-octene at 60° gave 90 g (\sim 90%) of catalyzate, which contained 40% of (Ia), 15% of (Ib), and 45% of a mixture of 5-methylene-tridecane (VIIb) and 6-methylenetridecane (VIIIb), bp 110-112° (11 mm), $n_D^{2°}$ 1.4357. Infrafed spectrum (ν , cm⁻¹): 890, 3080 (CH₂=C). PMR spectrum (δ , ppm): 0.85 m (6H, CH₃), 1.23 m (16H, CH₂), 1.90 m (4H, CH₂C=), 4.55 s (2H, CH₂=C). m/e 198.

Trimethylvinylsilane under analogous conditions is converted in 90% yield to trans-1,4bis(trimethylsilyl)-1-butene (VI) [10], bp 55-56° (1 mm), $n_D^{2°}$ 1.4375. Infrared spectrum (v, cm⁻¹): 710, 850-870, 1269 (Si(CH₃)₃), 975, 1620, 3030 (trans-CH=CH). PMR spectrum (δ , ppm): -0.02 m (9H, CH₃), 0.03 m (9H, CH₃), 0.54-0.68 m (2H, CH₂Si), 1.98-2.48 m (2H CH₂C=), 5.50-5.74 m (2H, CH=CH). m/e 200.

CONCLUSIONS

1. The system $Zr(OBu)_4$ -AEt₂Cl catalyzes the selective dimerization of the higher α -olefins to the corresponding methylenealkanes.

2. The yield of the dimers decreases with increase in the number of carbon atoms in the α -olefin, accompanied by a simultaneous decrease in the degree of migration of the double bonds in them.

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