Photolysis of  $Mn_2(CO)_{10}$  in the presence of di-t-butyl-orthophenylenequinol (VIII) and tributylphosphite results in the EPR spectrum shown in Fig. 4. Evidently, in this case two types of complex are formed differing in their HFC with the <sup>31</sup>P nucleus. The considerable difference in the HFC constants is explained by the different location of the TBP ligand relative to the p-orbitals carrying the unpaired electron. The greater HFC results from extra-nodal, and the lesser from nodal, location of the TBP ligand.

## EXPERIMENTAL

The rhenium- and manganese-containing radicals were prepared by photolysis of the corresponding  $M_2(CO)_{10}$  in the presence of orthobenzoquinones in evacuated ampuls directly in the resonance chamber of the spectrometer. EPR spectra were recorded on a Varian E-12A spectrometer.

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## STEREO- AND REGIOSELECTIVITY OF THE CATALYTIC SYSTEM MoCl<sub>5</sub>/SiO<sub>2</sub>-SnMe<sub>4</sub> IN THE REACTION OF METATHESIS AND COMETATHESIS

OF OLEFINS AND THEIR FUNCTIONAL DERIVATIVES

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It was shown that the catalytic system  $MoCl_5/SiO_2-SnMe_4$  has almost 100% regioselectivity with respect to olefins. The stereoselectivity of the system is not a function of the length of the  $\alpha$ -olefin chain, temperature, or addition of functional groups (COOEt, Cl). Addition of pentachlorophenoxy and 8hydroxyquinolyl ligands significantly reduces the activity of the catalytic system with a slight increase in the stereoselectivity with respect to the cis-isomer.

The reaction of cometathesis of olefins and their derivatives is a promising method of synthesis of the components of pheromones [1-3], aromatic substances [4, 5], and plant growth stimulators [6]. The development of research in this area is dependent on the creation of accessible catalytic systems with elevated activity, stability, and regio- and stereoselectivity to a significant degree. The last index is especially important for synthesis of the components of natural compounds, many of which are individual cis- or transisomers. Unfortunately, there are currently no catalytic systems which satisfy all of these requirements, and there is no unified point of view on the mechanism of stereoregulation. This situation is stimulating the development of research to study the stereoregulation in the reaction of metathesis [7, 8].

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It was previously shown in [9, 10] that the catalytic system  $MoCl_5/SiO_2-SnMe_4$  exhibits elevated regioselectivity in metathesis of  $\alpha$ -olefins, which is not a function of the temperature, reaction time, or degree of deactivation of the catalyst. It was unclear whether the presence of small amounts of by-products in the catalyzates was caused by migration of double bonds or the presence of impurities of isomers of the position of the double bond in the starting  $\alpha$ -olefin.

Using different  $\alpha$ - and  $\beta$ -olefins with a controllable concentration of isomers for metathesis, it was found in the present study that the observed regioselectivity for reactants with a purity of 99.0% is close to this value. In metathesis of chemically pure 1-pentadecene (I), the catalyzate has the following composition, wt. %: (I) 25.38, 2-hexadecene 0.25, 3-heptadecene 0.07, 4-octadecene 0.04, 5-nonadecene 0.03, 6-cosene 0.09, 7-uncosene 0.05, 8-docosene 0.05, 9-tricosene 0.12, 10-tetracosene 0.03, 11-pentacosene 0.02, 12-hexacosene 0.04, 13-heptacosene 0.73, 14-octacosene 73.04 (II). The observed regioselectivity is 98.42%. In the case of pure 1-decene, the regioselectivity is 92.3%, and it is 94.2% for pure 1-hexene (X). In metathesis of 2-octene,\* the composition of the catalyzate is the following, wt. %: hexenes 1.33, heptenes 4.59, octenes 16.15, nonenes 13.69, decenes 9.00, undecenes 14.89, dodecenes 24.30, tridecenes 14.23, tetradecenes 1.82. The regioselectivity is 40.45%. It follows from the above that the catalytic system exhibits regioselectivity of ~100%, and the presence of by-products in the catalyzates is due to the presence of impurities of isomers.

The catalytic system also has high regioselectivity with respect to derivatives. It was shown in [3] that the observed regioselectivity in the reaction of cometathesis of 5-decene (III) and ethyl oleate (IV) prepared from olive oil is 90.0%, while the value is 40.0% for "ethyl oleate," a pure reagent from the Khar'kov Plant. In addition to the target products 9-tetradecenoic acid ethyl ester (V) and 5-tetradecene (VI), there are 6-undecenoic acid ethyl ester (VIII) in the catalyzates. The petroselinic acid (IX) (6-octadecenoic acid) present in the raw material is apparently responsible for the formation of the last two compounds. The general scheme of the transformations can be represented as follows:



This example demonstrates the possibility of using the reaction of cometathesis for the analysis of the composition of unsaturated fatty acids contained in lipids.

It was shown that the stereoselectivity of reactions of metathesis and cometathesis is almost independent of the  $\alpha$ -olefin chain length in the presence of the MoCl<sub>5</sub>/SiO<sub>2</sub>-SnMe<sub>4</sub> system [3]. Metathesis of (X), 1-octene (XI), 1-decene (XII), and (I) results in a mixture of cis- and trans-isomers of 5-decene (III), 7-tetradecene (XIII), 9-octadecene (XIV), and (II), respectively, with a 16 ± 2% concentration of the cis-isomer. Varying the temperature from 0 to 50°C [metathesis of (X)] did not affect the ratio of cis- and trans-isomers in 5-decene. Addition of functional groups (C1, COOEt) also does not change stereoselectivity. Thus, cometathesis of 5-decene with ethyl oleate or 9-chloro-1-decene (XV) gives similar results to  $\alpha$ -olefin for the ratio of cis- and trans-isomers in the final products: 9-tetradecenoic acid ethyl ester and 14-chloro-5-tetracene (XVI). It should be noted that the high concentration (<98.0%) of the cis-configuration of the double bond in ethyl oleate had virtually no effect on the final ratio of cis-, trans-isomers (18/82).

\*The pure reagent from the Khar'kov Plant contains the following according to the GLC and PMR data: 16.0-16.7% 1-octene; 60.5-61.5% 2-octene; 23.5-21.8% total 3-octene and 4-octene.

TABLE 1

Structure of site	Conversion of 1-hexene, wt. %	Reaction time, min	Ť.°C	1-Hexene:Mo molar ratio	Ratio of cis-, trans-5-decenes
(XVII) (XVIII) (XIX) (XX)	73 10 15 35	$10 \\ 60 \\ 120 \\ 180$	$25 \\ 25 \\ 25 \\ 25 \\ 25 \\ 25$	300 300 300 150	16/84 30/70 21/79 16/84

It was shown in [8] that the ratio of cis-,trans-butenes-2 formed in metathesis of cis-2-pentene changes as a function of the nature of the ligand. We investigated the effect of pentachlorophenoxy, 8-hydroxyquinolyl, and dimethylsiloxy ligands on the ratio of cisand trans-isomers in 5-decene prepared with the reaction of metathesis of (X). The probable structures which are precursors of active sites are shown below.



The results of the experiments are reported in Table 1.

Note that addition of ligands significantly reduces the activity of the catalytic system with an increase in the stereoselectivity toward formation of the cis-isomer.

## EXPERIMENTAL

The composition of the starting compounds and products of the reactions was determined by GLC on a LKhM-8MD chromatograph with an FID and an ITs-26 integrator. Columns 25 m  $\times$ 0.16 mm, SE-30, and 50 m × 0.22 mm, SKTFT-50 or SKTFT-100, were used. The carrier gases were Ar and H<sub>2</sub>. The standard error of the GLC analysis for two measurements was  $\leq$ 5% for concentrations >1%, 11% for concentrations <1%, and 30% for concentrations <0.1%. The PMR spectra were recorded on a Bruker WP-200 spectrometer (200.13 MHz) in the form of 5% solutions in CCl4 with TMS as the internal standard. The IR spectra were made on a Specord IR-75 in a thin layer. The mass spectra were made on an LKB-2091 (electron energy of 70 or 12 eV). The products were separated by rectification or on a Pye Unicam preparative chromatograph ( $2 \text{ m} \times 8 \text{ mm}$  column, 10% SE-30). The determination of the ratio of cis- and trans-isomers was based on the data from the IR, PMR, and GLC analyses. The error in the determination of the concentration of cis- and trans-isomers by proton-proton resonance and GLC was 2%. The starting substances were dried over 5 Å Na, CaH<sub>2</sub> sieves in the absence of  $O_2$ . The methods of conducting metathesis, cometathesis, and preparation of the catalyst are described in [3, 9, 10]. The starting compounds (I), (X)-(XII), (XXI)-(XXIII) were pure reagents. The synthesis and properties of compounds (III)-(V), (XV), and (XVI) are described in [3]. Compounds (II), (VI)-(VIII), (XIII), and (XIV) were separated from the catalyzates in the form of mixtures of cis- and trans-isomers.

<u>14-Octacosene (II)</u> (16/84 cis/trans mixture) was obtained by metathesis of (I) and separated by rectification at 260°C (1 mm), purity of 98.3%, mp of 49-51°C (after recrystallization from EtOH). PMR spectrum ( $\delta$ , ppm): 0.85 m (6H, 2CH<sub>3</sub>), 1.25 br.s (44H, 22CH<sub>2</sub>), 1.90 br.s (4H, 2CH<sub>2</sub>-C=), 5.52 m (2H, 2CH), 5.50 (16%), cis-CH 5.54 (84%), trans-CH. Mass spectrum, m/z [relative intensity, % (12 eV)]: M 392 (66), 101 (83), 97 (100), 83 (50), 69 (16). <u>5-Tetradecene (VI)</u> was obtained by cometathesis of (IV) and (V) and separated by preparative chromatography, purity of 98.6%. PMR spectrum ( $\delta$ , ppm): 0.85 m (6H, 2CH<sub>3</sub>), 1.25 br.s (16H, 8CH<sub>2</sub>), 1.90 br.s (4H, 2CH<sub>2</sub>-C=), 5.52 m (2H, 2CH). Mass spectrum, m/z (relative intensity, %): M 196 (10), 140 (6), 126 (12), 102 (16), 98 (37), 83 (69), 69 (100), 56 (69).

<u>6-Undecenoic Acid Ethyl Ester (VII)</u> was prepared by cometathesis of "ethyl oleate" and (III) and separated by preparative chromatography, purity of 98.4%. PMR spectrum ( $\delta$ , ppm): 0.85 m (3H, CH<sub>3</sub>), 1.25 m (9H, 3H, CH<sub>3</sub>, 6H, 3CH<sub>2</sub>), 1.6 m (2H, CH<sub>2</sub>-C), 1.90 br.s (4H, 2CH<sub>2</sub>- $\overset{|}{C}$ = ), 2.15 t (2H, CH<sub>2</sub>- $\overset{|}{C}$ =). 4.05 q (2H, CH<sub>2</sub>-O), 5.30 m (2H, 2CH). Mass spectrum, m/z (relative intensity, %): M 212 (17), 168 (35), 124 (42), 96 (60), 84 (100).

<u>5-Heptadecene (VIII)</u> was obtained by cometathesis of "ethyl oleate" and (III) and separated by preparative chromatography, purity of 98.0%. PMR spectrum ( $\delta$ , ppm): 0.85 m (6H, 2CH<sub>3</sub>), 1.25 br.s (22H, 11CH<sub>2</sub>), 1.90 br.s (4H, 2CH<sub>2</sub>-C=). 5.52 m (2H, 2CH). Mass spectrum, m/z (relative intensity, %): M 238 (14), 126 (14), 112 (20), 84 (30), 69 (44), 55 (100), 41 (66). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 970 (trans-CH), 730 (cis-CH).

<u>7-Tetradecene (XIII)</u> (16/84 cis/trans mixture) was obtained by metathesis of (XI) and separated by rectification, 99.2%,  $n_D^{20}$  1.4357, bp 230°C (760 mm). PMR spectrum ( $\delta$ , ppm): 0.85 m (6H, 2CH<sub>3</sub>), 1.25 br.s (16H, 8CH<sub>2</sub>), 1.90 br.s (4H, 2CH<sub>2</sub>—C=). 5.52 m (2H, 2CH). Mass spectrum, m/z (relative intensity, %): M 196 (12), 140 (8), 126 (12), 102 (16), 98 (36), 83 (66), 56 (70). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 970 (trans-CH), 730 (cis-CH).

<u>9-Octadecene (XIV)</u> (16/84 cis/trans mixture) was obtained by metathesis of (XII) and separated by rectification, purity of 98.6%,  $n_D^{20}$  1.4432, bp 170°C (10 mm). PMR spectrum

( $\delta$ , ppm): 0.85 m (6H, 2CH<sub>3</sub>), 1.25 br.s (24H, 12CH<sub>2</sub>), 1.90 br.s (4H, 2CH<sub>2</sub>-C=), 5.52 m (2H, 2CH). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 970 (trans-CH), 730 (cis-CH). Mass spectrum, m/z [relative intensity, % (12 eV)]: M 252 (100), 237 (8), 153 (13), 125 (36), 97 (7), 83 (12), 69 (10), 57(15), 43 (14).

<u>Synthesis of Modified Catalytic Systems (XVIII) and (XIX)</u> was conducted by the following method. An equimolar amount of pentachlorophenol (XXI) or 8-hydroxyquinoline (XXII) (on conversion to one chlorine) in absolute  $CCl_4$  was added to a weighed portion of  $MoCl_5/SiO_2$  and held for 4 h at 80°C. The  $CCl_4$  was decanted, and the catalyst was washed with  $CCl_4$ . The  $CCl_4$  was then eliminated in a vacuum ( $0.5 \cdot 10^{-3}$  mm) at 80°C for 2 h. For an equimolar ratio, (XXI) or (XXII) completely reacts with the molybdenum chloride attached to the  $SiO_2$ .

Synthesis of (XX). A solution of  $Me_2SiCl_2$  in absolute hexane in a 20-fold excess with respect to the OH groups of SiO<sub>2</sub> was poured on a weighed portion of SiO<sub>2</sub> (previously annealed at 300°C,  $0.5 \cdot 10^{-3}$  mm, 4 h). It was held for 48 h at 25°C and 6 h at 70°C, the solution was decanted, and a weighed portion was evacuated (80°C,  $0.5 \cdot 10^{-3}$  mm, 2 h).\* The amount of  $\exists -0-Si-Me_2$  groups in (XXIII) was determined by titration of HCl after hydrolysis of

the weighed portion of SiO<sub>2</sub>. The number of  $\exists -0-Si-Me_2$  groupst in (XXIV) was determined OH

by the reaction with BuLi. Silica gel with the groups of (XXIV) reacted with MoCl<sub>5</sub> with the formation of  $\exists -0-Si-Me_2$  (XX).

OMoCl₄

\*After this treatment, there were virtually no OH groups.

+Siloxane groups were virtually not formed, since the amount of (XXIII) coincides with the amounts of (XXIV).

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