ORGANIC CHEMISTRY

COMPOSITION OF OLEFINS FORMED IN THE DEHYDROGENATION OF

n-DECANE OVER ALUMINUM-PLATINUM CATALYSTS

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A knowledge of the composition of the products of dehydrogenation of the higher paraffins is necessary to establish routes for the utilization of higher monoolefins [1]. According to Bursian et al. [2], dehydrogenation of higher straight-chain paraffins over Al-Pt catalysts affords α - and monoolefins with nonterminal double bonds. No systematic study has however yet been made into the quantitative proportions of the isomeric monoolefins formed by the dehydrogenation of n-paraffins over Al-Pt catalysts, and the available information is limited to the dehydrogenation of C₆-C₁₆ n-paraffins over Zn-Cr and Fe-Cr oxide catalysts [3].

We here report a study of the effects of catalyst composition and experimental conditions on the proportions of n-decenes in which the double bond occupies different positions, formed in the dehydrogenation of n-decane over modified Al-Pt catalysts.

EXPERIMENTAL

Al-Pt catalysts with added MnO, grain size 0.5-1.0 mm, were used. The Pt content of the samples varied from 0.1 to 1.0%, and the MnO content up to 40%. All the catalysts were prepared by impregnation [4].

A stainless steel flow reactor was charged with 0.5 g (~1 cm³) of catalyst diluted with quartz grains, diameter 1-2 mm, in a ratio of 1:4. The catalyst was heated in a stream of hydrogen to 500°C, kept at this temperature for 30 min, then brought to the reaction temperature. The dehydrogenation of n-decane containing 1.1% of isodecanes was carried out at 430-500°C, $p_{\rm H_2}$ 0.1-0.6 MPa, volume flow rate of hydrocarbon (v) 20-60 h⁻¹, and at dilutions of the latter with hydrogen at molar ratios ($\rho_{\rm H_2}$) up to 16. The catalyzate yield was close to 100%.

Liquid reaction products were analyzed by IR spectroscopy and GLC. GLC was used to determine the extent of conversion of the n-decane, and the total yields of monoolefins, dienes, aromatic hydrocarbons, isodecanes, and cracking products (<C10 hydrocarbons).

The composition of the olefins in the catalyzates was determined by IR spectroscopy [5, 6]. The spectra were obtained on a Specord-751R at 2200-400 cm⁻¹ in a KBr cell, optical layer thickness 0.1 mm. The reference cell contained pure n-decane. Optical densities were measured at the maxima of the characteristic absorption bands. The concentrations of the α - and trans-olefins in the catalyzates were measured by reference to the optical density of spectra of reference samples. The compounds used for this purpose were 1-decene of 96.6% purity, and trans-5-decene containing 20% of the cis isomer. The amounts of 1-decene and trans-decenes were found from the =CH₂ (910 cm⁻¹) and CH=CH (970 cm⁻¹) bands, respectively. These frequencies coincide with the absorption frequencies of the dienes. According to GLC, however, dienes are formed to a much smaller extent than monoolefins (Tables 1 and 2), and consequently the effects of dienes on the quantitative estimation of monoolefins was within the limits of experimental error. The accuracies of the GLC and IR analyses were within 10 rel.%.

Since the content of cis-decenes in these multicomponent mixtures could not be determined independently, the amounts were calculated as the difference between total monoolefins + dienes and trans-decenes + α -decenes.

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1. Effect of (ogenation of n- ate com- Conver-	fect of (ion of n- Conver-	7 N N I	Catalyst Decane	Compos (480°C, Compositi	sition on $\rho_{H_2} = 8$, $\rho_{H_2} = 8$, on of catalyz	the Amoun vol. flo	ts of Var w rate of C, 76	ious Pl n-deca Amount olefins ir	roducts ane 25 h of different	in the n ⁻¹ , P _H t forms of yzate, %	Cataly = 0.1 Ratio of decenes,	zate fr MPa) isomeric re. %	om the orms of
$\sqrt[n]{0}$ sion of n- $\sum_{\gamma \text{ distance}} \sum_{\gamma d$	decane, Σ mono- $\sum_{\Sigma \text{ diamas}} \sum_{z \text{ are } z \text{ zero}}$	2 mono- 7 dienes 2 mono-	T dienes	Σ mono		Σ aromatic	Σ cracking	by	IR				
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10 19,1 15,3 1,5 16,8	19,1 15,3 1,5 16,8	15,3 1,5 16,8	1,5 16,8	16,8		1,7	0,6	0,9	9,8	6,1	9	58	1
10 24,3 19,6 2,8 22,4	24,3 19,6 2,8 22,4	19,6 2,8 22,4	2,8 22,4	22,4		1,5	0,4	1,1	13,1	8,2	£	58	
10 20,0 16,1 2,0 18,1	20,0 16,1 2,0 18,1	16,1 2,0 18,1	2,0 18,1	18,1		1,4	0,5	0,9	11,5	5,7	വ	63	
10 20,7 14,3 2,2 16,5	20,7 14,3 2,2 16,5	14,3 2,2 16,5	2,2 16,5	16,5		3,6	0,6	0,8	0'6	6,7	ы	54	
0 14,6* 9,7 1,6 11,3	14,6* 9,7 1,6 11,3	9,7 1,6 11,3	1,6 11,3	11,3		2,5	0,4	0,7	5,3	5,3	9	47	
5 21,9 16,1 3,3 19,4	21,9 16,1 3,3 19,4	16,1 3,3 19,4	3,3 19,4	19,4		1,8	0,7	0,8	10,6	8,8	4	55	
10 20,7 14,3 2,2 16,5	20,7 14,3 2,2 16,5	14,3 2,2 16,5	2,2 16,5	16,5		3,6	0,6	0,8	9,0	6,7	5 C	54	-
40 25,5 28,9 3,1 22,0	25,5 18,9 3,1 22,0	8,9 3,1 22,0	3,1 22,0	22,0	_	3,2	0,3	1,1	12,5	8,4	n	57	ಹ
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*The reaction products also contained 0.4% of isodecanes.

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ן אר ו	forms of zate, %		CIS		4,5 9,2 9,6		10,6 8,3 3,7		8,3 7,0 5,1		11,8
1	of various f the cataly		trans		5,9 7,8 15,4		13,3 4,5 8,6 8,5 6,5 7 6		9,8 10,5 8,7		13,9 9.7
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(s03)	/ GLC, %	aromatic 2	iydrocar- I	=1,0 MPa; ρ		² ==8, <i>v</i> _n -c ₁₀ H ₂₄	2,5 1,0 0,6 0,6	°, рн ₂ =0,2 М	2,1 0,9 0,5	$p_{{\rm II}_2}=0,2~{\rm MP_5}$	15,7
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, Mn0 10%	osítion of ca	Σ mono-	otenns + dienes		11,0 23,2 26,2		, 25,0 10,9 8,3		19,2 18,4 14,6		26,9
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genation	Variable	parame- ters		T., °C	430 450 500	<i>р</i> н ₂₆ МРа	0,1 0,4 0,6 6 4	$v_{n-C_{10}H_{22}}$ h	20 60 60	$ ho_{ m H_2}$	04

Effects of Experimental Conditions on the Amounts of Products in Catalyzates from the Dehydro-TABLE 2. genation o



Fig. 1. Plots of the relative amounts of decenes in the olefinic fraction of the catalyzates versus temperature at $p_{H_2} = 0.1$ MPa (a), and versus pressure at 480°C (b). $(v_{n-C_{10}H_{22}} = 20 \text{ h}^{-1}; \rho_{H_2} = 8): 1$) trans-decenes; 2) cis-decenes; 3) 1-decene. The plots show the relative amounts of the isomeric decenes in equilibrium mixtures, and the points represent the experimental data.

DISCUSSION OF RESULTS

It will be seen from Tables 1 and 2 that the principal products of the dehydrogenation of of n-decane over Al-Pt catalysts under these conditions are monoolefins (8-23%). Comparisons of the IR spectra of the products with those of 1-decene and trans-5-decene showed the presence of olefinic C_{10} hydrocarbons with different positions of the double bond.

Calculation of the relative amounts of the isomeric decenes in the mixed olefins formed showed that decenes with an internal double bond constituted ~95 rel.%, the proportion of 1-decene being no greater than 6 rel.%. The trans forms of decenes with nonterminal double bonds usually predominated (47-64 rel.%) over the cis forms (35-47%). Changes in the composition of the A1-Pt catalyst or in the experimental conditions had little effect on the proportion of 1-decene in the monoolefins. The proportions of cis to trans forms of the monoolefins varied slightly in some instances, but the predominance of the trans forms was always maintained. For example, an increase in the charging rate of n-decane from 20 to 60 h⁻¹ resulted in a slight increase in the relative content of the trans-forms and a reduction in the cis forms of the decenes (Table 2). Increasing the reaction temperature or $p_{\rm H_2}$, or increasing the extent of dilution of the n-decane with hydrogen under the conditions employed had no effect on the proportions of all three forms of decenes. The ratios of concentrations of the isomeric decenes (Fig. 1a, b) were close to the values calculated by Eliseev et al. [7].

The observed proportions of the α -cis and trans forms of the olefins differed from those reported in [3] for the dehydrogenation of higher n-paraffins over Zn-Cr and Fe-Cr oxide catalysts. Thus, the proportion of α -olefins reported in [4] was 33-58 rel.% in the mixture of olefins formed, whereas olefins with a nonterminal double bond normally contained preferentially the cis forms, the trans forms in several instances being totally absent.

CONCLUSIONS

1. The amounts of α -, cis-, and trans-decenes formed by dehydrogenation of n-decane over an aluminum-platinum catalyst corresponded on average to the proportions 1:8:11, and they were little affected by changes in catalyst composition and reaction conditions.

2. Decenes with nonterminal double bonds were formed preferentially (~95 rel.%).

3. The proportions of the different forms of decenes were close to the calculated values.

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REGIOSELECTIVE REACTION OF FUNCTIONALLY SUBSTITUTED MONO-, DI-, AND TRIOLEFINS WITH ALKYLMAGNESIUM COMPOUNDS, CATALYZED BY Cp₂ZrCl₂

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We have recently carried out the selective reaction of α -olefins with Et₂Mg under mild conditions in the presence of catalytic quantities of Cp₂ZrCl₂[1]

 $R _ \checkmark + Et_2Mg \xrightarrow{[Zr]} R _ \checkmark -MgEt$

In order to expand the field of application of this method and to investigate the possibility of involving functionally substituted olefins in the reaction with alkylmagnesium compounds, we have studied the reaction of Et_2Mg and EtMgBr with di- and triolefins with different structures, and with 0-, N-, S-, and Si-containing unsaturated compounds. The reaction of the selected olefins with Et_2Mg proceeds with maximum selectivity and yield at 20-25° at a Mg:olefin ratio of 1.5:1. However, regardless of the initial reactant ratio, only one of the ethyl groups of the Et_2Mg molecule takes part in the reaction. Evidently, the asymmetrical higher dialkyl Mg derivatives formed in the reaction are less reactive.

Only the terminal double bonds enter into the reaction, while the di- and trisubstituted unconjugated double bonds have practically no effect on the course of the reaction and do not undergo isomerization.

Thus, 1,4-Z-hexadiene reacts with Et_2Mg and is converted to 2-ethyl-4Z-hexen-l-yl-ethyl magnesium (I), the hydrolysis of which leads to 5-methyl-2Z-heptene (II). Under analogous conditions 1,5-hexadiene reacts with Et_2Mg to form, depending on the concentration of the latter, mono-(III) and the adducts (IV):



It must be pointed out that the hydrolysis of (IV) gave a mixture of approximately equal amounts of two diastereomers of 3,6-dimethyloctane (VIa, b) which were identified by 13 C NMR spectroscopy.

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