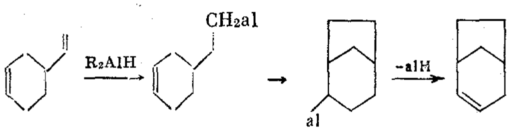
TRANSFORMATIONS OF SOME OLEFINS UNDER THE INFLUENCE OF ORGANOALUMINUM COMPOUNDS

V. P. Yur'ev, A. V. Kuchin,
I. M. Salimgareeva, G. A. Kozhevnikova,
V. I. Kleiner, and G. A. Tolstikov

UDC 542.97:547.313

Previously it was established that 4-vinylcyclohexene (VCH) when heated with triisobutylaluminum (TIBA) is converted in high yield to bicyclo[3,2,1]-2-octene (BCO) [1]. It seemed interesting to make a more detailed study of this reaction in order to transfer it to other olefins. In order to find the optimum isomerization agent we studied the comparative activity of some organoaluminum compounds of variable structure.

From the data given in Table 1 it can be seen that the most active agents for the isomerization of VCH to BCO are triethylaluminum (TEA), TIBA, diisobutylaluminum hydride (DIBAH), and triscyclohexenylethylaluminum (TCEA) [2]. Diethylaluminum chloride, diisobutylaluminum chloride, and ethylaluminum dichloride are much less active. Triphenylaluminum is completely inactive, which is explained by the following. The isomerization of olefins and, in particular, the isomerization of VCH begins with the hydroalumination of the vinyl group by a compound of the R_2AlH type. Compound (II), obtained as the result of exhaustive transalkylation, is converted to the bicyclooctane derivative (III) due to the intramolecular reaction of the C—Al bond with the double bond in the ring. The cleavage of aluminum hydride leads to BCO (I). As a result, triphenylaluminum, due to its inability to take part in the hydroalumination reaction, does not cause the isomerization of olefins.



al = Al/3 (II) (III) (I)

Since the best isomerization catalyst is DIBAH, the transformations of a number of olefins with its involvement were studied. 1,5-Cyclooctadiene (COD) when heated at 200°C in the presence of DIBAH is 70% isomerized to bicyclo[3,3,0]-2-octene (IV). This transformation opens up a route to the synthesis of difficultly available bicyclanes. Hydrocarbon (IV) was obtained previously by the isomerization of 1,3-cyclooctadiene on potassium hydride [3], and its constants coincided completely with those of the product obtained by us. The use of a 10-fold excess (molar) of the olefin relative to the DIBAH and a high temperature make it possible to direct the isomerization process toward the formation of bicyclene (IV).

However, if an equimolar ratio of TIBA : COD is used and the reaction is run in benzene at a lower temperature [4], then the process goes with the formation of the organoaluminum compound (VI). Its subsequent hydrolysis gives a mixture of the cis- and trans-methylethylcyclopentanes (VII), while reaction with ethylene leads to 1-methylene-2-vinylcyclopentane (VIII).

As a result, if the hydroalumination of the double bonds of COD occurs in one case, which can be judged [4] by the chemical transformations of compound (VI), then the isomerization process takes place in the case of using catalytic amounts of DIBAH. The direct preparation of bicyclo[3,3,0]-2-octene (IV) from the reaction mixture serves as proof of this.

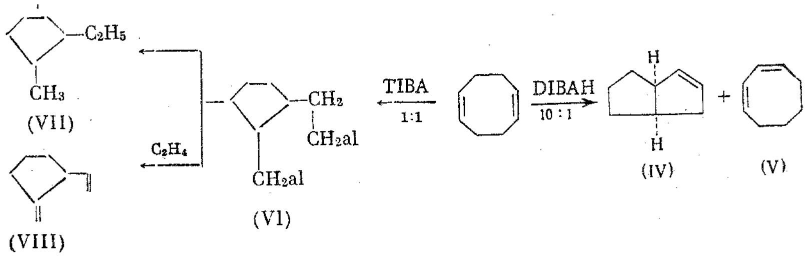
Institute of Chemistry, Bashkir Branch of the Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2553-2557, November, 1974. Original article submitted February 5, 1974.

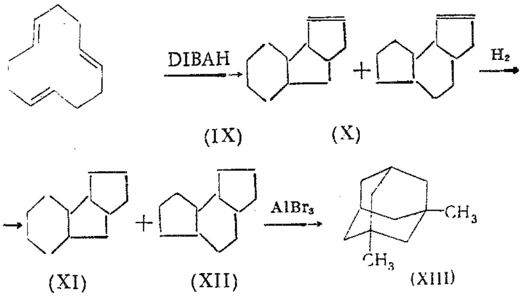
TABLE 1. Isomerization of 4-Vinylcyclohexene (VCH) on Organoaluminum Compounds (Mole ratio Al : VCH = 1 : 10, 150°C, 5 h, and a charge of 6.4 g of VCH)

Catalyst	TIBA	TEA	DIBAH	TCEA	TPA	DIBAC	DEAC	EADC	$LiAlH_4$	$NaBH_4$
VCH conversion, %	84,5	31,0	77	92,5	95,5	98,5	95,5	40,0	92,5	94,0
Yield of BCO, %	45,0	65,0	75,0	70,0	0	20,0	20,0	30,0	0	0

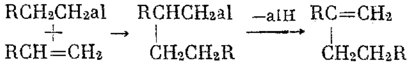
The isomerization of trans-trans-trans-1,5,9-cyclododecatriene proceeds even more easily, which after heating at 200°C for 5 h gives a mixture of tricyclo$[6,4,0,0^{3,7}]$-4-dodecene (IX) and tricyclo$[7,3,0,0^{3,7}]$-4-dodecene (X) in 85% yield. The structure of the tricyclenes is proved by the quantitative isomerization of the dehydro derivatives (XI) and (XII) to 1,3-dimethyladamantane (XIII) [5], and also on the basis of the physicochemical data. Thus, the mass spectrum of (IX) has a molecular peak (m/e 162) with an intensity of 30%, which indicates the cyclic structure of the hydrocarbon [6].

The cleavage of neutral fragments with a mass number of 67 and 68 is due to the presence of five-membered rings in the molecule. Based on the quantitative hydrogenation data, the degree of unsaturation is equal to one. The signals of two vinyl protons in the 5.30 ppm region are observed in the NMR spectrum.





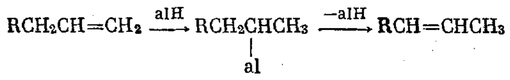
It seemed interesting to study the isomerization of some monoolefins. As is known, the heating of α-olefins in the presence of aluminum trialkylates leads to the formation of dimers. The dimerization proceeds due to the addition of the aluminum alkylates to the double bond in harmony with the Markovnikov rule [7].



$$\begin{array}{c} RCH_2CH_2al \\ + \\ RCH=CH_2 \end{array} \rightarrow \begin{array}{c} RCHCH_2al \\ | \\ CH_2CH_2R \end{array} \xrightarrow{-alH} \begin{array}{c} RC=CH_2 \\ | \\ CH_2CH_2R \end{array}$$

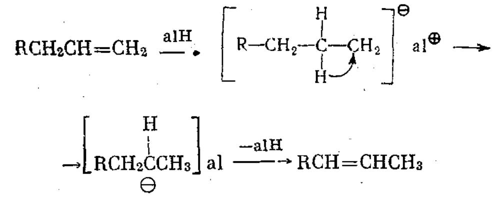
Under the conditions, described in [7] (heating the hydrocarbon with DIBAH at 148°C), 1-octene was converted to 2-hexyl-1-decene. In our experiments it was shown that 1-octene under more drastic conditions (200°C) is converted to a mixture of the Δ^2-, Δ^3-, and Δ^4-isomers. Vinylcyclohexane is isomerized completely to ethylidenecyclohexane and ethylcyclohexene. 1-Methyl-1-vinylcyclohexene remains completely unchanged. We were unable to isomerize olefins that contain a CH_2 group and a tri-substituted double bond. In particular, even after drastic treatment, 2,4,4-trimethyl-1-pentene, α-pinene, limonene, β-pinene, and Δ^3-carene are recovered unchanged.

In discussing the isomerization of di-substituted olefins it was assumed by Ziegler and co-workers [7] that the shift of the double bond can be explained by the reversible alH addition—cleavage reaction. If this scheme is used to explain the isomerization of α-olefins, then it must be assumed that the Markovnikov rule is upset in the addition of alH.



$$\mathrm{RCH_2CH{=}CH_2 \xrightarrow{alH} RCH_2\underset{\substack{|\\ al}}{C}HCH_3 \xrightarrow{-alH} RCH{=}CHCH_3}$$

It is more valid to assume a different isomerization scheme, based on the hydride shift, which proceeds under drastic conditions.



As a result, the heating of olefins with diisobutylaluminum hydride serves as a convenient method for the preparation of isomeric hydrocarbons, many of which are difficultly available.

EXPERIMENTAL

The NMR spectra were recorded on Varian A-60 and BS-487B instruments for solutions of the compounds in CCl_4, and using HMDS as the internal standard. The mass spectra were obtained on an MC-12-03 spectrometer using an electron ionization energy of 50 eV. The IR spectra were recorded on a UR-20 spectrophotometer. The UV spectra were measured on a Specord UV-VIS instrument using heptane solutions.

Isomerization of Vinylcyclohexene. Into a 25 ml steel autoclave were charged 6.5 g of vinylcyclohexene and 1.5 g of diisobutylaluminum hydride, and the mixture was heated at 150°C for 5 h. After fractional distillation in vacuo we obtained 5.0 g of bicyclo[3,2,1]-2-octene (I); bp 135-136°C (760 mm); n_D^{20} 1.4810. Infrared spectrum (ν, cm^{-1}): 760, 1450, 1650, 3030. m/e 108. The results of isomerizing vinylcyclohexene on the other catalysts are summarized in Table 1.

The isomerization of the following olefins was run at 200°C for 5 h, using a 10 : 1 ratio of the starting olefin and DIBAH.

1. From 6 g of 1,5-cyclooctadiene we obtained 5.5 g of a mixture, which, based on the GLC data, is composed of two isomers (IV) and (V) in a 7 : 3 ratio. After preparative separation we obtained: a) bicyclo[3,3,0]-2-octene (IV), bp 133-134°C (760 mm); n_D^{20} 1.4935. Infrared spectrum (ν, cm^{-1}): 700, 760, 1460, 3030. NMR spectrum (δ, ppm): 5.60 (2H), m/e 108; b) 1,3-cyclooctadiene (V), bp 60-61°C (65 mm); n_D^{20} 1.4901. Infrared spectrum (ν, cm^{-1}): 720, 1460, 1640, 1660, 3020. Ultraviolet spectrum: λ_{max} 230 nm, log ε 3.80. m/e 108; cf. [3].

2. From 6.3 g of trans-trans-trans-1,5,9-cyclododecatriene we obtained 5.3 g of a mixture, which contained 55% of (IX) and 45% of (X). After preparative separation of the mixture we obtained: a) tricyclo[6,4,0,$0^{3,7}$]-4-dodecene (IX), bp 80-81°C (8 mm); n_D^{20} 1.4962. Infrared spectrum (ν, cm^{-1}): 745, 1450, 3060. NMR spectrum (δ, ppm): 5.59 (2H). m/e 162; b) tricyclo[7,3,0,$0^{3,7}$]-4-dodecene (X), bp 83-85°C (8 mm); n_D^{20} 1.5048. Infrared spectrum (ν, cm^{-1}): 750, 1450, 3055. NMR spectrum (δ, ppm): 5.39 (2H). Mass spectrum, m/e M^+ (30%), 121 (41%), 96 (10.7%), 93 (48.1%), 82 (21%), 81 (48%), 80 (100%), 41 (32%).

Hydrogenation of Mixture of Compounds (IX) and (X). Into an autoclave were charged 12.5 g of a mixture of compounds (IX) and (X) and 1.0 g of Raney Ni. The hydrogenation was run for 5 h at 20°C and a H_2 pressure of 5 atm. We obtained 12.0 g of a mixture of tricyclanes (XI) and (XII), bp 85-86°C (6 mm); n_D^{20} 1.4903. Infrared spectrum (ν, cm^{-1}): 1380, 1460. M^+ 164 (by mass spectrometry).

Isomerization of Mixture of Tricyclanes (XI) and (XII). With stirring, to a mixture of 5.0 g of $AlBr_3$ and 4.0 g of compounds (XI) and (XII) was added 2.0 g of tert-butyl chloride, the mixture was kept at 60°C for 6 h, and then the product was extracted with pentane. After evaporation and distillation we obtained 3.5 g of dimethyladamantane (XIII), bp 100-102°C (25 mm); n_D^{20} 1.4785; cf. [8].

1. From 6 g of 1-octene we obtained 5.5 g of a mixture, which, based on the GLC data (identification using authentic specimens), consisted of 2-octene and 3-octene in a 1 : 1 ratio, bp (of the mixture) 122-122.5°C (760 mm); n_D^{20} 1.4140. Infrared spectrum (ν, cm^{-1}): 960, 1380, 1460, 3020. NMR spectrum (δ, ppm): 5.80 (2H), m/e 112.

2. From 6 g of vinylcyclohexene we obtained 2 g of a mixture, which, based on the GLC data (identification using a label), consisted of ethylidenecyclohexane and 1-ethylcyclohexene in a 1:3 ratio. A similar ratio was also obtained when the NMR spectrum of the mixture was examined.

CONCLUSIONS

1. Irreversible isomerization occurs when olefins are heated in the presence of diisobutylaluminum hydride.

2. Conditions were found for the conversion of 4-vinylcyclohexene to bicyclo[3,2,1]-2-octene, of 1,5-cyclooctadiene to bicyclo[3,3,0]-2-octene, and of 1,5,9-cyclododecatriene to tricyclo[6,4,0,$0^{3,7}$]dodecene and tricyclo[7,3,0,$0^{3,7}$]dodecene, and also for the isomerization of α-olefins with a shift of the double bond.

LITERATURE CITED

1. V. P. Yur'ev, G. A. Tolstikov, A. V. Kuchin, T. O. Yakovleva, E. G. Galkin, and S. R. Rafikov, Dokl. Akad. Nauk SSSR, 215, 1397 (1974).
2. V. P. Yur'ev, G. A. Gailyunas, and G. A. Tolstikov, Zh. Obshch. Khim., 42, 2111 (1972).
3. L. H. Slaugh, Tetrahedron, 32, 1774 (1966).
4. E. Marcus, D. L. MacPeek, and S. W. Tinsley, J. Org. Chem., 36, 381 (1971).
5. A. Schneider, R. W. Warren, and E. J. Jonoski, J. Org. Chem., 31, 1667 (1966).
6. A. A. Polyakova and R. A. Khmel'nitskii, Mass Spectrometry in Organic Chemistry [in Russian], Khimiya, Leningrad (1972), p. 287.
7. Organoaluminum Compounds [Russian translation], IL (1962), p. 175.
8. H. Koch and J. Franken, Chem. Ber., 96, 213 (1963).