ISOMERIZATION OF 1,5-CYCLODECADIENE DERIVATIVES BY TRIISOBUTYLALUMINUM

G. A. Tolstikov, U. M. Dzhemilev,
and S. S. Shavanov

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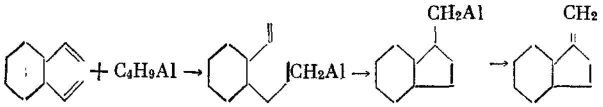
Previously we had shown that cis,trans-cyclodecadiene (I) can be isomerized quantitatively to cis-1-methyleneperhydroindan (II) in the presence of catalytic amounts (2-5%) of triisobutylaluminum (TIBA) [1]. In the present communication we present more detailed data on this new reaction of 1,5-cyclodecadiene derivatives.

The preparation of hydrocarbon (II) by the reaction of cis-1,2-divinylcyclohexane with a stoichiometric amount of TIBA was described in [2]. The organoaluminum compound (III) that is formed here, after treatment with excess ethylene under pressure, is converted to methyleneperhydroindan (II) and $AlEt_3$ by the following scheme:



Since the thermal isomerization of cis,trans-1,5-cyclodecadiene to 1,2-divinylcyclohexane proceeds very easily [3], it is logical to assume that the conversion of cyclodiene (I) to perhydroindan (II) proceeds via the step of forming 1,2-divinylcyclohexane and its subsequent conversion by the above-indicated scheme. However, it was unexpectedly established that 1,2-divinylcyclohexane when heated with 2-5% of TIBA gives the aluminumtrialkyl (III) in an amount that corresponds to the amount of used TIBA, whereas most of the hydrocarbon remains unchanged.

As can be seen from Fig. 1, cyclodecadiene is isomerized slowly even at 40°C. It is completely converted at 160° in 5 h and at 200° in 0.5 h. It is characteristic that cis,cis-1,6-cyclodecadiene (IV) is not isomerized to methyleneperhydroindan and is recovered unchanged after heating with 10% TIBA at 200° for 20 h. These facts caused us to examine more carefully the possible mechanism of the isomerization of the cis,trans-1,5-cyclodecadienes.

Of the two double bonds the transoid linkage is more reactive. Thus, we established that the epoxidation of 1,5-cyclodecadiene with tert-amyl hydroperoxide in the presence of $Mo(CO)_6$ gives a mixture of two oxides, (V) and (VI), in a 7:3 ratio. The cis-cyclodecenes (VI) and (VII) were obtained after hydrolysis when diene (I) is kept with an equivalent amount of $(i\text{-}C_4H_9)_2AlH$ at 40°. As a result, the isomerization of 1,5-cyclodecadiene begins with the hydroalumination of the transoid linkage, which gives compound (VIII).

An important detail of the experiment, which assures the complete isomerization of diene (I) to perhydroindan (II), is heating the hydrocarbon with the TIBA in a closed vessel. If the reaction is carried out in an open vessel, then the yield of the perhydroindan does not exceed 40%, while the remainder of the product is 1,2-divinylcyclohexane, which is formed by thermal isomerization. As can be seen, the isobutylene that is liberated in the reaction of TIBA with the hydrocarbon plays the role of displacing agent. Since 1,2-divinylcyclohexane fails to isomerize even when heated in a closed vessel, it may be assumed that the isobutylene is not in a condition to displace the methyleneperhydroindan from compound (III). Due to this the degree of divinylcyclohexane conversion to (III), which proceeds as hydroalumination and subsequent

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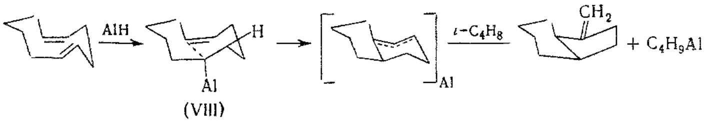
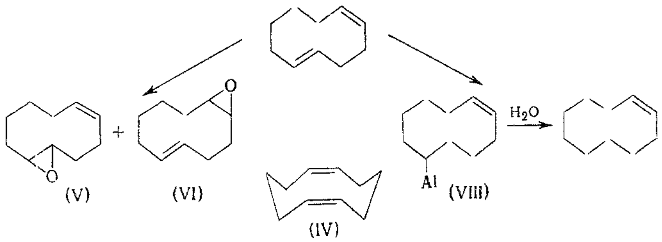
intramolecular carbalumination, is strictly limited by the amount of TIBA. These facts testify to the important differences in the cyclization mechanisms of cyclodecadiene and divinylcyclohexane. It may be assumed that the formation of (VIII) is followed by the synchronous processes of cyclization, bond rupture, and displacement of the Al–H element by isobutylene.

The resistance of cis,cis-1,6-cyclodecadiene to isomerization can be due to the low reactivity of the cisoid double bonds in the hydroalumination reaction.





The 9-methyl- and 9-phenyl-cis,trans-1,5-cyclodecadienes (IX)-(X) are isomerized very smoothly under the described conditions. The substituted methyleneperhydroindans (XI)-(XII) that are formed here are difficultly separable mixtures of the structural isomers. The ozonolysis of hydrocarbons (II) and (XI) gave the corresponding ketones (XIII)-(XIV), the stability of which toward alkaline reagents proves the cis coupling of the rings.

EXPERIMENTAL METHOD

The NMR spectra were recorded on a Tesla BS-480B instrument (CCl_4 or $CDCl_3$, internal standard = HMDS). The IR spectra were recorded on a UR-20 spectrophotometer (as a film). The GLC analysis was carried out on a Tswett-102 chromatograph using a flame-ionization detector, a 2 m × 3-mm column, a temperature of 120°, and nitrogen as the carrier gas at a flow rate of 40 mm/min. The mass spectra were taken on an MX 13-06 instrument with a temperature of 200° in the ionization chamber.

Compounds (VI) and (VII) were obtained in [4, 5], while hydrocarbon (IV) was synthesized by the isomerization of (I) in the presence of $Ni(acac)_2$ $AlEt_3$ [6].

Isomerization of Cyclodecadienes. a) A mixture of 1 g of TIBA and 10 g of cyclodecadiene was heated in a steel bomb at 160° for 5 h, after which the product was vacuum distilled. The yields of the chromatographically homogeneous methylenehydroindans were 90-95%. The hydrocarbons had the following constants.

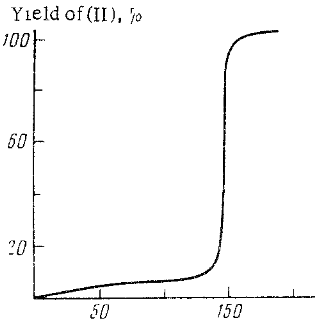


Fig. 1. Effect of temperature on conversion of cis,trans-1,5-cyclodecadiene to 1-methyleneperhydroindan.

1-Methyleneperhydroindan (II). bp 27° (1 mm); n_D^{20} 1.4869. Infrared spectrum (ν, cm^{-1}): 895, 3085 ($>C=CH_2$). NMR spectrum (δ, ppm): 1.25-1.57 m (2H) 2.22-2.41 M (3H), 4.70 (2H, methylene), m/e 136.

Methyl-1-methyleneperhydroindan (VII), bp 36-37° (1 mm); n_D^{20} 14932. Infrared spectrum (ν, cm^{-1}): 895, 3090 ($>C=CH_2$), 1380, 1450 (CH_3). NMR spectrum (δ, ppm): 0.91 d (3H), J=7 Hz), 1.25-1.57 m (10H), 2.24-2.42 m (3H), 4.70 (2H, methylene), m/e 150.

Phenyl-1-methyleneperhydroindan (VII), bp 94-95° (1 mm); n_D^{20} 1.5664. Infrared spectrum (ν, cm^{-1}): 710, 755, 1600, 3040 ($C_6H_5^-$); 885, 3075. NMR spectrum (δ, ppm): 1.57 m (13H), 4.7 (2H, $=CH_2$), 7.0 s (C_6H_5), m/e 212.

b) Mixtures of 5 g of (I) and 0.5 g of TIBA were placed in steel bombs, which were kept for 5 h at a definite temperature, and then the contents were analyzed by GLC. The results of the experiments are plotted in Fig. 1.

Hydroalumination of 1,5-Cyclodecadiene. A mixture of 6.8 g of (I) and 7.1 g of $(i\text{-}C_4H_9)_2AlH$ was kept at 40° for 20 h, and then the mixture was hydrolyzed by the addition of water. The usual workup gave 5 g of cis-cyclodecene [7] with bp 73° (15 mm), n_D^{20} 1.4885.

Epoxidation of (I) with tert-amyl hydroperoxide. To a solution of 27 g of (I) and 20 mg of $Mo(CO)_6$ in 100 ml of benzene at 80° was added in 30 min a 20% solution of 0.22 mole of TAHP in C_6H_6. The mixture was kept at 80° for 2 h, cooled, and washed with water. After removal of the solvent the product was vacuum distilled. The yield of the mixed (V) and (VI) was 27.5 g, bp 48-51° (1mm); n_D^{20} 1.4928. Infrared spectrum (ν, cm^{-1}): 710 (cis-CH=CH–), 980 (trans-CH=CH–). NMR spectrum (δ, ppm): 1.5 m (8H, –CH–); 2.3 m (4H, $>C=C-CH_2-$), 2.6 (2H, –C–O); 5.4 (2H, –CH=CH–), m/e 152.

General Ozonization Procedure. A stream of O_2, which contained 6-7% of ozone, was passed into a solution of 5 g of methyleneperhydroindan in 20 ml of CH_2Cl_2 at −50° until the ozone passed through. After adding 2 ml of dimethyl sulfide the mixture was left to stand overnight at ~20°, washed with water, and worked up in the usual manner. The ketones, purified by vacuum distillation, had the following constants.

Perhydroindanone (V), bp 32° (0.5 mm); n_D^{20} 1.4813. Infrared spectrum (ν, cm^{-1}): 1740 ($>C=O$), m/e 138. Oxime, mp 88-89°. Infrared spectrum (ν, cm^{-1}): 1684 (C=N–). Found: C 70.8; H 10.1; N 9.6; O 9.5%. $C_9H_{15}NO$. Calculated: C 70.5; H 9.8; N 10.5; O 9.2%.

Methylperhydro-1-indanone (IX), bp 76° (5 mm), n_D^{20} 1.4847. Infrared spectrum (ν, cm^{-1}): 1740 ($>C=O$), 1380, 1450 (CH_3), m/e 152. Semicarbazone, mp 193-194°. Found: C 62.9; H 9.1; N 20.3%. $C_{10}H_{17}N_3O$. Calculated: C 63.2; H 9.08; N 20.06%.

CONCLUSIONS

It was shown for the first time that the cis,trans-1,5-cyclodecadienes can be converted by triisobutylaluminum to the corresponding methyleneperhydroindans.

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