THE HYDROALUMINATION REACTION FOR SOME ALKENYLTRIMETHYLSILANES WITH DIISOBUTYLALUMINUM HYDRIDE

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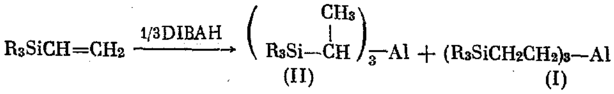
Vinyl- and allyltrialkylsilanes react with dialkylaluminum hydride to form organoaluminum compounds (OAC) which contain the silicon atom in the alkyl radical [1, 2]. In this case the formation of the less sterically preferable organoaluminum addition product (II) takes place because of the effect of $d_\pi-p_\pi$-conjugation between the Si and C atoms [3].

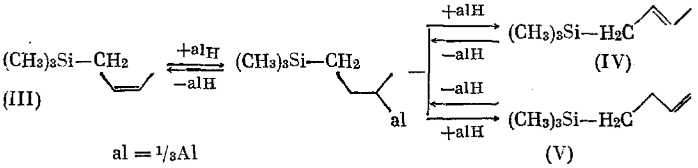


$$R_3SiCH{=}CH_2 \xrightarrow{1/3\,DIBAH} \underset{(II)}{\left(R_3Si{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}\right)_3{-}Al} + \underset{(I)}{(R_3SiCH_2CH_2)_3{-}Al}$$

The formation of a mixture of OAC was also observed in processes for the hydroalumination of stryene [4] and 6,6-dimethylfulvene [5].

In this work the reaction of diisobutylaluminum hydride (DIBAH) was studied with silicon-containing olefins which have different double bonds. The study of these compounds is also interesting because studies, which have appeared recently, indicate that it is possible, basically, to involve olefins with di- and trisubstituted double bonds in the hydroalumination process [6, 7].

Trimethylsilyl-cis-2-butene (III), upon reacting with 1/3 of a mole of DIBAH (80°, 6 h), does not form OAC. However, an analysis of the reaction products showed that the starting compound isomerized to a marked extent into a mixture of trimethylsilylbutenes in a ratio of (III) : (IV) : (V) = 27 : 68 : 5. The presence of the compound (V) in the mixture was established by the appearance of signals for the methylene protons at 2-C (2.00-2.12 ppm) in the PMR spectrum and the appearance of the 910- and 1000- cm^{-1} absorption bands in the IR spectrum. Because of the small concentration of the isomer (V) in the reaction mixture, it was not possible to isolate it, whereas the compounds (III) and (IV) were isolated by the method of preparative GLC. Heating with DIBAH (100°, 10 h) results in the formation of trimethylsilyl-trans-2-butene (IV) with an 89% yield. These experiments show that the reaction between the alkene (III) and DIBAH takes place in the form of reversible addition — the splitting off of the aluminum hydride — in the course of which the more thermodynamically stable trans isomer is accumulated. The addition of $Ti(OBU)_4$, which in a complex with DIBAH is an active catalyst for shifting the double bond [8], did not result in samples of any addition products.



al = $^1/_3$Al

The difficulty of adding R_2AlH to a disubstituted double bond in trimethylsilylbutenes can be explained by the interaction of the π-electrons with the 3d-vacant orbitals of the silicon atom because of their spatial approach [9]; the formation of the $d_\pi-p_\pi$ bond also shows a stabilizing effect.

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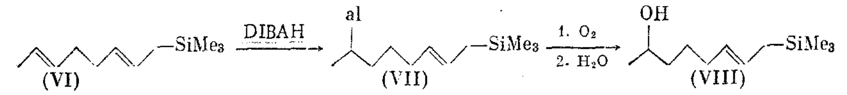
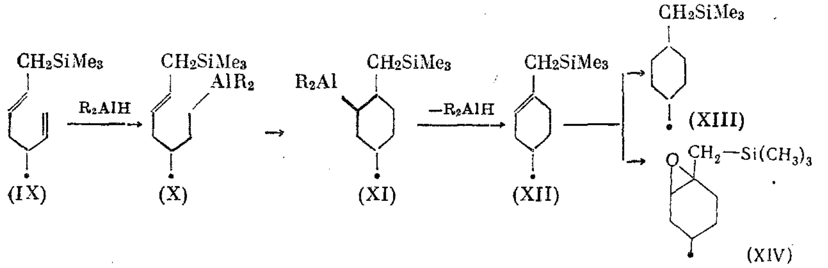
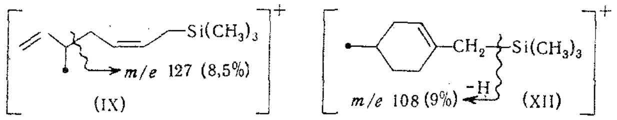
The reaction of 1/3 of a mole of DIBAH with trimethylsilyl-2,6-octadiene (VI) (130-140°, 10-12 h) gives tris-(8-trimethylsilyl-2-methyl-6-octenyl)aluminum (VII) with a 30% yield. The reaction takes place without a shift in the double bond to the end position as indicated by the structure of the alcohol (VIII), which is obtained by the oxidation of the OAC (VII) by air followed by hydrolysis with acidified water.



The reaction of DIBAH with trimethylsilyl-5-methyl-2,6-heptadiene (IX), which, in spite of the presence of a vinyl group, does not stop at the stage for the formation of the OAC (X), is quite interesting. The reaction product, which is obtained with an 80% yield, is 1-trimethylsilylmethyl-4-methylcyclohexene (XII). Apparently the reaction of the diene (IX) with the DIBAH begins in the process of the hydroalumination of the vinyl bond, resulting in the compound (X), which then undergoes intramolecular cyclization which takes place as the carbalumination of the disubstituted double bond. The cyclic compound (XI), which is formed in this way, is unstable and decomposes with the splitting off of the aluminum hydride. As we can see, the double bond which is in the β-position to the silicon atom is rather highly active in the carboalumination reaction. The addition of the aluminum hydrides is less typical for it. In every case the splitting off of the R_2AlH from the γ-alumosilanes takes place very easily.



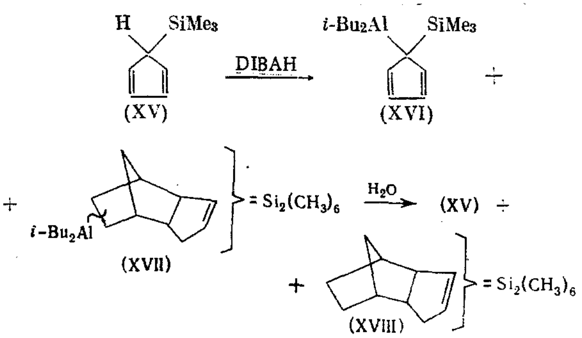
According to mass-spectrometric data, the compounds (IX) and (XII) have the same molecular ion 182 but with a different intensity: for the product (XII) the intensity of the peak for the molecular ion is two orders of magnitude greater than that for the aliphatic dienes, which indicates the cyclic structure of (XII) [10]. Moreover, the paths for the decomposition of the molecular ions for these compounds upon impact differ.



For the diene (IX) this is the formation of the $SiC_7H_{15}^+$ ion with m/e 127 and for the cycloalkene (XII) this is the rupture of the β-bond with respect to the ring to form C_8H_{12} ions with m/e 108. The PMR spectra for the compounds (XII) and (IX) differ.

The quantitative hydrogenation of the compound (XII) on Pd/C takes place with the absorption of 1 mole of hydrogen; the oxidation of (XII) with an equimolar amount of tert-amyl hydroperoxide in the presence of $Mo(CO)_6$ gives the oxide (XIV). The cyclization of the diene (IX) takes place also with the catalytic amount of DIBAH (~ 5-10%) giving the product (XII) with an 85% yield.

The reaction of DIBAH with an excess of trimethylsilylcyclopentadiene (XV) (100°, 6 h) takes place with the formation of the OAC (XVI) and (XVII) having the composition $C_{21}H_{41}AlSi_{1.6}$, the hydrolysis of which gives the initial diene (XV) and the mixture of isomers of bis(trimethylsilyl)tricyclo[5,2,1,$0^{2,6}$]-3(4)-decene (XVIII) in a 3 : 5 ratio. It may be assumed, from the presence of the compound (XV) in the hydrolysis products, that the diene (XV) undergoes direct metallization substitution with DIBAH with the formation of (trimethylsilylcyclopentadienyl)-diisobutylaluminum (XVI). This is explained by the fact that the proton, which is on the atom with the $Si(CH_3)_3$-substituting group, has an elevated acid nature because of the conjunction of the vacant d-orbitals of the Si with the occupied π-orbitals of the cyclopentadienyl and therefore it is replaced by the i-Bu_2Al group. Such a reaction was also observed during the hydroalumination of cyclopentadiene [11]. The isolation of the mixture of the (XVIII) isomers from the hydrolysis products shows that the process for the hydroalumination of the dimeric form of the diene (XV) by DIBAH takes place along the cis-disubstituted (norbornene) bond. The reaction conditions facilitate the migration of the double bonds and the $Si(CH_3)_3$ group in the diene (XV); therefore its dimers have a different isomeric composition. For this reason the dihydrotricyclene (XVIII) also is a mixture of isomers with different positions for the $Si(CH_3)_3$ groups.



EXPERIMENTAL METHOD

The IR spectra were obtained on the UR-20 spectrophotometer (film). The PMR spectra were recorded in CCl_4 on the "Tesla" VS-487-V apparatus with an operating frequency of 80 MHz with and without proton stabilization with respect to the HMDS. The mass spectra were obtained on the MKh-13-06 apparatus at 50 eV and at 200°. The GLC was carried out on the KhT-63 apparatus, phase KhE-60, 10% on Chromosorb W.

Reaction of Trimethylsilyl-cis-2-butene (III) with DIBAH. Fifteen grams of the compound (III) were added to 5.5 g of DIBAH at 80° in a stream of argon. The mixture was held at 120° for 5-10 h. After hydrolysis with acidified water 13.8 g of the product was obtained, the GLC analysis of which showed that the ratio of the isomeric trimethylsilylbutenes (III) : (IV) : (V) = 27 : 68 : 5. The boiling temperature of the mixture was 95-116° (760 mm); n_D^{20} 1.4060. The mixture was separated by preparative GLC. The cis-isomer (III), bp 115-116° (760 mm); n_D^{20} 1.4220, was isolated. The trans-isomer (IV) had a b. p. of 113-114° (760 mm); n_D^{20} 1.4240; IR spectrum (ν, cm^{-1}): 660, 690, 700, 720, 850, 970, 1250, 1660, 3030. The PMR spectra (δ, ppm): −0.12 (9H); 1.56 (3H), J = 6 Hz; 1.48 (2H): 5.25-5.50 (2H, vinyl); M^+ 128 (mass spectrometric). Found: C 68.1, H 12.3, Si 19.2%. $C_7H_{15}Si$. Calculated: C 68.3, H 12.3, Si 19.4%.

Reaction of Trimethylsilyl-2,6-octadiene (VI) with DIBAH. Using the method described above, tris-(8-trimethylsilyl-2-methyl-6-octenyl)aluminum (VII) was obtained with a yield of 30%. Found: C 76.0, H 13.0, Si 5.12, Al 5.0%. $C_{33}H_{69}SiAl$. Calculated: C 76.2, H 13.3, Si 5.3, Al 5.2%.

The oxidation of (VII) with atmospheric oxygen followed by hydrolysis yielded trimethylsilyl-2-octene-7-ol (VIII) with a bp 76° (2 mm); n_D^{20} 1.4553. IR spectrum (ν, cm^{-1}): 700, 770, 870, 970, 1160, 1250, 1470, 3020, 3380. PMR spectrum (δ, ppm): −0.05 (9H); 2.18 (6H); 1.13 (3H), J = 7 Hz; 1.60 (2H), J = 8 Hz; 5.40 (2H); 3.75 (H); 3.42 (OH); M^+ 200 (mass spectrometric). Found: C 65.9, H 12.2, Si 13.8%. $C_{11}H_{24}OSi$. Calculated: C 66.0, H 12.0, Si 14.0%.

1-Trimethylsilylmethyl-4-methylcyclohexene (XII). Heating the diene (IX) with DIBAH at 80-140° for 5-12 h gives (XII) with a yield of 76%, bp 62° (6 mm); n_D^{20} 1.4580. IR spectrum (ν, cm^{-1}): 700, 760, 840, 865, 1250, 1380, 1420, 1440, 1460, 1660, 3040. PMR spectrum (δ, ppm): −0.06 (9H); 0.82 (3H); J = 7 Hz; 1.42 (2H); 5.36 (H). Mass spectrum, m/e: M^+ 182 (7.6%), 167 (2.11%), 139 (2.0%), 108 (9.0%), 97 (3.5%), 95 (2.7%), 93 (6.8%), 79 (4.0%), 77 (2.5%), 73 (100%), 59 (11%), 58 (8.9%), 55 (13.0%), 45 (13.0%). Found: C 72.3, H 12.0, Si 15.2%. $C_{11}H_{22}Si$. Calculated: C 72.5, H 12.1, Si 15.4%.

1-Trimethylsilylmethyl-4-methylcyclohexane (XIII). The hydrogenation of (XII) on Pd/C in ether gives (XIII), bp 35° (1 mm), n_D^{20} 1.4400. IR-spectrum (ν, cm^{-1}): 700, 760, 870, 1190, 1250, 1380, 1460, 2880, 2920, 2970. PMR spectrum (δ, ppm): −0.06 (9H); 2.40 (10H); 0.92 (3H), J = 7 Hz; 0.51 (2H); M^+ 184 (mass spectrometric) Found: C 71.6, H 13.2, Si 14.9% $C_{11}H_{24}Si$. Calculated: C 71.7, H 13.0, Si 15.2%.

1-Trimethylsilylmethyl-4-methyl-1,2-epoxycyclohexane (XIV). Epoxidation of the compound (XII) with a one mole amount of tert-amyl hydroperoxide, catalyzed with $MO(CO)_6$, yields the oxide (XIV), bp 93° (7 mm); n_D^{20} 1.4600. IR-spectrum (ν, cm^{-1}): 700, 770, 870, 1240, 1380; M^+ 198 (mass spectrometric). Found: C 66.9, H 11.0, Si 13.8%. $C_{11}H_{22}OSi$. Calculated: C 66.7, H 11.1, Si 14.1%.

Reaction of Trimethylsilylcyclopentadiene (XV) with DIBAH. Ten grams of the diene (XV) were added to a solution of 9 g of DIBAH in 150 ml of heptane at 90-100° in the course of 2-3 h and it was held at this temperature for 6 h. After evacuation we got 18.5 g OAC (XVI)–(XVII). Found C 68.76, H 11.00, Al 7.11, Si 12.0%. $C_{11}H_{41}AlSi_{1.6}$. Calculated: C 69.1, H 11.2, Al 7.4, Si 2.3%.

The OAC (XVI)–(XVII) were hydrolyzed in abs. hexane, the organic layer was dried with $MgSO_4$, and the solvent was distilled off. By means of vacuum distillation we obtained 4.2 g (XV), bp 35° (12 mm); n_D^{20} 1.4658 and 7 g of product (XVIII), bp 60–65° (1 mm); n_D^{20} 1.4885. IR-spectrum (ν, cm^{-1}): 700, 760, 855, 1250, 3030. PMR spectrum (δ, ppm): −0.08 (9H); +0.12 (9H); 6.27 (1H olefin). M^+ 278 (mass spectrometric). Found C 69.25, H 10.8, Si 19.9%. $C_{16}H_{30}Si_2$. Calculated: C 69.0, H 10.8, Si 20.2%.

CONCLUSIONS

1. The disubstituted double bond in the β-position with respect to the silicon atom does not enter into the hydroalumination reaction because of the interaction of the π-electrons with the 3d-vacant orbitals of the silicon atom.

2. The disubstituted double bond, which is removed from the silicon atom, enters into the hydroalumination reaction without a shift in the vinyl position to form organoaluminum compounds which contain the silicon atom.

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