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THE DIMETHYLSILANE HYDROSILYLATION OF FUNCTIONAL OLEFINS

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Summary

Dimethylsilane hydrosilylation of some polar compounds has been carried out by the catalytic system $\text{Ni}(\text{acac})_2 + \text{AlR}_3 + \text{PPh}_3$. The interaction proceeded through only one Si—H bond. As an example the addition of dideuterodimethylsilane to acrylonitrile and vinyl butyl ether has been used for the proposed scheme of the process.

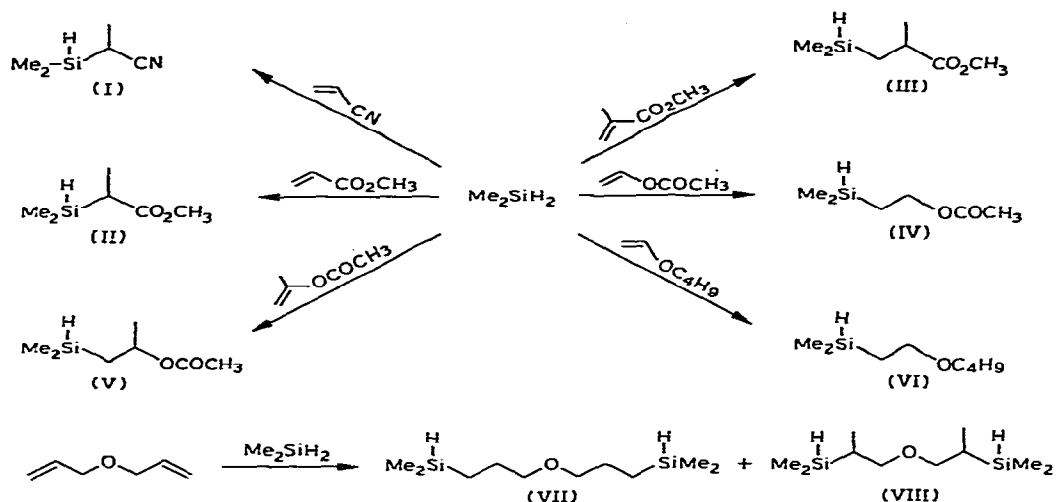
The alkylhalo- or trihalosilane hydrosilylation of functional olefins is usually carried out by a catalytic system in the presence of Pt [1], Rh [2], or Ni [3–5]. The silicon—halogen compounds obtained with different functional groups in the organic radical are most commonly inserted into following transformations through the Si—halogen bond.

The present work deals with procedures of the synthesis of the silyl monomers whose Si atom contains the Si—H bond apart from the functional polar bond, and the work also shows the Si—H bond activity. Towards this end dimethylsilane (DMS) has been used as a hydrosilylation agent. The catalytic system consisted of $\text{Ni}(\text{acac})_2$, triphenylphosphine (PPh_3) and organoaluminium compounds (OAC) such as tris(2-phenyl-1-ethyl)aluminium or perhydro[9b]aluminumphenolene as reductant. Triethyl- or triisobutyl-aluminium are not useful in this reaction because of the polymerization products which decrease the yield of the final product. This system has proved to be good in the hydrosilylation process of 1,3-dienes [8,9].

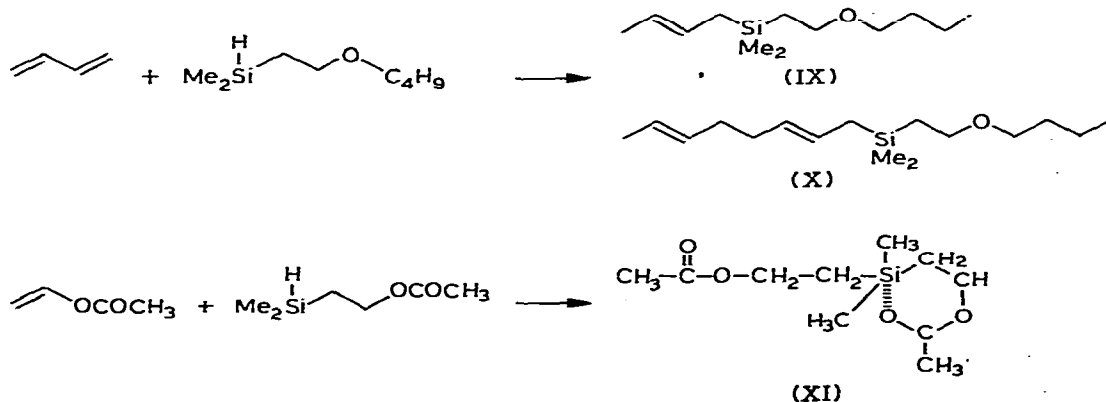
The interaction between DMS and acrylonitrile gave 1-(dimethylsilyl)-1-cyanoethane (I), methyl esters of acrylic and methacrylic acids gave, respectively, methyl esters of 2-(dimethylsilyl)- (II) and 2-methyl-3-(dimethylsilyl)-propionic acids (III). Vinyl- and isopropenylacetates converted to 2-(dimethylsilyl)ethylacetate (IV) and 1-(dimethylsilyl)isopropylacetate (V). The hydrosilylation products were obtained in 70–80% yield with conversions of 40–50%. Besides hydrosilanes (I–V) the formation of isomeric addition products of 5–10% was

observed in all cases. In the experimental section are set out the constants of single monomers obtained by preparative chromatography.

Vinyl butyl ether in a reaction with DMS gave the single 1-(dimethylsilyl)-3-oxaheptane (VI) in high yield and with good conversion. Diallyl ether did not react with DMS unambiguously, equal amounts of 1,7-bis(dimethylsilyl)- (VII) and 2,6-bis(dimethylsilyl)-4-oxaheptanes (VIII) were isolated from the reaction products.



Characteristic of these reactions is that hydrosilylation proceeds through one hydrosilylic bond under these conditions, and adduct formation through both bonds simultaneously was not observed. At the same time the Si-H bonds of products I-VIII are active enough to allow them to be used as hydrosilanes for the hydrosilylation of dienes in repeated reactions. For example, 1-(dimethylsilyl)-3-oxaheptane reacted with butadiene and the previously mentioned catalytic system to give either 5,5-dimethyl-5-sila-8-oxa-2-dodecene (IX) or 9,9-dimethyl-9-sila-12-oxa-2,6-hexadecadiene (X) depending on the conditions of the experiment. It is to be noted that hydrosilylation has been previously observed to be accompanied by the oligomerization process in studying the interaction between butadiene and DMS [4].



In an iterative reaction with vinylacetate under the same conditions the silane IV gave 1,5-diacetato-3,3-dimethyl-3-silapentanediol (XI) in 60% yield which has been isolated pure and characterized.

The IR spectrum of product XI showed equivalent absorption bands at 1745 and 1725 cm^{-1} which are characteristic of the acetate groups. The NMR spectrum of product XI showed the methyl protons of the acetate group to appear at 1.91 and 1.95 ppm as two singlets. This proves the two acetate groups to be different due to the formation of a six-membered ring in which magnetic non-equivalency of the protons is observed because of the $d_{\pi}-p_{\pi}$ interaction between 3d orbital of the silicon atom and p-electrons of the oxygen of one of the acetate groups.

The substitution of the inert solvent HCCl_3 by deuterated methanol removes the $d_{\pi}-p_{\pi}$ interaction and this spectrum shows a signal of a methyl group in the field of 1.91 ppm which is also peculiar to the product III.

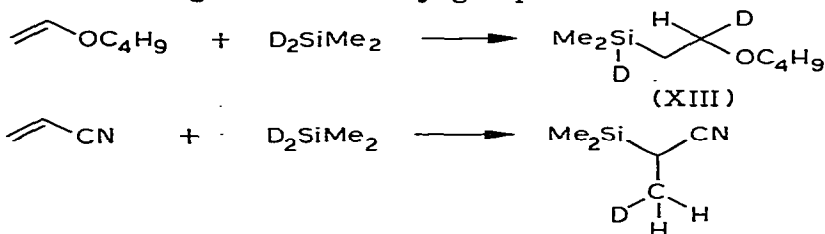
The proposed method can be good practice in the synthesis of bis-functional silicon derivatives.

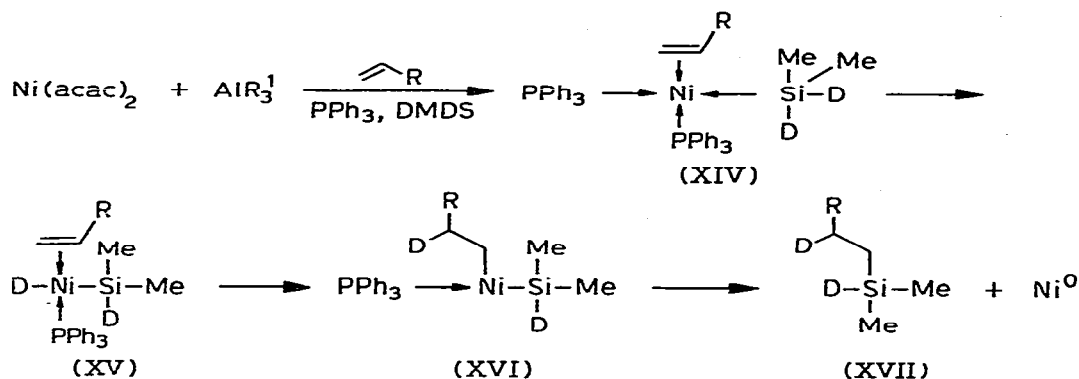
To establish a possible scheme of the hydrosilylation of functional derivatives of olefins the interaction between dimethyldideuterosilane (DMDS) and acrylonitrile and vinyl butyl ether has been studied.

The DMDS hydrosilylation of acrylonitrile was carried out under the same conditions, and the reaction proceeded selectively giving the adduct 1-(dimethyldeuterosilyl)-2-D-1-cyanoethane (XII) in 40% yield. In the NMR spectrum of product XII methyl protons at the silicon atom appear as a singlet at 0.05 ppm and a methine proton at C(1) interacting with the two protons at C(2) appears as a triplet at 1.75 ppm (J 6 Hz), while the same proton in compound I interacting with three methyl protons appears as a quartet. This proves one atom of deuterium to be at silicon and another at C(2).

The reaction of DMDS with vinyl butyl ethers leads to the addition product, 1-(dimethyldeuterosilyl)-2-D-3-oxaheptane (XIII). In the NMR spectrum of the adduct XIII the singlet at 0.05 ppm is assigned to the six methyl protons at the silicon atom. Methylene protons at C(2) appear as a doublet at 0.55 ppm (J 7 Hz) as opposed to the compound VI whose protons appear as a triplet in the equivalent field. According to these results one atom of deuterium is believed to be at C(2) and another at the silicon atom.

Thus, a possible interaction scheme suggests itself for this process: the interaction between $\text{Ni}(\text{acac})_2$ with the organoaluminium compounds in the presence of an olefin and PPh_3 leads to complex XIV. The subsequent insertion of metal through the Si-D bond leads to the complex XV of bivalent nickel. The deuterium addition through the double bond is accompanied by the formation of the C-Ni-Si σ bond and gives complex XVI. The deuterium attack of the α or β -carbon atom depends on its electronic density and substituent on the double bond. The migration of the silyl group leads to the silane XVII and nickel(0).





Experimental

Measurement

IR spectra were determined on a UR-20 spectrophotometer, NMR spectra were taken on Tesla BS-487B and JEOL-60C instruments using hexamethyldisiloxane as internal reference and CCl_4 as solvent. Mass spectra were recorded on an MX-13-03 spectrophotometer. The ionization energy was 200°C . GLC analysis was performed on an XT-instrument (l 3 m, d 4 mm); the solid carrier was Xromatone N, the liquid phase XE-60 (10%). The flow rate of the gas carrier (nitrogen) was 40 ml/min.

An example of hydrosilylation: the argon blown autoclave was charged with 5.4 g (0.1 mol) of butadiene, 16.0 g (0.1 mol) of 1-(dimethylsilyl)-3-oxaheptane (VI), 0.13 g (0.5 mmol) of $\text{Ni}(\text{acac})_2$, 0.13 g (0.5 mmol) of PPh_3 and 0.2 g (1 mmol) of perhydro[9b]alumophenolene. The mixture was kept for 8 h at 100°C . 17.1 g (80%) of the adduct was isolated containing the two compounds IX and X in 1/1 ratio according to GLC analysis. These products were distilled in vacuo under reflux.

5,5-Dimethyl-5-sila-8-oxa-2-dodecene (IX), b.p. $70-71^\circ\text{C}$ (3 mmHg), n_D^{20} 1.4515. IR (ν cm^{-1}): 840, 960, 1000, 1110, 1247, 3020. NMR (δ (ppm)): 0.05 s (6H, Si- CH_3), 0.50 t (2H, Si- CH_2 - CH_2 , J 7 Hz), 0.80 t (3H, CH_3 - CH_2 , J 6 Hz), 1.42 d (2H, Si- CH_2 -CH, J 7 Hz), 1.56 d (3H, CH_3 -CH, J 6 Hz), 1.95 m (4H, CH_2 -O- CH_2), 5.50 m (2H, CH=CH). m/e 214.

9,9-Dimethyl-9-sila-12-oxa-2,6-hexadecadiene (X), b.p. 125°C (2 mmHg), n_D^{20} 1.4643, IR (ν cm^{-1}): 850, 980, 1000, 1110, 1250, 3020. NMR (δ (ppm)): 0.06 s (6H, Si- CH_3), 0.45 t (2H, Si- CH_2 - CH_2 , J 7 Hz), 0.80 t (3H, CH_3 - CH_2 , J 6 Hz), 1.45 d (2H, Si- CH_2 -CH, J 7 Hz), 1.62 d (3H, CH_3 -CH, J 6 Hz), 2.05 m (8H, CH_2 - CH_2), 3.40 t (4H, CH_2 -O- CH_2 , J 7 Hz), 5.38 m (4H, CH=CH). m/e 268.

Hydrosilylation of the other compounds was carried out according to the method described.

The constants of the compounds obtained

The IR spectra of the products have the absorption bands for the functional groups, as well as the frequencies for the silyl fragments: 840, 1247, 2140 (Si- CH_2 , Si- CH_3 , Si-H) cm^{-1} .

1-(Dimethylsilyl)1-cyanoethane (I), 40% yield, b.p. 50°C (15 mmHg), n_D^{20} 1.4263, NMR (δ (ppm)): 0.05 d (6H, J 3 Hz), 1.27 d (3H, J 6 Hz), 1.87 q (1H, J 6 Hz), 4.38 q (1H, J 6 Hz). m/e 113.

Methyl ester of 2-(dimethylsilyl)propionic acid (II), 85% yield, b.p. 98°C (760 mmHg), n_D^{20} 1.4200, NMR (δ (ppm)): 0.05 d (6H, J 3 Hz), 0.84 q (1H, J 7 Hz), 1.14 d (3H, J 6 Hz), 3.55 s (3H), 3.88 q (1H, J 6 Hz). m/e 146.

Methyl ester of 2-methyl-3-(dimethylsilyl)propionic acid (III), 90% yield, b.p. 30°C (4 mmHg), n_D^{20} 1.4310, NMR (δ (ppm)): 0.05 d (6H, J 3 Hz), 0.83 d (2H, J 6 Hz), 2.43 q (1H, J 6 Hz), 3.48 s (3H), 3.75 q (1H, J 6 Hz). m/e 160.

2-(Dimethylsilyl)ethylacetate (IV), 80% yield, b.p. 106°C (760 mmHg), n_D^{20} 1.4170, NMR (δ (ppm)): 0.05 d (6H, J 3 Hz), 0.98 t (2H, J 6 Hz), 1.91 s (3H), 3.88 t (1H, J 6 Hz), 4.09 t (2H, J 6 Hz). m/e 146.

1-(Dimethylsilyl)isopropylacetate (V), 75% yield, b.p. 52°C (18 mmHg), n_D^{20} 1.4290, NMR (δ (ppm)): 0.05 d (6H, J 3 Hz), 1.80 d (3H, J 6 Hz), 0.98 d (2H, J 6 Hz), 2.63 q (1H, J 6 Hz), 3.88 q (1H, J 6 Hz). m/e 160.

1-(Dimethylsilyl)-3-oxaheptane (VI), 98% yield, b.p. 26°C (2 mmHg), n_D^{20} 1.4180, NMR (δ (ppm)): 0.05 d (6H, J 6 Hz), 0.81 t (2H, J 6 Hz), 0.92 t (3H, J 6 Hz), 2.35 m (4H), 3.31 t (4H, J 6 Hz), 3.73 t (1H, J 6 Hz). m/e 160.

1,7-Bis(dimethylsilyl)-4-oxaheptane (VII), 50% yield, b.p. 85°C (7 mmHg), n_D^{20} 1.4378, NMR (δ (ppm)): 0.05 d (2H, J 3 Hz), 0.75 t (2H, J 6 Hz), 1.40 t (4H, J 6 Hz), 1.60 (2H), 3.20 t (4H, J 6 Hz), 3.78 t (2H, J 6 Hz). m/e 218.

2,6-Bis(dimethylsilyl)-4-oxaheptane (VIII), 50% yield, b.p. 55°C (7 mmHg), n_D^{20} 1.4301, NMR (δ (ppm)): 0.05 d (12H, J 3 Hz), 0.90 m (2H), 1.50 d (6H, J 6 Hz), 3.31 d (4H, J 6 Hz), 3.48 t (2H, J 6 Hz), m/e 218.

1,5-Diacetato-3,3-dimethyl-3-silapentadiol (XI), 60% yield, b.p. 90°C (15 mmHg), n_D^{20} 1.4295, NMR (δ (ppm)): 0.25 s (6H), 1.13 t (4H, J 6 Hz), 1.91 s, 1.95 s (6H), 4.09 t (4H, J 6 Hz). NMR (δ (ppm)) (in CD₃OD): 0.06 s (6H), 0.99 t (4H, J 6 Hz), 1.91 s (6H), 4.09 t (4H, J 6 Hz). m/e 232.

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