SYNTHESIS OF UNSATURATED ORGANOSILICON COMPOUNDS FROM PROPARGYL ALCOHOL

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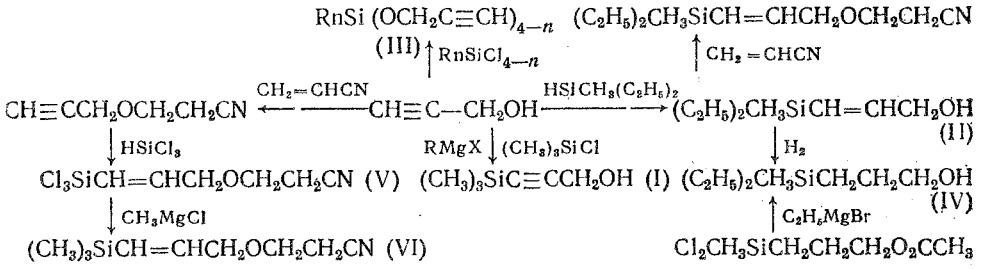
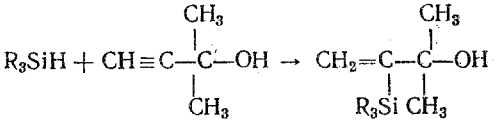
In the work of Petrov [1-6] and Shostakovskii [7-12] and their co-workers it was shown that there are wide possibilities of synthesizing various unsaturated organosilicon compounds from acetylenic alcohols. Dimethylethynylcarbinol and a series of its analogs and derivatives were used in these converisons. However, the possibilities of synthesizing organosilicon compounds from the simplest acetylenic alcohol, namely, propargyl alcohol, have still not been investigated. To fill this gap, in the present work we studied the series of conversions of propargyl alcohol given in the scheme below:



One should note the order of addition of R_3SiH to propargyl alcohol which we found in these conversions, and which did not correspond to the order of addition of these silanes to $(CH_3)_2C(OH)C{\equiv}CH$ [2,3].



EXPERIMENTAL

γ-(Trimethylsilyl)propargyl alcohol $(CH_3)_3SiC{\equiv}CCH_2OH$ (I). To the C_2G_5MgBr from 49 g of magnesium and 230 g of ethyl bromide in 0.6 liter of ether was added 40 g of propargyl alcohol. The contents of the flask were left overnight. On the following day, 70 g of trimethylchlorosilane was added and the ether distilled from the flask. The residue was heated on a boiling water bath for 3 hr. After the addition of 400 ml of ether, the complex was decomposed with very dilute acid. The ether layer was combined with ether extracts from the aqueous layer and dried with Na_2SO_4. After removal of the ether, vacuum distillation of the residue yielded 40 g of γ-(trimethylsilyl)propargyl alcohol with b.p. 65° (10 mm); n_D^{20} 1.4518; d_4^{20} 0.8753; found MR 39.50; calculated MR 39.48; yield 43.5%. Found: C 55.98; 56.09; H 9.34; 9.64; Si 22.29; 22.00%. $C_6H_{12}SiO$. Calculated: c 56.19; H 9.43; Si 21.90%.

Raman spectrum*. 148 (1), 173 (1 v. broad), 220 (v. broad), 261 (1), 382 (4), 438 (0), 600 (7), 645 (7), 693 (4), 763 (1), 832 (0), 975 (0), 1045 (0), 1191 (0), 1254 (4), 1404(0), 1445 (1), 2177 (10), 2200 (8), 2959 (8).

γ-(Diethylmethylsilyl)allyl alcohol $(C_2H_5)_2CH_3SiCH=CHCH_2OH$ (II). To a mixture of 24 g of diethylmethylsilane and 16 g of propargyl alcohol was added 0.1 ml of a 0.1 N solution of $H_2PtCl_6 \cdot 6H_2O$. Stirring formed an emulsion, which gradually disappeared on heating. Heating was stopped when the temperature of the mixture reached 140-145°. Vacuum distillation yielded 25g of γ-(diethylmethylsilyl)allyl alcohol (II) with b.p.99-100° (10 mm); n_D^{20} 1.4605; d_4^{20} 0.8734; found MR 49.69; calculated MR 49.69 yield 67.5%. Found: C 60.89, 60.92; H 11.61, 11.44; Si 18.03, 18.14%. $C_8H_{18}SiO$. Calculated: C 60.69; H 11.46; Si 17.74%

* The Raman spectra were plotted by L. A. Leites.

Raman spectrum. 245 (0), 268 (0), 403 (1 broad), 559 (5 broad), 594 (6 broad), 650 (0), 916 (0), 677 (0), 981 (2), 1019 (1), 1134 (0), 1241 (3 broad), 1305 (6 broad), 1418 (8), 1464 (9 broad), 1610 (3), 1623 (5), 2884 (10), 2909 (10), 2963 (10).

The addition product of acrylonitrile and alcohol (II) $(C_2H_5)_2$ $CH_3SiCH{=}CH$ $CH_2OCH_2CH_2CN$ was obtained in the usual way in 60% yield and had b.p. 155° (20 mm); n_D^{20} 1.4582; d_4^{20} 0.9124; found MR 63.24; Calculated MR 63.63. Found: C 62.55, 62.69; H 9.76, 9.82; Si 13.30, 12.86%. $C_{11}H_{21}SiNO$. Calculated: C 62.50; H 10.01; Si 13.28%.

γ-(Diethylmethylsilyl)propyl alcohol $(C_2H_5)_2CH_3SiCH_2CH_2CH_2OH$ (IV). Hydrogenation of 18.5 g of γ-(diethylmethylsilyl)allyl alcohol over Raney nickel in ethanol in a hydrogenation flask was continued until the theoretical amount of hydrogen had been absorbed (14 hr). Distillation yielded an alcohol with b.p. 86° (9 mm); n_D^{20} 1.4505; d_4^{20} 0.8626 Although the refractive index and boiling point of this alcohol differed somewhat from those of authentic γ-(diethylmethylsilyl) propyl alcohol [b.p. 92° (9 mm); n_D^{20} 1.4445; d_4^{20} 0.8630, obtained by the action of 5 moles of C_2H_5MgBr on $Cl_2CH_3SiCH_2$ $CH_2CH_2O_2CCH_3$], its Raman spectrum coincided with that of authentic γ-(diethylmethylsilyl)propyl alcohol apart from very weak additional lines: 873 (1); 905 (0); 1325 (0); 2851 (1).

Raman spectrum. 550 (0), 580 (10), 597 (1), 645 (2 broad), 661 (1 broad), 710 (0), 726 (0), 752 (2 broad), 795 (0), 861 (1), 972 (3 broad), 1015 (4 broad), 1056 (2 broad), 1112 (2 broad), 1139 (2 broad), 1184 (3 broad), 1232 (3), 1251 (1), 1302 (2 broad), 1380 (1), 1415 (5 broad), 1467 (6 broad), 2875 (10), 2903 (10), 2937 (3), 2956 (10).

Propargyloxytrimethylsilane $CH{\equiv}CCH_2OSi(CH_3)_3$ (III). Over a period of 3 hr, 110 g of trimethylchlorosilane was added with stirring to a mixture of 56.1 g of propargyl alcohol, 79.1 g of pyridine, and 250 ml of ether. The pyridine salt formed was then removed by filtration and washed with fresh ether. After treatment with dry HCl, the filtrate was refiltered and distilled on a column. We obtained 60 g of propargyloxtrimethylsilane with b.p. 110.8° (757 mm); n_D^{20} 1.4090; d_4^{20} 0.8333; found MR 38.05; calculated MR 38.55; yield 47%. Found: C 56.19; 56.19; H 9.26, 9.01; Si 21.85, 22.06%. $C_6H_{12}SiO$. Calculated: C 56.19; H 9.43; Si 21.90%.

Raman spectrum. 181 (6 broad), 217 (5 broad), 310 (5 broad), 475 (0), 614 (10 broad), 690 (1), 752 (0), 830 (0), 923 (0), 1033 (0), 1102 (0), 1185 (0), 1262 (0), 1379 (1), 1405 (1), 1452 (1), 2129 (10 broad), 2900 (10 broad), 2956 (10), 3107 (4).

The following compounds were synthesized analogously: $C_2H_5(CH_3)_2SiOCH_2C{\equiv}CH$: b.p. 134.8° (745 mm); n_D^{20} 1.4172; d_4^{20} 0.8339; found MR 42.92; calculated MR 43.20; $(CH_3)_2Si(OCH_2C{\equiv}CH)_2$: b.p. 73° (10 mm); n_D^{20} 1.4368; d_4^{20} 0.966; found MR 45.57; calculated MR 45.75; $C_2H_5Si(OCH_2C{\equiv}CH)_3$: b.p. 118° (10 mm); n_D^{20} 1.4550; d_4^{20} 1.0328; found MR 58.40; calculated MR 58.10.

β-(γ-Trichlorosilylallyloxy) propionitrile $Cl_3SiCH{=}CHCH_2OCH_2CH_2CN$ (V). A mixture of 20 g of β-propargyloxypropionitrile [b.p. 111° (15 mm); n_D^{20} 1.4450; d_4^{20} 0.9962], 32 g of trichlorosilane, and 0.5 ml of a 0.1 N solution of $H_6PtCl_6{\cdot}6H_2O_2$, in isopropanol was boiled for 3 hr. Vacuum distillation yielded 23 g of β-(γ-trichlorosilylallyloxy) propionitrile with b.p. 140° (7 mm); n_D^{20} 1.4780; d_4^{20} 1.2900; Found MR 53.5; calculated MR 53.67. Found: Cl 61.00; 60.89%. $C_6H_8NOCl_3Si$. Calculated: Cl 60.94%. Methylation with CH_3MgCl gave a 50% yield of β-(γ-trimethylsilyallyloxy) propionitrile (VI) with b.p. 94-96° (6 mm); n_D^{20} 1.4490; d_4^{20} 0.9084; found MR 54.13; calculated MR 54.61.

SUMMARY

γ-Trialkylsilylpropargyl and allyl alcohols, and also propargyloxysilanes were synthesized from propargyl alcohol.

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