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LETTERS TO THE EDITOR

Addition of Triorganosilanes to 1-Propargyloxy-2-glycidyloxypropane in the Presence of Chloroplatinic Acid

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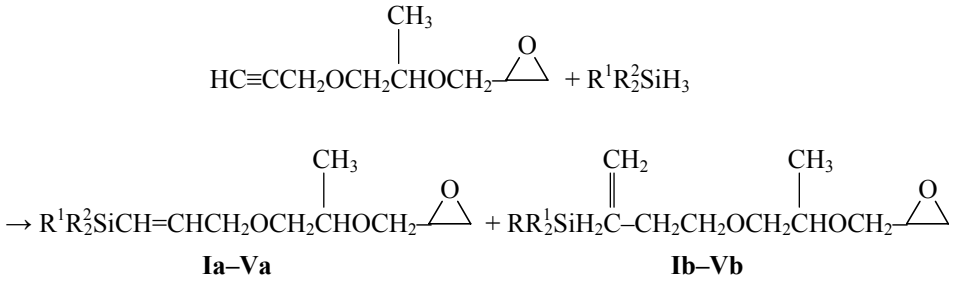
In continuation of the studies on the addition reactions of monohydrosilanes [1–5] the reaction of triorganosilanes with 1-propargyloxy-2-glycidyloxypropane in the presence of chloroplatinic acid is investigated. The reaction was shown to proceed with participation of the triple bond with the formation of the corresponding adducts **I–V** as a mixture of isomers in 75–87 % yield (Scheme 1).

Scheme 1.



Ia–Va **Ib–Vb**

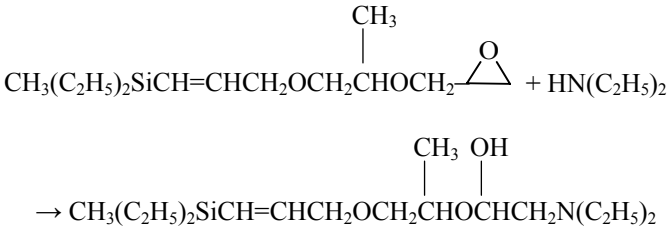
$R^1 = CH_3$, $R^2 = C_2H_5$ (**I**), C_3H_7 (**II**), OC_2H_5 (**III**), C_6H_5 (**IV**); $R^1 = C_6H_5$, $R^2 = CH_3$ (**V**).

The structure and composition of the reaction products was proved by the NMR spectroscopy data and by elemental analysis. Thus, in the ^{1}H NMR spectrum of compound **I** a broadened singlet of the C=CH_2 group of isomer **Ib** at 5.50 ppm and a multiplet at 5.86–6.24 ppm corresponding to the CH=CH group protons of isomer **Ia** were present. The protons of the SiCCH_2O group in isomer **Ib** appear as a singlet signal at 4.22 ppm, which is overlapped with the doublet signal of this group at 4.21 ppm belonging to isomer **Ia**. The ratio of the isomers according to the ^{1}H NMR spectroscopy data is **a** : **b** = 4 : 1.

The reaction of adduct **I** with diethylamine results in the opening of the epoxide ring with the formation of the secondary alcohol **VI** (Scheme 2).

1-(γ-Methyldiethylsilylallyloxy)-2-glycidyloxypropane (I). The mixture of 21.4 g of freshly distilled 1-propargyloxy-2-glycidyloxypropane, 40 mL of dry benzene, and 0.02 mL of the solution of chloroplatinic acid in isopropanol was heated to reflux, and 8.0 g of methyldiethylsilane was added. The obtained mixture was refluxed for 18 h. After removal of solvent, the residue was distilled in a vacuum. Yield 22.5 g (75%),

Scheme 2.



bp 122°C (0.5 mmHg), d_4^{20} 0.9412 g/cm^3, n_D^{20} 1.4611. IR spectrum, ν, cm^{-1}: 3055 (C–H), 1610 (C=C), 1259 (Si–C). Found; %: C 61.88; H 10.68; Si 10.48. MR_D 79.46. $C_{14}H_{28}O_3Si$. Calculated, %: C 61.72; H 10.35; Si 10.31. MR_D 79.49.

Similarly, compounds **II–V** were obtained.

1-(γ-Methyldipropylsilylallyloxy)-2-glycidyloxypropane (II). Yield 81%, bp 142°C (0.5 mmHg), d_4^{20} 0.9346 g/cm^3, n_D^{20} 1.4630. Found, %: C 64.14; H 10.85; Si 9.71. $C_{16}H_{32}O_3Si$. Calculated, % : C 63.95; H 10.73; Si 9.35.

1-(γ-Methyldiethoxylsilylallyloxy)-2-glycidyloxypropane (III). Yield 87%, bp 148°C (0.5 mmHg), d_4^{20} 1.0094 g/cm^3, n_D^{20} 1.4480. Found, %: C 55.43; H 9.38; Si 9.39. $C_{14}H_{28}O_5Si$. Calculated, %: C 55.23; H 9.27; Si 9.22.

1-(γ-Methyldiphenylsilylallyloxy)-2-glycidyloxypropane (IV). Yield 72%, bp 214.5°C (0.5 mmHg), d_4^{20} 1.0836 g/cm^3, n_D^{20} 1.5585. Found, %: C 73.39, H 9.76, Si 6.51. $C_{22}H_{28}O_3Si$. Calculated, %: C 73.25; H 9.56; Si 6.34.

1-(γ-Dimethylphenylsilylallyloxy)-2-glycidyloxypropane (V). Yield 77%, bp 169.5°C (0.5 mmHg), d_4^{20} 1.0241 g/cm^3, n_D^{20} 1.5099. Found, %: C 66.81; H 8.46; Si 9.35. $C_{17}H_{26}O_3Si$. Calculated, % : C 66.62; H 8.55; Si 9.16.

Reaction of epoxysilane I with diethylamine. The mixture of 13.6 g of compound **I**, 2 drops of water, and 12.3 g of diethylamine was stirred for 8 h at 45°C, and then distilled. 15.9 g (92%) of aminoalcohol **VI** was obtained, bp 167°C (0.5 mmHg), d_4^{20} 0.9356 g/cm^3, n_D^{20} 1.4625. IR spectrum, ν, cm^{-1}: 3415 (OH). Found, %: C 62.83; H 11.48; N 4.21; Si 8.37. MR_D 103.78. $C_{18}H_{39}NO_3Si$. Calculated, %: C 62.56;. H 11.37; N 4.05. Si 8.13. MR_D 103.73.

^{1}H NMR spectra were registered on a 487 B Tesla (80 MHz) spectrometer from solutions in CCl_4, internal reference HMDS. IR spectra were taken on a UR-20 spectrophotometer from thin layer.

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