LETTERS TO THE EDITOR

REACTION OF 1,3-DIOXANIUM PERCHLORATE WITH SILICON-CONTAINING JOSICH REAGENTS

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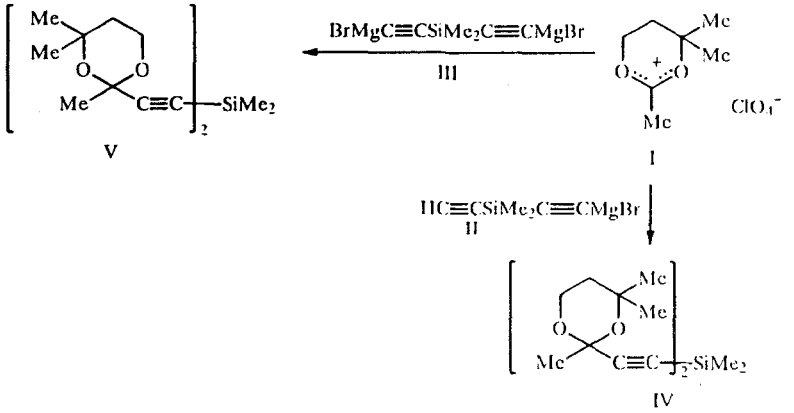
An original method is proposed for the synthesis of new derivatives of 1,3-dioxanes in which the 1,3-dioxane ring is bound at the carbon atom of the acetal fragment by a C–C bond with the silylethynyl substituent.

We have previously obtained similar 2-ethyl-substituted compounds, which are of interest as biologically active compounds, and as starting compounds for the synthesis of the difficultly accessible α-acetylene ketones [1].

We have found that under the conditions of an organomagnesium synthesis from dimethyldiethynylsilane and 2,4,4-trimethyl-1,3-dioxanium perchlorate, the corresponding silicon-acetylenic 1,3-dioxanes IV and V are readily formed.



The reaction was carried out at room temperature by adding perchlorate I in portions in the course of 20-30 min to the silicon-containing Josich complex obtained by a typical procedure. Compounds IV and V were obtained in a 60-80% yield.

Dimethyl(ethynyl)[(2,4,4-trimethyl-1,3-dioxan-2-yl)ethynyl]silane (IV, $C_{13}H_{20}O_2Si$). bp 146-148°C (14 mm Hg), d_4^{20} 0.9453; n_D^{20} 1.4596. IR spectrum: 1110, 1140, 1160, 1180 (O–C–O); 1260 (Si–CH_3); 2060, 2180 (C≡C); 3290 cm^{-1} (≡C–H). PMR spectrum (CCl_4): 0.05 [6H, s, $Si(CH_3)_2$]; 0.90, 1.16 [6H, s,s, $4(CH_3)_2$]; 0.9-1.6 (2H, m, 5-CH_2); 1.23 (3H, s, 2-CH_3); 2.3 (1H, s, ≡CH); 3.4-4.0 ppm (2H, m, 6-CH_2).

Dimethylbis-[(2,4,4-trimethyl-1,3-dioxan-2-yl)ethynyl]silane (V, $C_{20}H_{32}O_4Si$). mp 98°C (from ethanol). IR spectrum: 1110, 1140, 1160, 1185 (O–C–O); 1260 (Si–CH_3); 2170 cm^{-1} (C≡C); PMR spectrum (CCl_4): 0.2 [6H, s, $Si(CH_3)_2$]; 0.6-1.3 (4H, m, 5-CH_2); 0.83, 1.16 [12H, s,s, $4(CH_3)_2$]; 1.16 (6H, s, 2-CH_3); 3.38-3.9 ppm (4H, m, 6-CH_2).

REFERENCES

1. T. P. Kosulina and V. G. Kul'nevich, Inventor's Certificate No. 1601097 (USSR); Byull. Izobret., No. 39, 97 (1990).

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