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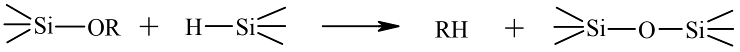
# LETTERS TO THE EDITOR

## NOVEL REACTIONS TO FORM AN Si–O–Ge GROUP

**L. Ignatovich, V. Muravenko, S. Grinberga, and E. Lukevics**

**Keywords:** alkoxygermanes, alkoxysilanes, hydrogermanes, hydrosilanes, siloxygermanes, tris(pentafluorophenyl)borane.

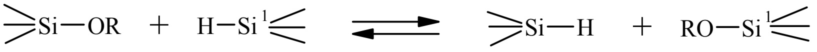
In study of O-silylation of hydroxyl-containing compounds [1-3] and hydrosilylation of the carbonyl group [3-6] in the presence of tris(pentafluorophenyl)borane [7], further reduction of the initially formed alkoxysilanes by excess hydrosilane has been observed:


(1)

This reaction was suggested for preparative reduction of the carbonyl group to a methylene [8] or methyl [3, 8, 9] group without preliminary separation of the intermediate alkoxysilanes.

Another group of researchers who were interested in organosilicon reaction products (1) suggested using it for synthesis of new siloxanes and polysiloxanes [10, 11].

In a study of the mechanism of the reaction of hydrosilanes with alkoxysilanes in the presence of $B(C_6F_5)_3$, the following competing reaction was found involving exchange of substituents on the silicon atoms, with formation of a new hydrosilane and a new alkoxysilane, which ultimately leads to formation of two symmetric and one nonsymmetric disiloxane [12].


(2)

Alkylhydrosilanes [1-3, 5, 6, 9, 10, 12], arylhydrosilanes [4-6], alkylarylhydrosilanes [6, 10-12], and hydrosiloxanes [8, 10] have been used in reactions (1) and (2).

We have shown that hetarylhydrosilanes, such as methyl(2-furyl)(2-thienyl)silane, also react with alkoxysilanes in the presence of $B(C_6F_5)_3$. Its reaction with methyltriethoxysilane occurs with stepwise substitution of one and two ethoxy groups (Table 1, runs 6 and 7). With excess hydrosilane (run 8), we observe formation of 1,3-di(2-furyl)-1,3-dimethyl-1,3-di(2-thienyl)disiloxane (*via* exchange according to reaction (2)).

Condensation of triethylsilane with 1-ethoxysilatrane (run 10), containing a five-coordinate silicon atom in the ring, occurred with significantly more difficulty.

For the first time, we have established that alkoxygermanes (3) and hydrogermanes (4) enter into a similar reaction, with formation of an Si–O–Ge group.

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Latvian Institute of Organic Synthesis, Riga LV-1006; e-mail: ign@osi.lv. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 299-302, February, 2006. Original article submitted January 20, 2006.

TABLE 1. Reaction of Hydrosilanes(germanes) with Alkoxysilanes(germanes)

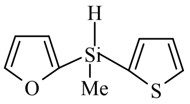
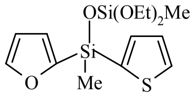
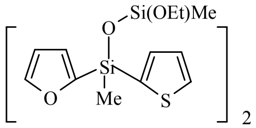
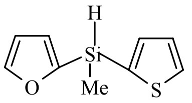
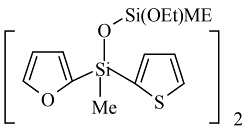
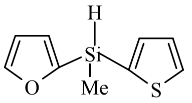
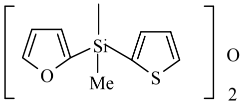
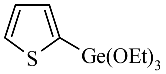
| Run | $\geqslant$M-OEt | $\geqslant$M-H | Hydrosilane equivalents | Reaction time, h | Major reaction products | % by GC/MS |
|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 1 | $Et_3SiOEt$ | $Et_3SiH$ | 1 | 1 | $Et_3SiOSiEt_3$ | 77 |
| 2 | $Et_3SiOEt$ | $Et_3GeH$ | 1 | 1 | $Et_3SiOGeEt_3$ | 66 |
| 3 | $MeSi(OEt)_3$ | $Et_3SiH$ | 3 | 1 | $MeSiOEt(OSiEt_3)_2$<br>$MeSi(OSiEt_3)_3$<br>$Et_3SiOSiEt_3$ | 30<br>40<br>10 |
| 4 | $MeSi(OEt)_3$ | $Et_3GeH$ | 3 | 3 | $MeSi(OEt)_2OGeEt_3$ | 55 |
| 5 | $MeSi(OEt)_3$ | $Et_3GeH$ | 4 | 3 | $MeSi(OEt)_2OGeEt_3$ | 60 |
| 6 | $MeSi(OEt)_3$ |  | 1 | 1 | <br> | 60<br>10 |

TABLE 1 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| 7 | MeSi(OEt)$_3$ |  | 3 | 1 |  | 80 |
| 8 | MeSi(OEt)$_3$ |  | 4.5 | 1 |  | 85 |
| 9 |  | Et$_3$SiH | 3 | 1 |  | 20 |
| 10 | N(CH$_2$CH$_2$O)$_3$SiOEt | Et$_3$SiH | 1 | 8 | N(CH$_2$CH$_2$O)$_3$SiOSiEt$_3$ | Traces |

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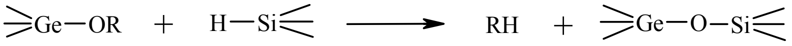
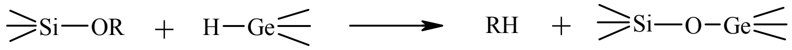
* Reaction temperatures 50°C (runs 1-9) and 80°C (run 10).



(3)



(4)

In this case, hydrogermanes proved to be less reactive than hydrosilanes. Thus triethylgermane reacted with triethylethoxysilane more slowly than triethylsilane (runs 1 and 2), and only one ethoxy group was substituted in methyltriethoxysilane (runs 4 and 5) under conditions where triethylsilane substituted two and three ethoxy groups (run 3). Only one ethoxy group was substituted by the triethylsiloxy group in 2-thienyltriethoxygermane, when treated with triethylsilane (run 9).

The reactions were carried out in 8 ml toluene under a dry argon atmosphere with 1.4 mmol alkoxysilane and 0.07 mmol $B(C_6F_5)_3$; the products were analyzed by chromatography/mass spectrometry on an HP 6890 GC/MS spectrometer (70 eV) equipped with an HP-5 capillary column (30.0 m × 250 μm × 0.25 μm).

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