Chemistry of Heterocyclic Compounds, Vol. 33, No. 2, 1997

SYNTHESIS OF THIENYLHYDROGERMANES AND THEIR TRANSFORMATIONS IN THE PRESENCE OF DI(*tert*-BUTYL) PEROXIDE

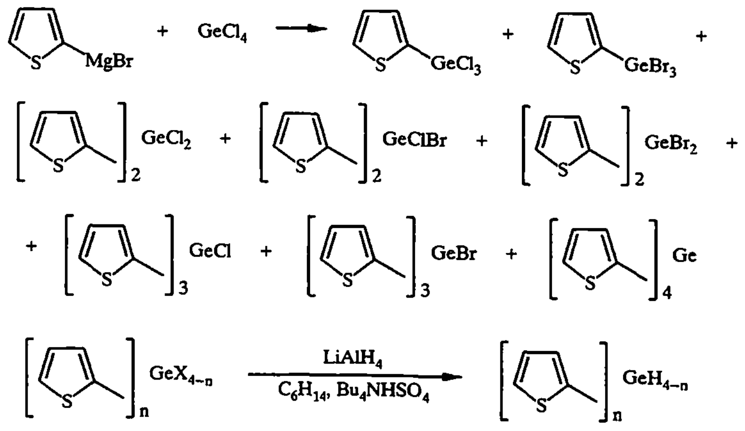
E. Lukevics, O. A. Pudova, I. Mazheika, and S. Grinberga

A method was developed for the synthesis of thienylhydrogermanes R_nGeH_{4-n} (where R = 2-thienyl, n = 1-3), involving the reduction of the corresponding ethoxygermanes by lithium aluminum hydride under the conditions of phase-transfer catalysis. The transformations of thienylhydrogermanes under the influence of di(tert-butyl) peroxide were studied. Features of the mass-spectrometric behavior of thienylethoxygermanes were analyzed.

Whereas methods for the production of thienylhydrosilanes and their chemical properties [1-3] have at the present time been studied fairly widely, thienylhydrogermanes [4, 5] and thienylethoxygermanes [5-7] have been investigated little. In this connection we undertook the synthesis of thienylhydrogermanes and studied their transformations in the presence of di(*tert*-butyl) peroxide.

In order to obtain the hydrogermanes we used the reduction of thienylhalogeno- and thienylethoxygermanes, which in turn we synthesized from 2-thienylmagnesium bromide. It was established by chromato-mass spectrometry that the reaction of 2-thienylmagnesium bromide with tetrachlorogermane in a molar ratio of 1:1 in absolute ether gave a complex mixture of (2-thienyl)chloro- and (2-thienyl)bromogermanes, which could not be separated by vacuum distillation. This mixture is easily reduced by lithium aluminum hydride under the conditions of phase-transfer catalysis (hexane, Bu_4NHSO_4, room temperature, 1-1.5 h [8, 9]) to a mixture of 2-thienyl-, di(2-thienyl)-, and tri(2-thienyl)germanes, which are also separated poorly during distillation.

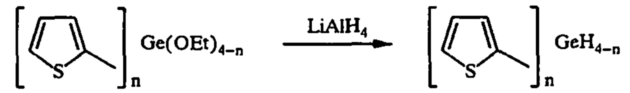
During alcoholysis of the mixture of thienylhalogenogermanes with ethanol in the presence of triethylamine the products from partial substitution of the halogen atoms [(2-thienyl)diethoxychloro- and di(2-thienyl)ethoxychlorogermane] are formed in addition to (2-thienyl)triethoxy-, di(2-thienyl)diethoxy-, and tri(2-thienyl)ethoxygermanes.



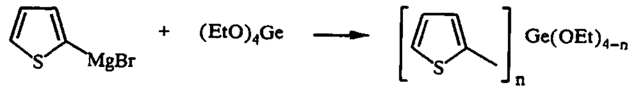
n = 1–3, X = Cl, Br

Latvian Institute of Organic Synthesis, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 198-201, February, 1997. Original article submitted November 11, 1996.

A more convenient method for the synthesis of thienyl-containing hydrogermanes is the reduction of the individual (2-thienyl)triethoxy-, di(2-thienyl)diethoxy-, and tri(2-thienyl)ethoxygermanes with lithium aluminum hydride (pentane, Bu_4NHSO_4, room temperature, 1 h). Under the indicated conditions the reduction takes place rapidly without cleavage of the $C_{thiophene}$—Ge bond as side process and, according to GLC, with a quantitative yield.



The initial thienylethoxygermanes in turn were obtained in the reaction of 2-thienylmagnesium bromide with tetraethoxygermane. The ratio of the 2-thienylmagnesium bromide and tetraethoxygermane in this reaction determines the ratio of the thienylethoxygermanes. Thus, with a ratio of 2:1 the main reaction product is tri(2-thienyl)ethoxygermane, while di(2-thienyl)diethoxy- and triethoxy(2-thienyl)germanes are only formed in small amounts. With the 2-thienylmagnesium bromide and tetraethoxygermane in a ratio of 1:1 (2-thienyl)triethoxy-, di(2-thienyl)diethoxy-, and tri(2-thienyl)ethoxygermanes are obtained with yields of 23, 30, and 10% respectively calculated on the reacted tetraethoxygermane.

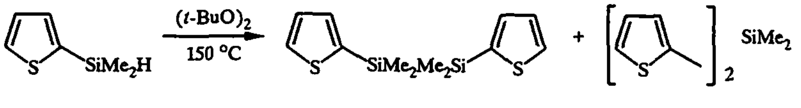


In a continuation of research into the dissociation of the furyl and thienyl derivatives of elements of group IVB under electron impact we obtained the mass spectra of (2-thienyl)ethoxygermanes $R_nGe(OEt)_{4-n}$ (where R = 2-thienyl, $n = 1, 2, 3$). Compared with the previously studied silicon analogs [10] the thienylethoxygermanes are less stable under electron impact. Their spectra do not contain a molecular peak, whereas the molecular ion peak in thienylethoxysilanes amounts to 20-100% of the maximum.

The destabilization of the molecular ion, together with the vigorous ejection of thiophene from its molecule (less characteristic of the thienylethoxysilanes), is due to the decrease in the π-accepting characteristics of germanium compared with silicon and, consequently, to the decrease in the delocalization of the positive charge in the thienylethoxygermanes. The main direction in the formation of the even-electron ions in the ethoxygermanes is the removal of the ethoxy radical. The intensity of the $(M - OEt)^+$ ions for the $R_nGe(OEt)_{4-n}$ is 90% ($n = 1$), 40% ($n = 2$), and 56% ($n = 3$). In the corresponding silanes the ejection of thiophene and the cleavage of the C—C bond in the ethoxy group take place in parallel with this process. The increase in the electropositivity of the germanium atom compared with silicon gives rise to an increase of the fraction of divalent germanium R_2Ge^+ (31 and 40% respectively for the compounds with $n = 2$ and 3), $RHGe^+$ (77 and 100% for the compounds with $n = 1$ and 2), and RGe^+ ions (23, 75, and 43% for thienyltriethoxy-, dithienyldiethoxy-, and trithienylethoxygermane) in the spectra.

The presence of the Ge—Cl bond in the molecules of $RGeCl(OEt)_2$ and $R_2GeCl(OEt)$ increases the stability of the molecular ions somewhat, and their intensities amount to 4 and 3% respectively. The initial dissociation of the molecular ions takes place exclusively with the formation of the even-electron ions in three parallel directions, i.e., ejection of the Cl, OEt, and R radicals. The intensity of the $(M - Cl)^+$ peaks amounts to 1 and 21%, the $(M - R)^+$ peaks to 25 and 25%, and the $(M - OEt)^+$ peaks to 100 and 54% respectively for thienylchlorodiethoxy- and dithienylchloroethoxygermane. The obtained data make it possible to conclude that the strength of the bonds decreases in the order Ge—Cl > Ge—2-thienyl > Ge—OEt. This order corresponds to the order of the strength of the bonds in the corresponding silicon compounds [11].

Earlier [12] we studied the transformation of phenyl- and thienylhydrosilanes under the influence of di(*tert*-butyl) peroxide. It was found that under radical conditions dimethyl(2-thienyl)silane forms a mixture of 1,1,2,2-tetramethyl-1,2-di(2-thienyl)disilane and dimethyldi(2-thienyl)silane with low yields (~30%) in a ratio of 3:1.



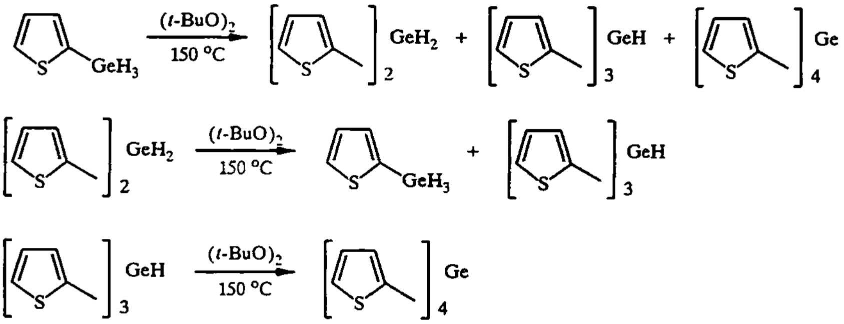
Under these conditions triethylgermane is converted with a high yield into a mixture of hexaethyldigermane and hexaethyldigermoxane (6:1).

In light of the results indicating the possible formation of Si—Si and Ge—Ge bonds in radical reactions we undertook an investigation into the chemical transformations of thienylhydrogermanes under the influence of di(*tert*-butyl) peroxide. However, the experiments showed that 2-thienylgermane in the presence of di(*tert*-butyl) peroxide (10% of the

TABLE 1. Physicochemical Characteristics of Thienylgermanes (R = 2-thienyl)

Compound	bp, °C (mm Hg)	δ ^{1}H, ppm (CDCl$_3$)				Mass spectrum, m/z (intensity, % of maximum)
		H(5)	H(4)	H(3)	others	
RGe(OEt)$_3$	82(2)	7,62	7,19	7,40	1,22 (9H, t, CH$_3$); 3,89 (6H, q, OCH$_2$)	247 [M^+ - OEt, 90]
R$_2$Ge(OEt)$_2$ [5]	124(2)	7,64	7,20	7,42	1,24 (6H, t, CH$_3$); 3,89 (4H, q, OCH$_2$)	285 [M^+ - OEt, 40]
R$_3$GeOEt	173(2)	7,64	7,20	7,44	1,21 (3H, t, CH$_3$); 3,84 (2H, q, OCH$_2$)	323 [M^+ - OEt, 56]
RGeH$_3$	136...138	7,53	7,19	7,30	4,40 (3H, s, Ge—H)	160 [M^+, 30], 85 (70), 74 (24), 54 (100), 39 (48)
R$_2$GeH$_2$ [5]	93(3)	7,57	7,20	7,32	5,49 (2H, s, Ge—H)	242 [M^+, 41], 157 (80), 97 (59), 85 (59), 74 (45), 52 (100), 39 (35)
R$_3$GeH	148(4)	7,61	7,21	7,34	6,01 (1H, s, Ge—H)	324 [M^+, 17], 241 (25), 157 (24), 134 (100), 108 (27), 51 (31)

peroxide, 150°C, Pierce microreactor, 1 h) gave a mixture of di(2-thienyl)-, tri(2-thienyl)-, and tetra(2-thienyl)germanes in ratios of 10:15:3; products with a Ge—Ge bond were not detected. Under analogous conditions di(2-thienyl)germane disproportionates with the formation of 2-thienyl- and tri(2-thienyl)germanes. Tri(2-thienyl)germane is transformed by the action of di(*tert*-butyl) peroxide into tetra(2-thienyl)germane.



Thus, thienylhydrogermanes react like phenylhydrosilanes [12] in radical processes. As in the case of triethylgermane, the formation of digermanes was not observed.

EXPERIMENTAL

The PMR spectra were recorded on a Bruker WH-90/DS spectrometer at 90 MHz in deuterochloroform with trimethylsilane as internal standard. The mass spectra were recorded on a Kratos MS-25 GC/MS instrument at 70 eV. The reactions and the purity of the products were monitored by GLC on Khrom-4 instrument with a flame-ionization detector in a glass column (1.2 m × 3 mm) with Chromosorb W-PH containing 5% of OV-17. The carrier gas was helium, and the column temperature was 250°C.

Synthesis of (2-Thienyl)ethoxygermanes. To 25.2 g (0.1 mole) of tetraethoxysilane in 100 ml.of absolute ether while stirring we added a solution of 2-thienylmagnesium bromide, obtained from 16.3 g (0.1 mole) of 2-bromothiophene and 2.4 g (0.1 mole) of magnesium. The reaction mixture was left overnight at room temperature. The precipitated magnesium salt was filtered off, the solvent was evaporated, and the residue was distilled under vacuum. During distillation we obtained 6.7 g (23%) of triethoxy(2-thienyl)germane, 4.9 g (30%) of diethoxy(2-thienyl)germane, and 1.2 g (10%) of ethoxytri(2-thienyl)germane.

Synthesis of Thienylhydrogermanes. To a suspension of 1 g of lithium aluminum hydride in 50 ml of pentane we added 6.5 g (0.02 mole) of triethoxy(2-thienyl)germane and 0.74 g of Bu_4NHSO_4. The mixture was stirred at room temperature for 2 h. The precipitate was filtered off, and the filtrate was distilled. We obtained 2.6 g (81%) of 2-thienylgermane.

Di(2-thienyl)germane [5] and tri(2-thienyl)germane were obtained similarly in hexane solution.

Reactions of (2-Thienyl)hydrogermanes with Di(*tert*-butyl) Peroxide. A mixture of 0.01 mole of thienylhydrogermane and 0.15 g (0.001 mole) of di(*tert*-butyl) peroxide was heated at 150°C in a Pierce reactor for 1 h. The product was analyzed by GLC and chromato-mass spectrometry.

The constants of the obtained compounds and also the PMR and mass spectra are given in Table 1.

REFERENCES

1. E. Ya. Lukevics, O. A. Pudova, and N. P. Erchak, Advances in Organosilicon Chemistry, MIR Publishers, Moscow (1985), p. 153.
2. E. Lukevics, R. Ya. Sturkovich, and O. A. Pudova, J. Organomet. Chem., **292**, 151 (1985).
3. E. Lukevics, O. A. Pudova, R. Ya. Sturkovich, and A. P. Gaukhman, J. Organomet. Chem., **346**, 297 (1988).
4. E. Lukevits [Lukevics], R. Ya. Sturkovich, and O. A. Pudova, Zh. Obshch. Khim., **58**, 815 (1988).
5. E. Lukevics, S. Belyakov, and O. Pudova, J. Organomet. Chem., **523**, 41 (1996).
6. E. Lukevits [Lukevics], S. Germane, O. A. Pudova, and N. P. Erchak, Khim. Farm. Zh., **13**, No. 10, 52 (1979).
7. E. Lukevics, L. Ignatovich, N. Porsiurova, and S. Germane, Appl. Organomet. Chem., **2**, 115 (1988).
8. V. N. Gevorgyan, L. M. Ignatovich, and E. Lukevics, J. Organomet. Chem., **284**, C31 (1985).
9. V. Gevorgyan and E. Lukevics, J. Chem. Soc. Chem. Commun., No. 18, 1234 (1985).
10. S. Kh. Rozite, I. B. Mazheika, A. P. Gaukhman, N. P. Erchak, and E. Lukevits [Lukevics], Izv. Akad. Nauk Latv. SSR. Ser. Khim., No. 1, 102 (1985).
11. I. Mazheika, S. Grinberg, and E. Lukevits [Lukevics], Khim. Geterotsikl. Soedin., No. 7, 891 (1993).
12. E. Lukevits [Lukevics], O. A. Pudova, L. I. Borisova, and V. N. Gevorgyan, Izv. Akad. Nauk Latv. SSR. Ser. Khim., No. 5, 597 (1989).