ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 7, pp. 1187–1189. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © D.L. Myalochkin, T.A. Kochina, D.V. Vrazhnov, V.V. Avrorin, E.N. Sinotova, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 7, pp. 1103–1105.

Synthesis of Dimethylditritiogermane Me_2GeT_2

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Received March 7, 2007

Abstract—A microsynthetic procedure for preparing tritium-labeled alkyl-substituted germanes is developed. The resulting dimethylditritiogermane can be used as a source of dimethylgermylium ions. The synthesis was performed by the reduction of dibromodimethylgermane with lithium tritide in presence of $AlBr_3$.

DOI: 10.1134/S1070363207070080

Carbocations have been thoroughly studied throughout the entire preceding century, whereas their isoelectronic analogs, Group IV heavy element cations R_3M^+ (M = Si, Ge, Sn), still remain extremely poorly explored[1].

The formation of germylium ions were first reported more than fifty years ago [5], but nowadays the information on the properties and reactivity of these intermediates is scarce and controversial. Specifically, ion cyclotron resonance studies of reactions of Me_3Ge^+ ions with nitrogen- and oxygen-containing compounds showed that the adducts formed by these reactions are more stable than the corresponding adducts of Me_3Si cations [6]. At the same time, it was shown that the association energy of R_3M^+ cations with water decreases in the series $R_3Si^+ > R_3Ge^+ > R_3Sn^+$ [7]. Note that the few gas-phase studies [6–13] were all carried out by means of mass spectrometry and ion cyclotron resonance spectroscopy, whose possibilities are limited by rarefied gases and charged products. Moreover, these studies dealt exclusively with unsubstituted (H_3Ge^+) or fully substituted (R_3Ge^+) germylium cations. Reactions of germylium cations in the condensed phase have never been studied.

To solve this fundamental problem, we offered a nontraditional radiochemical approach involving a nuclear chemical method for generation of cations and radiochemical studies of their reactions. This approach we developed and applied for generation and studies of transformations of sylilium ions [4, 14]. In the present work, an attempt was made to extend this approach to free germylium cations, that is to make use of the β-decay of tritium in tritium-containing organogermanium compounds for generating free germylium cations according to the following scheme.

$$R_3GeT \xrightarrow{\beta} [R_3Ge\text{–}He]^+ \longrightarrow R_3Ge^+ + He.$$

For accomplishing this process it was necessary to prepare a tritium-containing organogermanium compound, a precursor of the corresponding cations. The aim of this work was to synthesize dimethylditritiogermane, a source of dimethylgermylium cations. The need in at least doubly labeled precursors arises from the fact that one tritium atom undergoes decay to generate a cation, while the second one acts as a label which allows to trace transformations of this cation. The probability of simultaneous decay of two tritium atoms in one molecule is negligible. It is determined by the squared tritium decay constant equal to 1.8×10^{-9} s[1]. Furthermore, by detecting reaction products by their radioactivity we can distinguish them from unlabeled radiolysis products. The synthesis of the target product was based on the reduction of dibromodimethylgermane with lithium tritide in the presence of $AlBr_3$.

$$Me_2GeBr_2 + 2LiT \xrightarrow{AlBr_3} Me_2GeT_2 + 2LiBr.$$

The isotope purity of the starting lithium tritide should be no less than 90%. Since such tritide is commercially unavailable, it was prepared by the reaction of butyllithium with molecular tritium (isotope purity 99.8%) in the presence of tetramethylethylenediamine.

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[1] Much recent attention has been attracted to generation and properties of sylilium ions [1–4].

$$T_2 + BuLi \xrightarrow{(CH_3)_2NCH_2CH_2N(CH_3)_2} LiT + BuT.$$

To this end, we modified the procedure in [5] suggesting use of large amounts of tritium for operation with small amounts of tritium in an isolated system. For reliable synthesis of labeled compounds, the procedure of microsynthesis should be worked out by multiply repeating model syntheses with protium or, if necessary, deuterium instead of tritium. The target product obtained in model experiments was identified as Me_2GeH_2 by gas chromatography, NMR spectroscopy, and mass spectrometry. The presence of a single peak in the chromatogram gave evidence for the formation of an individual substance. The ^1H NMR spectrum ($CDCl_3$, 25°C) contained a triplet (δ 0.3 ppm) and a septet (δ 3.7 ppm) with intensities characteristic of a structure containing two methyl groups and two hydrogen atoms directly bound with germanium. The spectrum agrees with reported data [16].

The mass spectra of organogermanium compounds are difficult to interpret strictly quantitatively because of the large number of native isotopes of germanium (5). Nevertheless, the mass spectrum of our synthesized compound (electron impact, 20 and 70 eV) confirmed the formation of dimethylgermane. The most abundant peaks belong to Me_2HGe^+ and MeH_2Ge^+ ions. Besides the mass spectrum contains a molecular ion peak $Me_2H_2Ge^{+\cdot}$ with an extremely low intensity and peaks of ions formed by deeper fragmentation ($Me_2Ge^{+\cdot}$ and $H_2Ge^{+\cdot}$), which agrees with published mass spectra of other organogermanium compounds [17].

EXPERIMENTAL

Chromatographic analysis of unlabeled and tritium-labeled products was carried out on a Tsvet 500 gas chromatograph equipped with thermal conductivity and radioactivity detectors, column 3000 × 2 mm, sorbent Poropak R, carrier gas helium (15 ml min^{-1}), quenching gas methane/argon (10 ml min^{-1}). The ^1H NMR spectra were taken on a Bruker Avance 300 DPX spectrometer ($CDCl_3$, 25°C). The mass spectra were obtained on an MX 1321 spectrometer, ionizing energy 30 and 70 eV.

The synthesis of dimethylditritiogermane was carried by strictly following the procedure developed in model experiments. The reaction device was an evacuated isolated system consisting of a reaction ampule, an ampule with preliminary activated CaA zeolite, and an ampule with gaseous tritium (2.5 Ci), connected with one another. The total volume of the reaction ampule and that with zeolite was no more than 2 ml. The reaction ampule was charged with butyllithium, 0.1 ml of a 1 M hexane solution, and 20 μl of tetramethylethylenediamine. The ampule with tritium was opened by means of a magnetic striker, and tritium was absorbed with zeolite at –196°C. After that the ampule with tritium was sealed off to minimize the reaction volume, the ampule with zeolite was heated to room temperature, and the reaction mixture was shaken for 4 h.

After completion of the first stage the solvent and tritiated butane C_4H_9T formed together with lithium tritide LiT were collected in the ampule with zeolite cooled to –196°C. The ampule with LiT was sealed off and opened under a dry inert atmosphere. A solution of $AlBr_3$ in dibutyl ether (0.2 ml, *c* 0.05 M) was added, and the ampule was cooled to –196°C and evacuated. Then it was heated to room temperature, and 0.1 ml of a 0.5 M Me_2GeBr_2[2] solution in dibutyl ether with a syringe through a vacuum rubber nipple.

The reaction mixture was kept at room temperature until the pressure in the system no longer increased and then cooled to –20°C (to reduce the partial vapor pressure of dibutyl ether), and the dimethylditritiogermane formed was condensed into a cylinder with xenone of spectral grade (V 400 ml, P_{Xe} 350 mm) cooled to –196°C.

Identification of the product and its chemical and radiochemical purity were determined by gas chromatography with thermal conductivity and radioactivity detectors. Identification was carried out by comparing the retention times of the labeled product and dimethylgermane synthesized in model experiments. The absence of noticeable amounts of radioactive and nonactive admixtures was established.

The yield of dimethylditritiogermane was 19% by volumetry and 8% by actinometry (per tritium). The activity was measured by the liquid scintillation technique on a Beta-2 device. The molar activity of the labeled dimethylgermane was 53 Ci $mmol^{-1}$, label multiplicity 1.8.

ACKNOWLEDGMENTS

The work was carried out under the Research Programs of the Department of Chemistry and Materials

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[2] For complete utilization of radioactive preparations (T_2 and LiT) compounds containing no tritium were taken in a 2–3-fold excess.

Sciences of the Russian Academy of Sciences (no. 1) and St. Petersburg Research Center of the Russian Academy of Sciences.

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