

---

LETTERS  
TO THE EDITOR

---

## Synthesis of 1-Hydrogermatrane Labelled with Tritium on the Ge–H Bond

V. V. Avrorin<sup>a</sup>, T. A. Kochina<sup>b\*</sup>, I. S. Ignat'ev<sup>a</sup>, and Yu. E. Ermolenko<sup>a</sup>

<sup>a</sup> St. Petersburg State University, Universitetskaya nab. 7–9, St. Petersburg, 198504 Russia

<sup>b</sup> I.V. Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences,  
nab. Makarova 2, St. Petersburg, 199034 Russia

\*e-mail: t-kochina@mail.ru

Received April 19, 2018

**Abstract**—The method of preparation of 1*H*-germatrane labelled with tritium on the germanium–hydrogen bond was elaborated with specific activity of 0.3 mCi/mg (~70 mCi/mmol).

**Keywords:** germatrane, tritium, tritium-labelled compounds

**DOI:** 10.1134/S1070363218100365

During many years we investigated ion-molecular reactions of three-coordinated cations of the 14th group elements in gas and condensed phases using nuclear-chemical method of generation of positively charged reactive species, cations [1]. The essence of the method consists in the processes accompanying  $\beta$ -decay of tritium in organic and organoelemental compounds according to equation (1).



Here,  $R^1$  and  $R^2$  are organic radicals, M is an element of the 14th group. The method allows to generate varying in composition free cations with the desired position of the charge, and to investigate their behavior in the reactions with nucleophilic substrates in any aggregate state not complicated with such accompanying factors as the effects of the solvent, catalyst, counter-ion, etc. The presence of tritium atom in the formed cation allows, firstly, applying the methods of chromatography in combination with very sensitive method of detection of the products of the reactions of these ions with various substrates by the method of radiometry, and, secondly, to ignore the radiation-chemical processes, unavoidably occurring in the system substrate/radioactive compound, leading to the formation, mainly, the products which do not contain radioactive label.

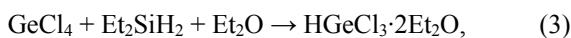
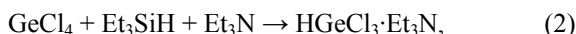
Unfortunately, this practical method of investigation is not applicable to generation of cations, whose

precursors are compounds with only one hydrogen atom at the central atom. We faced such situation when trying to generate silatranylium and germatranylium cations  $^+[M(OCH_2CH_2)_3N]$  ( $M = Si$  or  $Ge$ ), whose precursors are the corresponding 1*H*-silatrane and 1*H*-germatrane labelled with tritium on the element–hydrogen bond. Cations, arising upon the decay of tritium contained in these compounds do not contain radioactive label, so, it is impossible to use the method of radiometry for their detection. However, analytical capabilities of modern chromatomass spectrometry, apparently, allow solving this problem. Indeed, the system substrate/tritium-labelled precursor with activity of 1 mCi generates about  $5 \times 10^{-10}$  moles of cations in a reasonable time (~100 days). Modern mass spectrometers allow reliable detection of such and even much smaller (by 1–2 orders of magnitude) amounts of compounds.

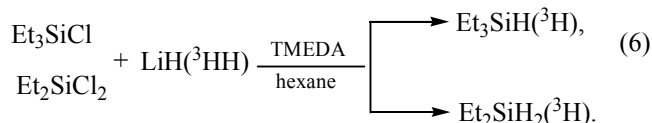
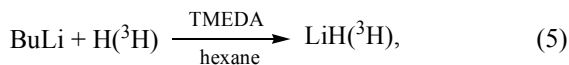
To check the applicability of this method to generation and investigation of ion-molecular reactions of the cations of this type, in particular, germatranylium cations, we need a procedure for introduction of tritium label into 1*H*-germatrane on the Ge–H bond. The goal of the present work was to work out such a procedure.

Three methods for preparation of 1*H*-germatrane were described in the literature [2–4]. All of them are based on the halogen–hydrogen exchange reaction

between germanium tetrachloride and silane with the formation of trichlorogermane. To stabilize unstable trichlorogermane, the formation of its complexes with amine or diethyl ether is used with subsequent conversion of the formed aminate or etherate to germatrane. As a source of hydrogen, trichlorosilane or di- or tri-substituted alkylsilanes can be used. The labelled 1*H*-trichlorosilane can be obtained by reactions (2)–(4).



The introduction of tritium label by reactions (2) and (3) requires two supporting reactions with tritium to be performed: the synthesis of lithium tritide by catalytic hydrogenation of butyllithium [reaction (5)] and its use for the reduction of substituted chlorosilanes to the corresponding hydrides [reaction (6)].

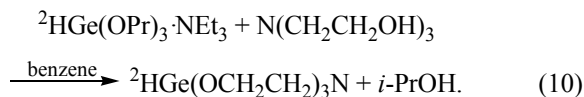
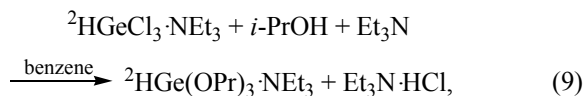
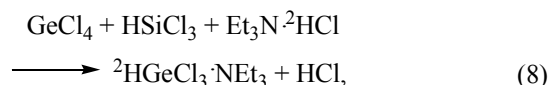
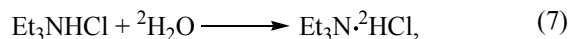


Reactions (5) and (6), when carried out on a micro-scale with stoichiometric amounts of the reagents, lead to the formation of the corresponding labelled silanes in no more than 10% yield [5]. Taking into account that the yield of 1*H*-germatrane in subsequent reactions does not exceed 15–20%, the total yield turns out to be unacceptably small.

In view of this, the most promising for introduction of tritium into the initial germanium compound is the use of reaction (8). This reaction proceeds rather fast and in nearly quantitative yield (80–90%). The source of tritium is triethylamine hydrochloride; introduction of tritium in this molecule is easily achieved by the isotope exchange between triethylamine hydrochloride and tritium-containing water.

The synthetic procedure was worked out on the reactions (7)–(10), using deuterium as the isotope label.

Introduction of the label into trichlorogermane aminate occurs due to the replacement of hydrogen chloride in the molecule of triethylamine hydrochloride by trichlorogermane, as a stronger acid. Therewith, complex  $^2\text{HGeCl}_3 \cdot \text{Et}_3\text{N}$  isomerizes to the salt product  $[\text{Et}_3\text{N}^2\text{H}]^+ [\text{GeCl}_3]^-$ . This mechanism was developed in [3] and



proved recently by our quantum-chemical calculations [6]. This causes practically the same degree of labelling of trichlorogermane aminate and triethylamine hydrochloride, which was proved by  $^2\text{H}$  NMR spectroscopy.

The ESI mass spectrum of germatrane prepared by the elaborated procedure contains a group of lines ( $M + \text{Na}^+$ ) with the isotope distribution typical for germanium compounds, the most intense lines being 244.005 (100), 242.005 (75), 240.005. The experimental mass spectrum practically coincides with the calculated one. The  $^1\text{H}$  NMR spectrum in chloroform contains three groups of signals (5.79 s, 1H, GeH; 3.83 t, 6H,  $\text{CH}_2\text{O}$ ; 2.88 t, 6H  $\text{CH}_2\text{N}$ ). In the spectrum of this compound in DMSO- $d_6$ , the Ge–H signal is shifted upfield to 5.44 ppm. In the  $^{13}\text{C}$  NMR spectrum, two signals appear at 51.56 and 56.40 ppm, characteristic of the atrane ring. The obtained spectra prove the structure of the synthesized compound as 1-hydrogermatrane and are nicely consistent with the earlier reported data [2].

When registering the  $^2\text{H}$  NMR spectrum, a singlet at 5.44 ppm is observed, which proves the presence of deuterium in the Ge–H bond of 1*H*-germatrane, although it turned out that the degree of deuterium labelling in the obtained compound is substantially lower than in trichlorogermane aminate. We have no explanation of this fact, the more so that we did not register deuterium in the  $^2\text{H}$  NMR spectrum of triethylamine hydrochloride formed in the reaction of trichlorogermanium aminate with isopropanol and triethylamine [reaction (9)]. Nevertheless, in spite of the loss of the isotope label, this method allows the preparation of the labelled germatrane in ~10% yield to the used hydrogen isotope; this yield is notably higher than when using labelled hydrosilanes.

## EXPERIMENTAL

Experimental procedure. Glass ampule connected with the tube filled with copper oxide and the ampule with gaseous tritium (0.5 Ci) was charged with 0.5 g of triethylamine hydrochloride. The system was evacuated, copper oxide heated to 400°C. The ampule with triethylamine hydrochloride was cooled with liquid nitrogen, the ampule with tritium was opened by magnetic peen and the tritium-containing water formed by the contact of tritium with copper oxide was condensed to the cooled ampule; to the same ampule, 500 µL of chloroform was condensed in a vacuum. The ampule was sealed and heated for some minutes for complete dissolution of the salt. Chloroform was removed from the reaction mixture in a vacuum and the labelled triethylamine hydrochloride was dried by gradually increasing the temperature to 150–160°C. The dried labelled triethylamine hydrochloride was transferred in a vial with screwed cap, 0.40 mL of trichlorosilane and 0.45 mL of germanium tetrachloride was added. The vial was tightly closed with screwed cap and kept in a boiling water bath till disappearance of the solid phase and the formation of two unmixed layers (~2 h). After cooling to room temperature, to the mixture 2 mL of dry hexane was added, the mixture was vigorously stirred by shaking, the hexane layer was separated and rejected. The residue of trichlorogermane aminate was washed with hexane, 2×2 mL, dissolved in 4 mL of benzene, the solution was cooled with ice water, and 0.75 mL of anhydrous isopropanol and 1.2 mL of triethylamine was successively added dropwise with intense stirring in an argon flow. The precipitate of triethylamine hydrochloride was filtered off in a vacuum. The transparent mother liquor was cooled again, and 0.25 mL of freshly distilled triethanolamine was added dropwise at stirring in an argon atmosphere. The reaction mixture was kept in a closed vial overnight in refrigerator. The formed precipitate was separated by centrifugation, the mother liquor was evaporated to half of the volume in a vacuum. The formed precipitate was separated again by centrifugation. The precipitates were combined, washed successively with hexane and

a small amount of cooled benzene. The obtained product was purified by crystallization from benzene to give 130 mg of dry product, yield 16% with respect to the used triethylamine hydrochloride. Total activity of the obtained product was ~40 mCi, the yield to the used tritium 8%.

Mass spectra were taken on a “MaXis” Bruker mass spectrometer. NMR spectra were registered on a Bruker 400 Avance spectrometer in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> solution. The activity of the synthesized compound was measured on the liquid β-radiometer “Beta-2.”

## ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (grant no. 16-03-00660). The authors thank the colleagues from the Scientific Park of St. Petersburg University for registering the NMR and mass spectra.

## CONFLICT OF INTERESTS

No conflict of interests was declared by the authors.

## REFERENCES

1. Kochina, T.A., Vrazhnov, D.V., Sinotova, E.N., and Voronkov, M.G., *Russ. Chem. Rev.*, 2006, vol. 75, no. 2, p. 95. doi 10.1070/RC2006v075n02ABEH002480
2. Mironov, V.F., Khromova, N.Yu., and Gar, T.K., *Zh. Obshch. Khim.*, 1981, 51, no. 4, p. 954.
3. Nametkin, N.S., Korolev, V.K., and Kuzmin, O.V., *Dokl. Akad. Nauk SSSR*, 1972, vol. 205, no. 5, p. 1111.
4. Karlov, S.S., Shutov, P.L., Akhmedov, N.G., Lorbort, Y., and Zaitseva, G.S., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 6, p. 1053.
5. Kochina, T.A., Vrazhnov, D.V., Nefedov, V.D., and Sinotova, E.N., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 6, p. 967.
6. Ignat'ev, I.S., Avrorin, V.V., Kochina, T.A., and Ermolenko, Yu.E., *Russ. J. Gen. Chem.*, 2018, vol. 88, no. 3, p. 470. doi 10.1134/S1070363218030131
7. Nametkin, N.S., Kuz'min, O.V., Chernysheva, T.I., Korolev, V.K., and Lepetukhina, N.A., *Dokl. Akad. Nauk SSSR*, 1971, vol. 201, no. 5, p. 1016.