ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 11, pp. 1888–1890. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © A.A. Alferova, T.A. Kochina, V.V. Avrorin, E.N. Sinotova, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 11, pp. 1925–1927.

LETTERS TO THE EDITOR

Synthesis of Diethylditritiumstannane Et_2SnT_2, a Generator of Stannylium Cations

A. A. Alferova[a], T. A. Kochina[b], V. V. Avrorin[a], and E. N. Sinotova[a]

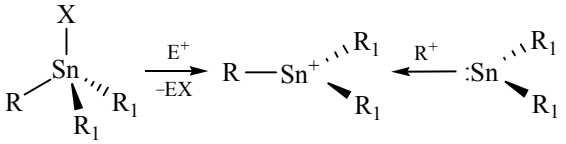
[a] *St. Petersburg State University, Department of Chemistry, Universitetskii pr. 26, St. Petersburg, 198504 Russia*
e-mail: radiochem@yandex.ru

[b] *Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, 199034 Russia*
e-mail: t-kochina@mail.ru

Received June 4, 2012

DOI: 10.1134/S1070363212110308

In recent decades tricoordinated cations of heavy elements of the 14-th group of the Periodic table, R_3M^+ (M = Si, Ge, Sn) are objects of intense study [1–4]. Despite the fact that the existence of R_3M^+ cations in gas phase was proved convincingly, their identification in the condensed phase remains a challenge. This is due to the unique ability of the heavy elements of 14th group to expand their coordination sphere in the reactions with the nucleophiles of any kind. Recent progress in this area relates to the development of the chemistry of anions with extremely low nucleophilicity, such as carborane anion $[CB_{11}X_{12}]^-$, X = halogen, H [5], borane dianion $[B_{12}X_{12}]^{2-}$, X = Cl, Br [6], perfluorotetraalkylborates $[B(C_6F_4X)_4]$, X = F, SiR_3 [7]. Use of such anions, solvents with low nucleophilicity, and suitable methods of generating allowed, finally, to synthesize and characterize some tricoordinated cations R_3M^+. So, the tin cations of low coordination were obtained in two ways: by splitting a Sn–C bond in tetraorganylstannanes [8] and by the addition of an R^+ cation to stannylene [9].



An alternative method for generating and studying stannylium cations is the nuclear chemistry method, which was developed initially to generate the carbenium and silylium ions [10] and which we extended to their germanium analogs [11]. At the present time an attempt was made to extend this approach to the generation and study of free stannylium cations. The method is based on the use of the processes of tritium β-decay in the tritium-labeled stannanes.

The nuclear chemistry method has several unique features, one of which is the ability to generate free cations of a desired composition and structure, without a counterion, with a strictly fixed charge localization, both in the gas phase in a wide range of pressures, and in the condensed phase. Moreover, the ions can be obtained with the initial localization of the charge not corresponding to its most stable state. For example, at the decay of tritium included in the multiple labeled substituted stannane the stannilium cations are formed in accordance with the scheme:

$$R_{4-n}Sn^3H_n \rightarrow R_{4-n}Sn^3H_{n-1} + {}^3He^0, \text{ where } n \geq 2.$$

The resulting cations contain one or more tritium atoms, so their further transformations such as interaction with nucleophiles, isomerization, and fragmentation can be traced by measuring radioactivity of final products.

As noted above, the source of the cations is a stannane multiple labeled with tritium. In this study we selected the diethylstannane, one of the simplest organotin compounds containing two tritium atoms, which allows us to observe the processes of isomerization of the formed cations. The choice of ethyl substituents is also connected with our previous studies of diethylsilyl and diethylgermyl cations. The study of diethylstannyl cations would allow to compare the properties of various cations of 14th group elements.

The aim of this work was to develop a method of the the micro synthesis of diethylditritiumstannane, the source of diethylstannyl cations. The synthesis was based on the following reaction [12]:

$$Et_2SnCl_2 \xrightarrow{LiAlT_4} Et_2SnT_2.$$

For obtaining the doubly tritiated diethyldihydrogentin we required lithium tritide of high isotopic purity. Since such a lithium tritide is not commercially available, it was prepared by reacting *n*-butyllithium with molecular tritium of the isotopic purity 99.8% in the presence of tetramethylethylenediamine, and then it was converted into $LiAlT_4$.

$$BuLi \xrightarrow{T_2} LiT \xrightarrow{AlBr_3} LiAlT_4.$$

For the preparation of tritiated diethylstannane Et_2SnT_2, the procedure for the synthesis diethyldihydrogentin Et_2SnH_2 described in the literature [12] was modified by us to operate with small quantities of reagents.

For the reliable obtaining the labeled compounds a technique of the micro synthesis should be developed by repeated performing the model syntheses using protium (or, if necessary, deuterium) instead of the tritium under identical conditions. The product synthesized in the model experiments was identified as Et_2SnH_2 by gas chromatography, NMR spectroscopy, and mass spectrometry. The presence of a single peak in the chromatogram indicated the formation of individual substances.

In the ^1H NMR spectrum ($CDCl_3$, 25°C) three groups of lines were observed: a triplet, a sextet, and a quintet, with the intensities corresponding to the structure containing two methyl, two methylene groups, and two hydrogen atoms Sn–H.

The exact quantitative interpretation of mass spectra of organic tin compounds is difficult due to the large number (10) of the natural isotopes of tin. In the mass spectrum (EI, 18 and 70 eV) there are the groups of lines corresponding to the elimination of one hydrogen atom and the ions corresponding to splitting off of one or two ethyl groups. The set of results obtained confirms the structure of the synthesized compound as Et_2SnH_2.

The chromatographic analysis was performed on a chromatograph Tsvet-500 equipped with a thermal conductivity and radioactivity detectors; a column 2000×2 mm with stationary phase 5% SE-30 on INERTON-AW. The rate of carrier gas (He) flow 20 ml min^{-1}, of quenching gas (CH_4/Ar) 10 ml min^{-1}, oven temperature 35°C.

NMR spectra were recorded on a Bruker Avance-300 DPX spectrometer ($CDCl_3$, 25°C). The mass spectrometric studies were carried out on a chromato-mass spectrometer Polaris 125 (electron impact and chemical ionization).

The synthesis of the labeled compounds was performed on a vacuum apparatus designed for the storage of gaseous tritium and various operations. Synthesis of diethylditritiumtin was performed strictly in accordance with the procedure developed in model experiments.

The synthesis was carried out in an evacuated closed system consisting of interconnected reaction ampule and an ampule with pre-activated CaA zeolite. The total volume of the reactor and the ampule with zeolite was ~2 ml.

The reactor ampule was charged with 50 ml of 1.5 M solution of *n*-butyllithium in hexane and 18 ml of tetramethylethylenediamine. The molecular tritium obtained from the uranium tritide (2.5 Ci) was adsorbed with the zeolite at –196°C. Then the ampule with zeolite was warmed and the tritium was transferred to the reactor cooled to –196°C. The content of the reactor was stirred for 1 h at room temperature (ampule with zeolite was blocked to prevent adsorption of hexane from the reactor). At the end of the first stage of the synthesis, the access to the ampule with zeolite was opened, and the solvent together with butane formed in the first step and together with lithium tritide were condensed in the ampule by cooling (freezing) it at –196°C, and then it was replaced with an empty ampule.

The ampule with the obtained LiT was opened in an atmosphere of dry argon, and to it was charged 40 ml of diethyl ether containing 2 mg of $AlBr_3$, and evacuated while cooling with liquid nitrogen, then warmed to room temperature. The system was filled with argon to atmospheric pressure, and through the connecting tube (vacuum rubber) was added 10 ml of the ethereal solution containing 1 mg of diethyltin dichloride. The reactor was evacuated at cooling to –196°C, warmed to room temperature, and diethyl-ditritiumstannane with diethyl ether was distilled into the empty ampule cooled with liquid nitrogen. The

isolation and purification of diethylditritiunstannane was performed using the technique of preparative gas chromatography. The isolated product was collected in a cylinder with a spectrally pure xenon [V = 250 ml, P(Xe) = 100 mm Hg].

Identification of the synthesized product and determination of its chemical and radiochemical purity were performed using gas chromatography on a Tsvet-500 chromatograph with thermal conductivity and radioactivity detectors by comparing the retention times of the labeled product with the retention time of Et_2SnH_2. The analysis showed the absence of appreciable amounts of both radioactive and inactive impurities. The activity of the product was measured by liquid scintillation technique on a Beta 2 radiometer. The yield with respect to the molecular tritium used in the synthesis was 10%. This yield is quite satisfactory for the two-stage synthesis of the twice labelled compound with the fixed charge localization. The found labeling multiplicity was 1.8±0.2.

ACKNOWLEDGMENTS

This work was supported by Russian Foundation for Basic Research, grant no. 12-03-00383. The authors thank the administration and staff of the Khlopin Radium Institute for the opportunity to carry out the synthesis of labeled products.

REFERENCES

1. *The Chemistry of Organic Germanium, Tin, and Lead Compounds*, Rappoport, Z. and Apeloig, Y., Eds., Chichester: Wiley & Sons, 2002, vol. 2, pp. 633, 961.
2. Kost, D. and Kalikhman, I., *Adv. Organomet. Chem*., 2004, vol. 50, p. 1.
3. Müller, T., *Adv. Organomet. Chem*., 2005, vol. 53, p. 155.
4. Reed, C.A., *Acc. Chem. Res*., 2010, vol. 43, p. 121.
5. Geis, V., Guttsche, K., Knapp, C., Schere,r H., and Uzun, R., *Dalton Trans*., 2009, vol. 38, p. 2687.
6. Jia, L., Jang, X., Stern, C.L., and Marks, T.J., *Organometallics*, 1997, vol. 16, p. 842.
7. Zharov, I., Weng, T.-C., Orendt, A.M., Penner-Hahn, D.H., Grant, D.M., Havlas, Z., and Michl, J., *J. Am. Chem. Soc*., 2004, vol. 126, p. 12033.
8. Lambert, J.B., Lin, L., Keinan, S., and Müller, T., *J. Am. Chem. Soc*., 2003, vol. 125, p. 6022.
9. Sekiguchi, A., Fukawa, T., Lee, V.Ya., and Nakamoto, M., *J. Am. Chem. Soc*., 2003, vol. 125, p. 9250.
10. Nefedov, V.D., Kochina, T.A., and Sinotova, E.N., *Usp. Khim*., 1986, vol. 55, no. 5, p. 749.
11. Myalochkin, D.L. and Kochina, T.A., *Khimicheskie posledstviya beta-raspada tritiya v sostave molekul. Yaderno-khimicheskoe generirovanie dialkilgermilievykh kationov i radiokhimicheskoe izuchenie ikh reaktsii* (Chemical Effects of the Beta Decay of Tritium in a Molecule. Nuclear-Chemical Generation of Dialkylgermylium Cations and Radiochemical Study of Their Reactions), Berlin: LAMBERT Academic Publishing, 2011, p. 200.
12. Dillard, C.R., VcNeill, E.H., Simmons, D.E., and Veldell, J.D., *J. Am. Chem. Soc*., 1958, vol. 80, p. 3607.