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Note

Reaction of germanes and digermanes with triflic acid: The route to novel organooligogermanes

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ABSTRACT

Novel germanium containing triflates were prepared from the reactions of trifluoromethanesulfonic acid with tetraphenylgermane (**1**) and digermanes ($Ph_3GeGeMe_3$ (**4**), $Ph_3GeGePh_3$ (**5**)). The improved procedures for synthesis of known organogermanium compounds (Ph_4Ge (**1**), Ph_3GeCl (**2**), $Ph_3GeGeMe_3$ (**4**), $Ph_3GeGePh_3$ (**5**)) were also presented. The crystal structure of Ph_3GeOTf (**6**) and $Ph_2Ge(OTf)Ge(OTf)Ph_2$ (**7**) was studied by X-ray analysis. In **7** each germanium atom is pentacoordinated due to intramolecular interaction with O atom of the neighboring triflate group.

1. Introduction

In the last few years chemistry of organogermanium compounds attracts intent attention of researchers and especially interest is given to oligogermanes [1,2]. This interest is based not only on academic investigations [3–5] but also on a search of new unique properties of these compounds such as thermochromism, absorption in UV/visible spectral region [6–15], conductivity, luminescence [16]. Besides organogermanium compounds may be used as precursors for synthesis of new materials for example nanostructures [17]. The main problem in chemistry of oligogermans consists in limitation of reliable synthetic methods for obtaining compounds with required structure and properties. The reaction of hydrogermolysis developed by Weinert et al. [15] and also application of alkaline organogermanium reagents investigated by Marschner, Baumgartner et al. [14] partially solved this problem. Meanwhile, a search of new techniques for modification of organogermanium compounds and improvement of synthesis of known widely used compounds may be regarded as a topic for investigation.

It is known that the action of trifluoromethanesulfonic acid (HOTf) on organogermanium compounds containing aromatic groups results to electrophilic substitution of one Ar group [6,18] but commonly triflates obtained are used subsequently without isolation in reactions occurring with nucleophilic substitution of OTf group. The investigations of such intermediate triflate compounds are very rare [6]. Meanwhile, triflate group is strong electron acceptor and it's introduction in organogermanium molecule, especially in oligogermane substances, may result to substantial changing of structural parameters of these molecules, for example of Ge–Ge bond. In this work we used modified procedures for synthesis of mono- and digermanes. The compounds obtained were investigated in reaction with trifluoromethanesulfonic acid.

2. Results and discussion

Using modified procedures we synthesized several germanes and digermanes (Scheme 1) which would be used than for interaction with triflic acid. All compounds were obtained in high yields as analytically pure samples.

In the course of this work we interested in the investigation of substitution of two aryl groups at one germanium atom in oligogermanes by action of HOTf. As a model compound for studying of

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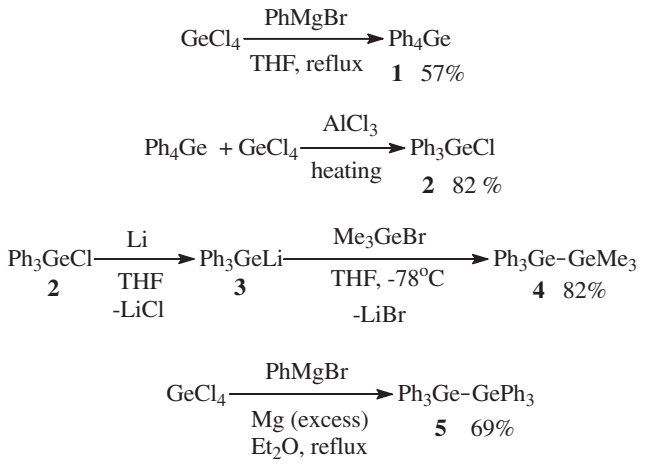


Scheme 1.

this process we used tetraphenylgermane Ph_4Ge (**1**). The possibility of substitution of two phenyl groups in tetraphenylgermane was shown earlier [19], but methods of structure establishing were not reliable. It is significant that in such reaction the mild conditions (room temperature, short time) are necessary especially in the case of oligogermanes due to lability of Ge–Ge bond.

We established that action of two equivalents of HOTf on Ph_4Ge (**1**) results exclusively to formation of Ph_3GeOTf (**6**) (Scheme 2). The increase of the time of the reaction to several days did not result to changing the product nature. According to NMR the byproducts formed in the course of this reaction represent a mixture of unidentified compounds. In the control experiment with one equivalent of HOTf the triphenylgermaniumtriflate (**6**) was also obtained but with greater yield.

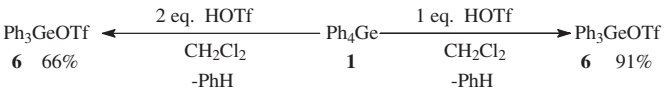
Evidently, introduction of two triflate groups to one Ge atoms is impossible in the course of this method due to the electron acceptor ability of OTf that complicate sequential electrophilic substitution at C atom.

The crystal structure of the compound (**6**) was investigated by X-ray analysis (Fig. 1, Table 2).

The germanium atom in Ph_3GeOTf (**6**) has a slightly distorted tetrahedral coordination. The Ge–O bond length is sufficiently increased in comparison with related compounds containing Ge–O bond (1.9225(17) *vs*. 1.86(1) Å in $Ph_3GeO_2CCF_3$ [20], 1.767(2) Å in $(Ph_3Ge)_2O$ [21]) what denotes the significant ionic character of this bond in **6**. Similar increasing the length of the covalent Ge–O bond was found in pentacoordinated germanium compounds (for example, in $C_{10}H_6(OMe)(Ge(H)(OTf)(NpOMe))$, 1.988(3) Å [22]) where weakening covalent bonds are admitted.

At the action of two equivalents of HOTf on the hexaphenyldigermane (**5**) the new complex $(OTf)Ph_2GeGePh_2(OTf)$ (**7**) was obtained with high yield (Scheme 3).

In this case it is interesting to note the retention of Ge–Ge bond and the rupture of two Ge–C_6H_5 bonds at the neighboring germanium atoms (compare bond energy Ge–C (255 kJ/mol) and Ge–Ge (163 kJ/mol)) [23]. We believed that the main reasons of predominant rupture of Ge–C bonds consist in steric hindrances for attack on the Ge–Ge bond and the formation of the thermodinamically advantageous product which contained two strong



Scheme 2.

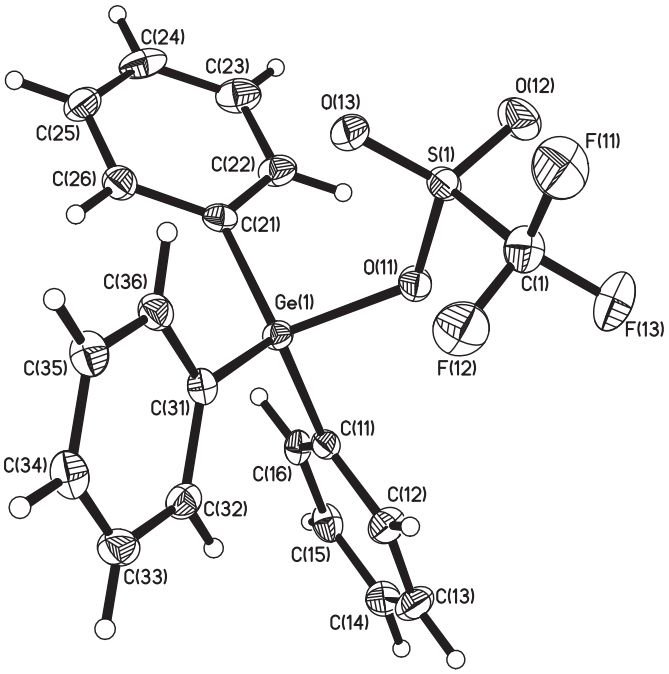


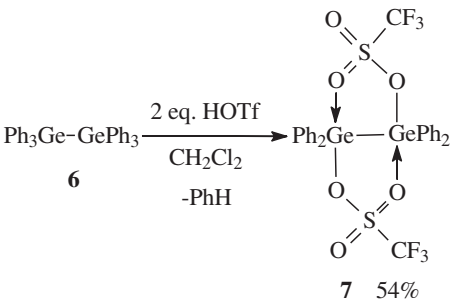
Fig. 1. Molecular structure of compound Ph_3GeOTf (**6**). Selected bond length (Å) and angles (°): Ge(1)–O(11) 1.9225(17) Å, Ge(1)–C(21) 1.919(2) Å, Ge(1)–C(11) 1.921(2) Å, Ge(1)–C(31) 1.931(2) Å, O(11)–Ge(1)–C(11) 96.99(9)°, O(11)–Ge(1)–C(21) 102.73(9)°, O(11)–Ge(1)–C(31) 107.21(9)°, C(21)–Ge(1)–C(11) 116.98(10)°, C(21)–Ge(1)–C(31) 116.38(10)°, C(11)–Ge(1)–C(31) 113.31(10)°. There are two independent molecules in crystal. Only one independent molecule is presented in Figure.

intramolecular interactions. It should be noted that this reaction is occurred under more mild conditions (room temperature) than the synthesis of related derivative of the trichloroacetic acid **8** (prolonged reflux in toluene; see Scheme 4) [24].

The structure of the compound **7** was established by X-ray analysis (Figs. 2 and 3, Table 2).

In the centrosymmetric structure of **7**, both germanium atoms possess trigonal bipyramidal coordination environment. The triflate oxygen atoms occupy axial positions, while phenyl groups and neighboring germanium atom lie in equatorial sites. The Ge–O bond lengths in almost linear O–Ge–O fragment are significantly different (2.065(3) and 2.344(4) Å). This fragment may be considered as **3c**–**4e** bond. As expected, both the Ge–O bonds are longer than ordinary germanium-triflate **2c**–**2e** bond in the complex **6** (1.9225(17) Å).

The Ge–Ge distance in **7** (2.4635(12) Å) is somewhat longer than in parent compound $Ph_3GeGePh_3$ (**1**) ($Ph_3GeGePh_3$ (2.437(2) Å) [25], $Ph_3GeGePh_3{}^*2C_6H_6$ (2.446(1) Å) [26]). The latter may be caused by sterical requirements of the bridging triflate ligands.



Scheme 3.