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Abstract

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SYNTHESIS OF NEW MIXED ORGANOGERMANIUM COMPOUNDS OF THE TYPES $(C_6H_5)_3GeR$ AND $(C_6H_5)_3Ge—C_6H_4X$

(Presented by Academician A. N. Nesmeyanov, October 25, 1962)

The chemistry of organogermanium compounds has so far been little studied; however, this field is attracting the attention of many investigators ($^{1-3}$), etc. The latter is explained not only by theoretical but also by practical interests. The present work is connected with the general problem of the synthesis of new mixed organoelement compounds being carried out by one of us (^{4,5}). A number of types of organogermanium compounds are known only in the form of a few representatives.

We decided to synthesize new organogermanium compounds of the type $(C_6H_5)_3GeR$, where R is an aliphatic (saturated and unsaturated) and alicyclic radical. Until now, compounds of such a structure had been described only as several substances in which R is methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-amyl (^{6}). As for compounds of this type with an alicyclic, as well as an unsaturated, radical, they have hitherto not been known in the literature. It was desirable to clarify the influence of homologous differences in the aliphatic saturated radical, as well as of cyclohexyl and allyl radicals, on the physicochemical properties.

Secondly, in order to study the influence of a substituent in the nucleus, we also undertook the synthesis of compounds of the type $(C_6H_5)_3Ge—C_6H_4X$ (where X is a substituent in the benzene nucleus). Compounds of similar structure have been described only as three substances, where X is methyl, dimethylamino, and methoxy groups (^{7}).

The starting material for the planned syntheses was germanium tetrachloride, obtained by us from germanium dioxide by the method described (^{8}). Tetraphenylgermane was obtained by the Grignard reaction. In this connection, we showed that at a ratio of germanium tetrachloride to phenylmagnesium bromide of 1 : 4, mainly triphenylgermanium chloride is obtained (yield 40%). Tetraphenylgermane was obtained in good yield (70–75%) only at a ratio of 1 : 5, which contradicts the data of Worrall (^{9}).

Tetraphenylgermane was converted into triphenylgermanium bromide by a briefly described method (^{10}), the conditions of which we refined; in this case the product was isolated in good yield (75–80%).

For the first time, we developed the direct iodination of tetraphenylgermane in boiling decalin. The reaction proceeded according to the following scheme:

$$(C_6H_5)_4Ge + J_2 \xrightarrow{\text{decalin}} (C_6H_5)_3GeJ + C_6H_5J. \tag{1}$$

The yield of the product was 30%. In solvents of lower boiling point, the process of dearylation of tetraphenylgermane by iodine does not occur. As is known, dearylation by iodine of tetraphenyllead and tetraphenyltin proceeds already in absolute ether, which is evidently explained by the lower energy of the Me–C bond.

Comparing the yields and the method for obtaining triphenylgermanium bromide, chloride, and iodide (see above), we decided to choose triphenylgermanium bromide for further work.

We carried out the synthesis of compounds of the type $(C_6H_5)_3GeR$ by the Grignard method. By the reaction of a Grignard reagent with triphenylbromogermane we succeeded in obtaining ten new substances. The reaction proceeded in the direction:

$$(C_6H_5)_3GeBr + Mg\underset{R}{\overset{Br}{\langle}} \rightarrow (C_6H_5)_3GeR + MgBr_2, \tag{2}$$

where R is isopropyl, tert-isobutyl, tert-isoamyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-nonyl, *n*-decyl, allyl, and cyclohexyl. The syntheses were carried out, as usual, in anhydrous ether. To complete the reaction, the ether was distilled off, replaced with dry toluene, and the reaction mixture was heated for 2 hours on an oil bath at a temperature of 110-120°.

The products obtained are white crystalline substances, possessing a characteristic pleasant odor, insoluble in water, and readily soluble in organic solvents (less readily in ethyl alcohol).

The products obtained were confirmed by analysis for germanium (6), and for most of them IR spectra were studied. The yields of the products range from 45 to 63% (see Tables 1, 2).

By comparing the physical properties of compounds of the type $(C_6H_5)_3GeR$ (see Table 1), certain regularities can be established. All the compounds obtained with a normal aliphatic radical are thermostable, are readily distilled in vacuum, after which they crystallize, and have a low melting point in the range 48-65°. It is characteristic that products with an iso radical are less thermostable and distill in vacuum with difficulty, with partial decomposition. All the substances obtained are fairly stable and do not undergo the process of radical redistribution (symmetrization).

Table 1

Formulas of substances	Yield, %	B.p., °C	M.p., °C	Ge, % found	Ge, % calculated	n_D^x
$(C_6H_5)_3$Ge-*iso*-C_3H_7	48.6	decomposes	126-127	20.68; 20.87	20.94	–
$(C_6H_5)_3$Ge-*iso*-C_4H_9	45.3	164-165 (3 mm)	124-125	19.49; 19.67	20.13	–
$(C_6H_5)_3$Ge-*iso*-C_5H_{11}	47.0	183-184 (3 mm)	65-66	19.52; 19.40	19.07	n_D^{70} 1.5691
$(C_6H_5)_3$Ge-*n*-C_6H_{13}	62.7	200-202 (5 mm)	65-66	18.96; 18.85	18.68	n_D^{71} 1.5560
$(C_6H_5)_3$Ge-*n*-C_7H_{15}	50.6	204-205 (5 mm)	51-52	17.75; 17.67	18.03	n_D^{65} 1.5586
$(C_6H_5)_3$Ge-*n*-C_8H_{17}	60.6	210-211 (3 mm)	63-64	17.43; 17.43	17.42	n_D^{75} 1.5495
$(C_6H_5)_3$Ge-*n*-C_9H_{19}	52.9	216-217 (5 mm)	48-49	16.90; 17.31	16.86	n_D^{65} 1.5558
$(C_6H_5)_3$Ge-*n*-$C_{10}H_{21}$	48.5	220-222 (3 mm)	51-52	15.76; 15.84	16.32	n_D^{65} 1.5205
$(C_6H_5)_3Ge-C_3H_5$*	51.2	173-175 (3 mm)	59-60	20.70; 20.78	21.067	n_D^{75} 1.5989
$(C_6H_5)_3Ge-C_6H_{11}$	47.4	220-221 (8 mm)	95-96	18.655; 18.72	18.77	–
$(C_6H_5)_3$Ge-*n*-$C_6H_4OC_2H_5$	58.3	–	129-130	17.41; 17.38	17.098	–
$(C_6H_5)_3$Ge-*o*-$C_6H_4CH_3$	45.0	–	110-111	18.95; 18.81	18.39	–

* Molecular weight determined cryoscopically by Rast’ s method: found 355.7, calculated 344.6.

Table 2

Some spectroscopic data on new organogermanium compounds

Formulas of substances	Brief characterization
$(C_6H_5)_3Ge$-*n*-C_6H_{13} $(C_6H_5)_3Ge$-*n*-C_7H_{15} $(C_6H_5)_3Ge$-*n*-C_8H_{17} $(C_6H_5)_3Ge$-*n*-C_9H_{19} $(C_6H_5)_3Ge$-*n*-$C_{10}H_{21}$	1630, 1570, 1485 cm^{-1}—stretching vibrations of the —C—C—bond of the aromatic ring;1375 cm^{-1}—symmetric deformation vibrations of methyl groups;1457 cm^{-1}—deformation vibrations of methylene groups (on going from lower to higher homologs the intensity of the vibration increases)
$(C_6H_5)_3Ge{-}CH_2{-}CH{=}CH_2$	1487, 1560, 1626 cm^{-1}—correspond to stretching vibrations of the —C—C—bonds of the aromatic ring;1545 cm^{-1}—stretching vibrations of the —C=C—bond of the allyl radical
$(C_6H_5)_3Ge$-*n*-$C_6H_4OC_2H_5$	700, 736 cm^{-1}—out-of-plane deformation vibrations of —C—H in monosubstituted benzene rings;921 cm^{-1}—vibration of the ethoxy group;1488, 1502, 1570, 1594 cm^{-1}—stretching vibrations of the —C—C—bonds of the aromatic ring;812, 823 cm^{-1}—out-of-plane deformation vibrations of —C—H of para-disubstituted aromatics

The synthesis of new compounds of the type $(C_6H_5)_3Ge{-}C_6H_4X$ was also carried out by the Grignard method. By the interaction of bromotriphenylgermane with the Grignard reagent we obtained new substances. The reaction proceeded according to the following scheme:

$$Mg\genfrac{}{}{0pt}{}{/\ C_6H_4X}{\backslash\ Br} + (C_6H_5)_3GeBr \rightarrow (C_6H_5)_3Ge{-}C_6H_4X + MgBr_2, \qquad (3)$$

where X is the *o*-methyl and *p*-ethoxy groups. The reaction was carried out in anhydrous ether; then the ether was distilled off and replaced with dry benzene, after which the mixture was boiled for four hours. After the benzene had been distilled off, the reaction mass was heated for 2 hours at a temperature of 110-120° in an oil bath.

The products obtained are white crystalline substances, readily soluble in organic solvents and insoluble in water. They were confirmed by analysis for germanium and partly spectroscopically. The yields range within 45-60%.

Subsequently we attempted to obtain substances of the indicated type in which X is bromine, phenoxy, and allyl groups. However, in all cases we isolated a product of the following composition–$(C_6H_5)_3Ge–O–Ge(C_6H_5)_3$; it was confirmed by analysis for germanium and by the IR spectrum. A mixed sample with the deliberately obtained substance gave no depression of the melting point.

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