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# Contributions to the Chemistry of Silicon and Germanium. XV.[1a] Preparation of Symmetrical Phenyldigermanes

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$(C_6H_5)_2GeHCl$ reacts with magnesium in tetrahydrofuran with the formation of $(C_6H_5)_2GeHGeH(C_6H_5)_2$. This compound is converted with condensed HBr to *dl*- and *meso*-$C_6H_5GeHBrGeHBrC_6H_5$ in high yield. Hydrogenation to $C_6H_5GeH_2GeH_2C_6H_5$ was successfully carried out using $Al(i\text{-}C_4H_9)_2H$ in ether. Mass spectra and $^1H$ nmr spectroscopic investigations were carried out on all investigated compounds.

## Introduction

From our work on phenylsilanes,[1] we were able to show that the reaction

$$C_6H_5SiH_2SiH_2SiH_3 \xrightarrow[-80°]{HBr} SiH_3SiH_2SiH_2Br + C_6H_6$$

proceeds in 100% yield without cleavage of the Si–Si bond. Similarly, $(C_6H_5)_2SiHSiH(C_6H_5)_2$ is converted to $C_6H_5SiHBrSiHBrC_6H_5$ with HBr.[1b]

Until the time of this work,[1b] it was only known that phenyl derivatives of monosilanes react with condensed hydrogen halides to give halogen substitution of the phenyl groups.[2] Using $(C_6H_5)_2GeHGeH(C_6H_5)_2$, we intended to investigate the behavior of the Ge–Ge bond when allowed to react with condensed HBr.

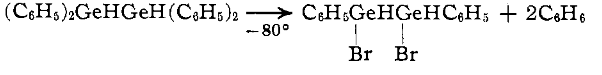
## Results

$(C_6H_5)_2GeHGeH(C_6H_5)_2$ has been mentioned in the literature once.[3] Only its decomposition point is given, whereas neither a mass spectrum nor an nmr spectrum is reported. We attempted to synthesize $(C_6H_5)_2GeHGeH(C_6H_5)_2$ by the reaction path

$$(C_6H_5)_2GeH_2 + Cl_2 \xrightarrow[-40°]{CFCl_3} (C_6H_5)_2GeCl + HCl \qquad (1)$$

$$2(C_6H_5)_2GeHCl + Mg \xrightarrow[+40°]{THF} (C_6H_5)_2GeHGeH(C_6H_5)_2 + MgCl_2 \qquad (2)$$

For reaction 1, it was important that carbon tetrachloride was not used as a solvent for the chlorine, as was possible for the chlorination of $(C_6H_5)_2SiH_2$. The Grignard reaction, eq 2, must not be allowed to proceed under refluxing THF, as $(C_6H_5)_2GeH_2$ would result. The synthesis continued



$$(C_6H_5)_2GeHGeH(C_6H_5)_2 \xrightarrow[-80°]{HBr} C_6H_5\underset{\displaystyle Br}{\underset{|}{Ge}}H\underset{\displaystyle Br}{\underset{|}{Ge}}HC_6H_5 + 2C_6H_6 \qquad (3)$$

$$C_6H_5GeHBrGeHBrC_6H_5 + 2(i\text{-}C_4H_9)_2AlH \longrightarrow C_6H_5GeH_2GeH_2C_6H_5 + 2(i\text{-}C_4H_9)_2AlBr \qquad (4)$$

$C_6H_5GeHBrGeHBrC_6H_5$ represents the first digermanium hydride which exists in *dl* and meso forms due to asymmetric Ge atoms. The *dl* and meso compounds exhibit slightly different singlets in the nmr spectrum.

From comparison with the spectrum of $C_6H_5SiHBrSiHBrC_6H_5$, it is found that the $A_2$ system of the Ge–H protons is shifted downfield with respect to that of the Si–H protons, corresponding to the positions in the periodic table. Hydrogenation of $C_6H_5GeHBrGeHBrC_6H_5$ was carried out with aluminum diisobutyl hydride which had proved a very good hydrogenation agent for phenyltin–halogen compounds.[3] The physical properties of $C_6H_5GeH_2GeH_2C_6H_5$ were found to be very similar to those of the silicon analog. $C_6H_5GeH_2GeH_2C_6H_5$ has only been isolated once before[4] when it was formed as a by-product in another reaction. The reported boiling point of 113° (0.3 mm) could not be reproduced by us because of the fact that the $C_6H_5GeH_2GeH_2C_6H_5$ decomposed.

## Experimental Section

**Preparation of $(C_6H_5)_2GeHCl$.**—A 115-g amount (0.5 mol) of $(C_6H_5)_2GeH_2$ was dissolved in 200 ml of $CFCl_3$ and treated with a $Cl_2$–$CFCl_3$ solution (35 g of $Cl_2$ in 100 ml of $CFCl_3$) at −40°. To avoid loss of chlorine, the chlorine solution was added to the $(C_6H_5)_2GeH_2$ solution by means of a "metal capillary bridge."[5] After the reaction, the solvent was removed and the $(C_6H_5)_2GeHCl$ was distilled using a heatable column (bp 101° (HV)); yield after distillation, 84%. Very pure $(C_6H_5)_2GeHCl$ was required for the next step. The purity was tested by nmr spectrum ($(C_6H_5)_2GeH_2$) and mass spectrum ($(C_6H_5)_2GeCl_2$).

**Preparation of $(C_6H_5)_2GeHGeH(C_6H_5)_2$.**—An 82-g amount (0.5 mol) of $(C_6H_5)_2GeHCl$ was brought together with 24.3 g (1 g-atom) of Mg for 1 hr at 60°. Without stirring, 30 ml of absolute THF was added under pure nitrogen and the reaction was initiated by the addition of 0.25 ml of $C_2H_5I$. The addition was made under the Mg turnings by means of a long injection needle. After the reaction had begun, the mixture was cooled to 40°, and a further 60 ml of absolute THF was added from a dropping funnel within a period of 10 hr. Then, after the addition of 200 ml of ether, the solution was filtered through glass wool and finally shaken with 0.5 *N* HCl. The solution was shaken with water three times and dried over $CaCl_2$, and the ether was taken off. Crystallization was accomplished from a hexane–benzene mixture (10:1) at 10° by scratching the walls with a glass rod; yield 41%; colorless crystals; mp 64–69°. *Anal.* Calcd: Ge, 31.92. Found: Ge, 31.1.

**Preparation of $C_6H_5GeHBrGeHBrC_6H_5$.**—Under an atmosphere of pure nitrogen, 50 ml of liquid HBr was condensed onto 9.2 g (0.02 mol) of $(C_6H_5)_2GeHGeH(C_6H_5)_2$ and kept for 3 hr at −80° with frequent shaking. After reaction, excess remaining HBr was volatilized by slight warming and the benzene was taken off

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[1] (a) Part XIV: F. Fehér, P. Plichta, and R. Guillery, *Tetrahedron Lett.*, **33**, 4443 (1970); (b) F. Fehér, P. Plichta, and R. Guillery, *ibid.*, **33**, 2889 (1970).

[2] G. Fritz and D. Kummer, *Z. Anorg. Allg. Chem.*, **306**, 194 (1960).

[3] K. Kühlein and W. P. Neumann, *Justus Liebigs Ann. Chem.*, **702**, 17 (1967).

[4] P. Riviere and J. Satgé, *Bull. Soc. Chim. Fr.*, 4039 (1967).

[5] F. Fehér, G. Kuhlbörsch, and H. Luhleich, *Z. Anorg. Allg. Chem.*, **303**, 294 (1960); *Z. Naturforsch.*, **14b**, 466 (1959).

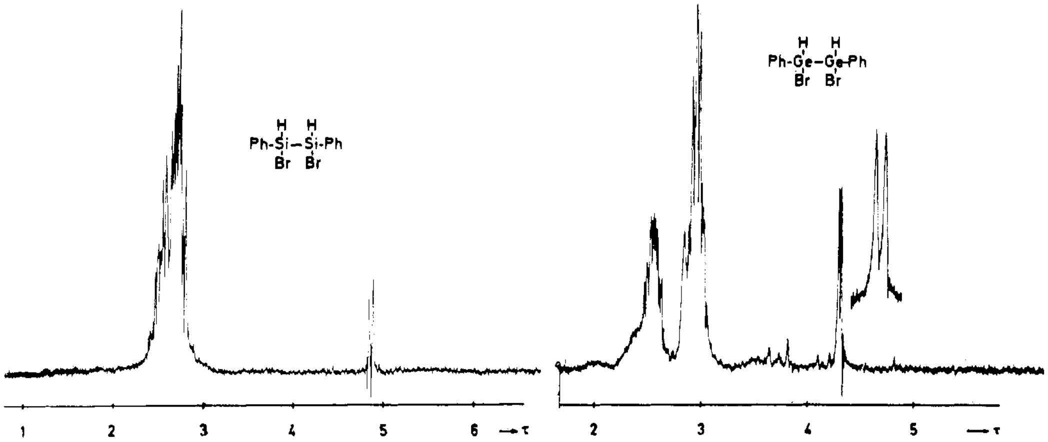

Figure 1.—Nmr spectra of $C_6H_5SiHBrSiHBrC_6H_5$ and $C_6H_5GeHBrGeHBrC_6H_5$.

in a rotavapor under high vacuum. The light brown solid was washed with ice-cold hexane under nitrogen; mp 58–66°; yield after washing, 96%. *Anal.* Calcd: Ge, 31.49; Br, 34.66. Found: Ge, 30.9; Br, 34.8.

**Preparation of $C_6H_5GeH_2GeH_2C_6H_5$.**—A 4.84-g amount (0.01 mol) of $C_6H_5GeHBrGeHBrC_6H_5$ was dissolved in 30 ml of absolute ether. A 3.12-g sample (0.022 mol) of $(i\text{-}C_4H_9)_2AlH$ was dropped into the solution with stirring. After a further 0.5 hr of being stirred, the solution was diluted with 100 ml of ether and shaken with 1 *N* HCl. The ethereal solution was then extracted three times with water and dried over $CaCl_2$, and then the ether was taken off. The residue was taken up in hexane and filtered through fired $Na_2SO_4$. The hexane was removed, leaving a colorless oil which exhibits an identical odor in high dilution to that of $C_6H_5SiH_2SiH_2C_6H_5$;[1] yield 73%. *Anal.* Calcd: Ge, 47.89. Found: Ge, 47.1.

*Warning!* All germanium compounds here described as well as $(C_6H_5)_2GeH_2$ irritate the mucous membranes and the skin very strongly, so that these compounds should be handled carefully.

## Spectroscopic Investigations

Hydrogen-1 nmr spectra of the phenyldigermanes in benzene-$d_6$, using TMS as internal standard, were measured. Mass spectroscopic investigations were also carried out.

(1) **$(C_6H_5)_2GeHGeH(C_6H_5)_2$.**—Nmr spectrum: Ge–H, $\tau$ 4.42 ppm; aromatic protons, multiplets at $\tau$ 2.5 and 2.8 ppm. Mass spectrum: the isotopic pattern of the parent ion was found to be grouped around *m/e* 456. Cracking of the parent ion leads mainly to fragments $(C_6H_5)_2Ge_2H_{0,1,2})^+$.

(2) **$C_6H_5GeHBrGeHBrC_6H_5$.**—Nmr spectrum: Ge–H, the *dl* and meso forms each exhibit a singlet at $\tau$ 4.305 ppm and $\tau$ 4.328 ppm (Figure 1). Mass spectrum: the isotope cluster of the molecular ion lies around *m/e* 460. Strongly intense ion fragments of compositions $(Ge_2Br_2H_{0,1,2})^+$ and $(Ge_2Br_2C_6H_5H_{0,1,2})^+$ were observed.

(3) **$C_6H_5GeH_2GeH_2C_6H_5$.**—Nmr spectrum: Ge–H, $\tau$ 5.50 ppm; aromatic protons, multiplets at $\tau$ 2.6 and 2.9 ppm. Mass spectrum: at 70 eV, the only peaks of substantial intensity are the parent ion and ions formed by the loss of one and two phenyl groups, respectively.

## Discussion

The symmetrical phenyldigermanes here described are stable against water (except $C_6H_5GeHBrGeHBrC_6H_5$) and air at room temperature, showing some similarity to the corresponding disilanes. The inherent mucous membrane active effect of $(C_6H_5)_2GeHGeH(C_6H_5)_2$ probably stems from traces of $(C_6H_5)_2GeH_2$ which, like $(C_6H_5)_2SnH_2$, has an extremely unpleasant effect on the skin. With liquid HBr, $C_6H_5GeH_2GeH_2C_6H_5$ reacts similarly to the corresponding silane, both phenyl groups splitting off to form $BrGeH_2GeH_2Br$[6] which, in contrast to $BrSiH_2SiH_2Br$, is very unstable.[7] The stability of the phenylsilanes and phenylgermanes may be attributed to the stabilizing influence of the phenyl groups, which becomes unimportant with phenyltin hydrides.

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(6) F. Fehér and P. Plichta, to be published.

(7) P. Plichta, Thesis, Cologne, 1969.