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Preliminary communication

ENHANCED REACTIVITY OF THE GERMANIUM — GERMANIUM BOND IN HEXAKIS(PENTAFLUOROPHENYL) DIGERMANE

M.N. BOCHKAREV, G.A. RAZUVAEV, N.S. VYAZANKIN and O.YU. SEMENOV
Institute of Chemistry, U.S.S.R. Academy of Sciences, Gorky (U.S.S.R.)

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Summary

Unlike hexaphenyldigermane, hexakis(pentafluorophenyl)digermane, $(C_6F_5)_3GeGe(C_6F_5)_3$, reacts with water, methanol, hydrogen chloride, acetic acid, trifluoroacetic acid, mercury chloride, sulphur and selenium via cleavage of the germanium—germanium bond. The reactions proceed in tetrahydrofuran (THF) but under identical conditions do not take place in non-polar solvents such as hexane, benzene, toluene etc.

Hexaphenyldigermane is known to be inert towards many reagents. In particular it is unreactive towards water, air and iodine even in boiling benzene or xylene [1]. It is unaffected by acetic acid at 140° even in the presence of aluminium chloride [2] and by monochloroacetic acid in boiling xylene [3]. An electrophilic attack by substituted acetic acid, CX_3COOH (X = Cl or F), on hexaphenyldigermane affords $Ph_3GeGePh_2(OCOCX_3)$ or $Ph_2Ge(OCOCX_3)_2$ which does not change the nature of the Ge—Ge bond [3]. Elemental chalcogens (S_8, Se_8, Te_n) do not react with hexaethyldigermane [4] and with hexaphenyldigermane as shown in the present work. Insertion of chalcogens (S_8 or Se_8) into the Ge—Ge bond was observed only in the case of strained heterocyclic compound, 1,1,2,2-tetraethyl-1,2-digermacyclopentane [5].

We have found that the germanium—germanium bond of hexakis(pentafluorophenyl)digermane (I) [6] is more reactive than that in the non-fluorinated compound, $Ph_3Ge—GePh_3$. For example, under the mild conditions (60-70°, 20-30 min) the digermane I reacts with water, methanol and hydrogen chloride in THF or acetone according to eqn. 1. As shown in Table 1, the yields of

$$\underset{\text{(I)}}{(C_6F_5)_3Ge{-}Ge(C_6F_5)_3} + HX \xrightarrow{\text{THF}} (C_6F_5)_3GeH + (C_6F_5)_3GeX \qquad (1)$$

$X = OH, OMe, Cl, OCOCH_3, OCOCF_3$

$(C_6F_5)_3GeH$ and $(C_6F_5)_3GeX$ were usually greater than 70-80%. Unlike hexaphenyldigermane [3] the reaction of the digermane I with trifluoroacetic acid in THF (100°, 1h) gives 70% of $(C_6F_5)_3GeH$ and 65% of $(C_6F_5)_3GeOCOCF_3$, i.e. the reaction involves a heterolytic cleavage of the Ge—Ge bond. Acetic acid reacts analogously.

TABLE 1

CONDITIONS AND YIELDS OF REACTION PRODUCTS OF HEXAKIS(PENTAFLUOROPHENYL) DIGERMANE IN THF

Reactant	Reaction temp. (°C)	Reaction time (h)	Reaction products (yields, %)
H_2O	70	0.25	$(C_6F_5)_3GeH$ (94) + $(C_6F_5)_3GeOH$ (93)
MeOH	60	0.25	$(C_6F_5)_3GeH$ (97) + $(C_6F_5)_3GeOMe$ (85)
HCl	70	0.5	$(C_6F_5)_3GeH$ (98) + $(C_6F_5)_3GeCl$ (98)
CH_3COOH	100	1	$(C_6F_5)_3GeH$ (92) + $(C_6F_5)_3GeOCOCH_3$ (69)
CF_3COOH	100	1	$(C_6F_5)_3GeH$ (70) + $(C_6F_5)_3GeOCOCF_3$ (65)
$HgCl_2$	70	1	$(C_6F_5)_3GeCl$ (99) + Hg_2Cl_2 (100)
S	60	3	$[(C_6F_5)_3Ge]_2S$ (52)
Se	100	5	$[(C_6F_5)_3Ge]_2Se$ (41)

Cleavage of the Ge—Ge bond in I is also observed in the reaction with mercury chloride in THF solution. Analogously to hexakis(2-biphenylyl)distannane [7] I in this reaction reduces $HgCl_2$ to Hg_2Cl_2 (eqn. 2).

$$\underset{\text{(I)}}{(C_6F_5)_3GeGe(C_6F_5)_3} + 2\,HgCl_2 \xrightarrow[60^\circ]{\text{THF}} 2\,(C_6F_5)_3GeCl + Hg_2Cl_2 \qquad (2)$$

It is interesting that in diethyl ether the reaction of I with water occurs under essentially more vigorous conditions (100°, 6h) than in THF, whereas in hexane, benzene or toluene I does not react with the mentioned compounds under identical conditions.

Analogously, we found that I does not react with sulphur in toluene on heating to 100° (3h). However, treatment of I in THF with one equivalent of a chalcogen at 60° (3h) gave hexakis(pentafluorophenyl)digermthiane as crystalline product, m.p. 165-168°, from hexane. A similar reaction with selenium gave $[(C_6F_5)_3Ge]_2Se$, m.p. 158-161° (eqn. 3). In contrast, an attempt to prepare

$$\underset{\text{(I)}}{(C_6F_5)_3GeGe(C_6F_5)_3} + 1/8\,X_8 \xrightarrow{\text{THF}} (C_6F_5)_3GeXGe(C_6F_5)_3 \qquad (3)$$

$$X = S, Se$$

hexaphenyldigermthiane by heating of hexaphenyldigermane with sulphur in THF at 100° (4h) failed, only starting materials were isolated.

Hexakis(pentafluorophenyl)digermane employed was obtained in 85% yield from $(C_6F_5)_3GeBr$ and lithium amalgam in diethyl ether at −20 – 0°.

All reactions were carried out in evacuated sealed ampoules. The volatile products [e.g. $(C_6F_5)_3GeH$, $(C_6F_5)_3GeCl$ etc.] were identified by GLC.

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