# 688. *Hexa-aryldigermanes.*

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The formation of hexa-aryldigermanes from germanium tetrachloride and an aryl magnesium halide is shown to proceed *via* the germyl Grignard reagents, $Ar_3Ge{\cdot}MgX$. If free magnesium is present this is formed primarily by reaction 3 (below), but for sterically hindered halides, $Ar_3GeX$, in the absence of magnesium, a slow reaction 6 (below) is postulated. Hydrolysis of *o*-, *m*-, or *p*-$(C_6H_4Me)_3Ge{\cdot}MgX$ gives the corresponding hydrides, $(C_6H_4Me)_3GeH$, whilst carbonation of (*p*-$C_6H_4Me)_3Ge{\cdot}MgX$ gives the acid, (*p*-$C_6H_4Me)_3Ge{\cdot}CO_2H$. The formation of disilanes is interpreted by the same reaction scheme.

Hexa-aryldigermanes and hexa-alkyldigermanes frequently result from the " reductive coupling " of a germanium(IV) halide and an excess of a Grignard reagent under defined experimental conditions.[1,2] In such reactions the tetrasubstituted germane is also formed by reactions 1 and 2 (below), and often predominates: $GeCl_4 + RMgX \longrightarrow R_6Ge_2 + R_4Ge$. One mechanism proposed[2] for the reaction between germanium tetrachloride and vinylmagnesium bromide which gave hexavinyldigermane (25%) and tetravinylgermanium (31%) required the reduction of germanium tetra- to di-chloride, followed by conversion into the magnesium derivative, $R_3GeMgX$:

$$GeCl_4 + 2RMgX \longrightarrow R_2 + GeCl_2$$

$$GeCl_2 + 3RMgX \longrightarrow R_3Ge{\cdot}MgX$$

$$R_3Ge{\cdot}MgX + R_3GeCl \longrightarrow R_6Ge_2$$

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[1] *Inorg. Synth.*, 1957, **5**, 72.

[2] Soyferth, *J. Amer. Chem. Soc.*, 1957, **79**, 2738.

We feel rather sceptical of the first stage in the above mechanism since germanium tetrachloride often reacts with Grignard reagents to give very high yields of the germane $R_4Ge$ and negligible amounts of the digermane, $R_6Ge_2$. Convincing evidence for the existence of triphenylgermylmagnesium halides has been obtained by Gilman and Zuech[3] from the reaction between triphenylgermane and allylmagnesium chloride: $Ph_3GeH + CH_2{:}CH{\cdot}CH_2{\cdot}MgCl \longrightarrow Ph_3Ge{\cdot}MgX \longrightarrow Ph_3Ge{\cdot}[CH_2]_4{\cdot}OH$, the latter reaction involving cleavage of the solvent, tetrahydrofuran. In following as closely as possible the experimental conditions reported for the preparation of hexaphenyldigermane[1] we encountered considerable variation in the yield of product (0—60%), as also have Gilman and Gerow.[4] This suggested that the reductive coupling stage might primarily involve reaction with metallic magnesium—perhaps that present as a reactive sludge—which is not always removed by decantation or rough filtration. If this view is correct, then appreciable yields of the digermane are to be expected only if substitution of the halogen in $R_3GeX$ is slow owing either to steric effects or to the relatively low reactivity of a particular Grignard reagent.

We have examined the reaction of germanium(IV) chloride with several Grignard reagents, (*a*) completely free from any excess of magnesium and (*b*) containing a large excess of magnesium, and we interpret the results in terms of the following reactions:

$$GeX_4 + RMgX \longrightarrow R_3GeX \qquad (1)$$

$$R_3GeX + RMgX \longrightarrow R_4Ge \qquad (2)$$

$$R_3GeX + Mg \longrightarrow R_3Ge{\cdot}MgX \qquad (3)$$

$$R_3Ge{\cdot}MgX + R_3GeX \longrightarrow R_6Ge_2 \qquad (4)$$

$$R_3Ge{\cdot}MgX + H_2O \longrightarrow R_3GeH \qquad (5)$$

$$R_3GeX + RMgX \longrightarrow R_3Ge{\cdot}MgX + RX \qquad (6)$$

The highly reactive benzylmagnesium bromide gave high yields (85—90%) of tetrabenzylgermane in both cases (reactions 1 and 2). However, phenyl- and *p*-tolyl-magnesium bromide gave, in addition, the digermane, but only when an excess of magnesium was present (reactions 1, 3, and 4). Addition of sodium wire to phenylmagnesium bromide did not materially affect the yield of hexaphenyldigermane. Using tetrahydrofuran in place of ether as solvent in the absence of free magnesium gave only tetraphenylgermane (85%), and this is probably the most efficient preparative method. Evidence for the existence of the triarylgermyl Grignard reagent in reactions involving an excess of magnesium (reaction 3) was obtained for the *o*-, *m*-, and *p*-tolyl derivatives since, on hydrolysis, the corresponding hydrides were isolated in appreciable yield (reaction 5), and, in the reaction involving *p*-tolylmagnesium bromide and an excess of magnesium, carbonation led to the isolation of the acid, $(p\text{-}C_6H_4Me)_3Ge{\cdot}CO_2H$. It follows that reaction 3 is faster than the coupling reaction 4. It was confirmed that the hydrides, $R_3GeH$, do not arise from magnesium–acid reduction of the halides.[5]

*m*-Tolylmagnesium bromide gave a mixture of tetra-*m*-tolylgermane and hexa-*m*-tolyldigermane when an excess of magnesium was present, but even in the absence of magnesium some 6% of the digermane was isolated. With *o*-tolylmagnesium bromide only the digermane was isolated either in the presence or in the absence of an excess of magnesium, though it is significant that with an excess of magnesium the hydride was also obtained whilst in the absence of free magnesium bromotri-*o*-tolylgermane was the only other product isolated. Under more drastic conditions, with zinc chloride and *o*-tolylmagnesium bromide, tetra-*o*-tolylgermane is produced.[6]

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[3] Gilman and Zuech, *J. Org. Chem.*, 1961, **26**, 3035.

[4] Gilman and Gerow, *J. Amer. Chem. Soc.*, 1955, **77**, 5509.

[5] West, *J. Amer. Chem. Soc.*, 1953, **75**, 6080.

[6] Simons, Wagner, and Müller, *J. Amer. Chem. Soc.*, 1933, **55**, 3705.

Formation of the digermane in the complete absence of free magnesium, in these two cases, cannot be explained in terms of reactions 1—5 and we are led to consider reaction 6. This will only be significant in the absence of magnesium metal and in cases, particularly for *o*-tolyl, where the halide $R_3GeX$ is sterically hindered towards the introduction of a fourth R-group, and hence may be converted slowly into the digermane by reaction 4. The slow reaction rate is reflected in the recovery of $R_3GeBr$ from the *o*-tolyl reaction when no free magnesium is present. Reaction 6 could be considered to involve an equilibrium, although it is probable that RX would in most cases undergo a Wurtz-type of coupling with an excess of the Grignard reagent: $RX + RMgX \longrightarrow R_2 + MgX_2$.

Some further support for this view is to be found in silicon analogues. Gilman and his co-workers [7,8] have shown that hexa-aryldisilanes result from the reaction between triarylchlorosilanes and magnesium in tetrahydrofuran, and conclude that the Grignard reagent $Ar_3SiMgX$ is an intermediate. Selin and West [9] reported that chlorotriphenylsilane and cyclohexylmagnesium bromide interact to give hexaphenyldisilane in 67% yield. Other Grignard reagents behaved similarly. We have repeated this work in the presence and the absence of free magnesium and find a close parallel to the case of germanium: with free magnesium present the disilane is produced in about 75% yield, whereas in the complete absence of magnesium under the same conditions only 8% of hexaphenyldisilane is obtained, and much chlorotriphenylsilane remained unchanged. On the basis of reaction 6 we expect hexaphenyldisilane to be produced slowly in the presence of any Grignard reagent, unless direct substitution is possible.

## EXPERIMENTAL

*Tetraphenylgermane.*—Germanium tetrachloride (10 g.) in tetrahydrofuran (60 c.c.) was added in 10 min. to a filtered (grade 4 sinter) solution of phenylmagnesium bromide prepared from bromobenzene (88 g.) and magnesium (15·6 g.) in tetrahydrofuran (180 c.c.). After 18 hr. under reflux the crude tetraphenylgermane was separated by filtration (without hydrolysis), washed with dilute acetic acid, and crystallised from toluene; it had m. p. 237—238° (yield, 15·3 g., 85%). No hexaphenyldigermane was isolated.

*Tetrabenzylgermane.*—Benzylmagnesium chloride from benzyl chloride (65 g.), magnesium (15 g.), and ether (330 c.c.) was treated with germanium tetrachloride (13 g.) in toluene (100 c.c.) either with or without separation of an excess of magnesium. After 8 hr. at the b. p., hydrolysis and isolation in the normal way gave tetrabenzylgermane, m. p. 107—110° (24—25 g.).

*Hexaphenyldigermane and Tetraphenylgermane.*—(*a*) *In presence of an excess of magnesium.* Germanium tetrachloride (18 g.) in toluene (200 c.c.) was added in 15 min. to a solution of phenylmagnesium bromide prepared from bromobenzene (159 g.), magnesium (28 g.), and ether (500 c.c.). The mixture was refluxed for 4 hr., then filtered without hydrolysis, and the white solid washed with dilute acetic acid and dried. Soxhlet extraction by chloroform gave hexaphenyldigermane, m. p. 352—354° (18·3 g., 69%).

(*b*) In an analogous experiment the Grignard solution was passed through a grade 4 sintered disc, giving a clear amber solution to which was added the germanium tetrachloride (18 g.). Filtration and isolation as described under (*a*) gave tetraphenylgermane, m. p. 236—238° (22 g., 69%).

p-*Tolylmagnesium Bromide and Germanium Tetrachloride.*—The solution of *p*-tolylmagnesium bromide resulting from *p*-bromotoluene (137 g.), magnesium (30 g.), and ether (500 c.c.), was divided into two equal parts (*a*) and (*b*). Part (*a*), containing the excess of magnesium was treated with germanium tetrachloride (10 g.) in toluene (100 c.c.) and refluxed for 2 hr. Hydrolysis of the brown solution gave hexa-*p*-tolyldigermane, m. p. 345° (from toluene) (3·4 g.). Distillation of the brown oily residue gave *tri-*p*-tolylgermane* (4·5 g.), b. p. 160°/$10^{-3}$ mm., m. p. 81° [from light petroleum (b. p. 40—60°)] (Found: Ge, 21·8. $C_{21}H_{22}Ge$ requires Ge, 20·9%), $\nu_{max.}$ 2034 cm.$^{-1}$ (Ge–H stretch). The residue from the distillation gave some tetra-*p*-tolylgermane, m. p. 224—225°.

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[7] George, Peterson, and Gilman, *J. Amer. Chem. Soc.*, 1960, **82**, 403.

[8] Stendel and Gilman, *J. Amer. Chem. Soc.*, 1960, **82**, 6129.

[9] Selin and West, *Tetrahedron*, 1959, **5**, 97.

Part (*b*), after passing through a grade 4 sintered disc, was treated as described above. Hydrolysis of the yellow solution gave tetra-*p*-tolylgermane, m. p. 222—225° (10·6 g., 52%). The mother-liquors gave both bromotri-*p*-tolylgermane, m. p. 128—129°, and chlorotri-*p*-tolylgermane, m. p. 121°.

*Tri-*p*-tolylgermanecarboxylic Acid.*—*p*-Tolylmagnesium bromide from *p*-bromotoluene (68 g.), magnesium (15 g.), and ether (280 c.c.), containing the excess of magnesium, was treated with germanium tetrachloride (10 g.) in toluene (110 c.c.) in 10 min. The mixture was refluxed for 2 hr., poured on solid carbon dioxide under nitrogen, and hydrolysed with water. Acidification of the aqueous layer gave only *p*-toluic acid (32·5 g.). The organic layer wa extracted, with sodium hydroxide and on acidification gave the crude germanecarboxylic acsid (2·0 g.) from which *p*-toluic acid was separated by sublimation (85°/10$^{-3}$ mm.). Pure *tri-*p*-tolylgermanecarboxylic acid* (0·4 g.) had m. p. 141—143° with evolution of carbon monoxide (Found: C, 67·2; H, 5·7; Ge, 18·4%; equiv., 389. $C_{22}H_{22}GeO_2$ requires C, 67·6; H, 5·7; Ge, 18·6%; equiv., 391). Hexa-*p*-tolyldigermane (3·0 g.) was isolated from the neutral organic fraction.

*m-Tolylmagnesium Bromide and Germanium Tetrachloride.*—(*a*) *In presence of an excess of magnesium.* *m*-Tolylmagnesium bromide, from *m*-bromotoluene (68 g.), magnesium (15 g.), and ether (250 c.c.), was treated with germanium tetrachloride (10 g.) in toluene (110 c.c.), and the mixture was heated under reflux for 20 hr. Hydrolysis of the viscous solution with dilute acetic acid gave, from methylcyclohexane, hexa-*m*-tolyldigermane, m. p. 177—179° (3·5 g., 21·5%). Distillation of the viscous residue gave after a forerun of 3,3′-dimethylbiphenyl, *tri-*m*-tolylgermane*, b. p. 160—170°/10$^{-3}$ mm. (6·0 g.) (Found: C, 72·8; H, 6·6; Ge, 20·8. $C_{21}H_{22}Ge$ requires C, 72·7; H, 6·4; Ge, 20·9%), $\nu_{max.}$ 2034 cm.$^{-1}$. A higher-boiling fraction (~210°/10$^{-3}$ mm.) yielded tetra-*m*-tolylgermane, m. p. 146—147° (0·4 g.).

(*b*) An identical experiment in which the *m*-tolylmagnesium bromide was passed through a grade 4 sintered disc gave, after hydrolysis, tetra-*m*-tolylgermane, m. p. 148—149° (from light petroleum) (10·5 g., 52%) (Found: C, 76·6; H, 6·6. Calc. for $C_{28}H_{28}Ge$: C, 76·9; H, 6·5%). The material insoluble in light petroleum (b. p. 60—80°) gave *hexa-*m*-tolyldigermane* (from methylcyclohexane), m. p. 177—179° (1·0 g., 6%) (Found: C, 72·0; H, 5·4; Ge, 20·9. $C_{42}H_{42}Ge_2$ requires C, 72·9; H, 6·1; Ge, 21·0%).

*o-Tolylmagnesium Bromide and Germanium Tetrachloride.*—The solution of *o*-tolylmagnesium bromide resulting from *o*-bromotoluene (137 g.), magnesium (30 g.), and ether (500 c.c.) was treated as described for the *para*-isomer. Part (*a*), containing the excess of magnesium gave *hexa-*o*-tolyldigermane*, m. p. 284—286° (4·0 g.) (Found: C, 72·7; H, 6·7; Ge, 21·4%). Distillation of the mother-liquors gave *tri-*o*-tolylgermane*, b. p. 120—150°/10$^{-3}$ mm., which separated from light petroleum as fine white needles, m. p. 102—103° (2·0 g.) (Found: Ge, 20·9%), $\nu_{max.}$ 2050 cm.$^{-1}$ (Ge–H stretch).

Part (*b*), free from magnesium, gave hexa-*o*-tolyldigermane (3·8 g.) (from methylcyclohexane), m. p. 284—286°, and an oily residue containing 2,2′-dimethylbiphenyl, b. p. 110°/10$^{-2}$ mm., and bromotri-*o*-tolylgermane, b. p. 195°/10$^{-2}$ mm., m. p. 119—120° (from hexane) (Found: C, 59·7; H, 5·2. Calc. for $C_{21}H_{21}BrGe$: C, 59·2; H, 5·0%).

*Chlorotriphenylsilane and Cyclohexylmagnesium Bromide.*—Chlorotriphenylsilane (14·7 g.) in tetrahydrofuran (155 c.c.) was added to a filtered (grade 4 sinter) solution of cyclohexylmagnesium bromide from cyclohexyl bromide (16·3 g.) and magnesium (2·9 g.) in tetrahydrofuran (95 c.c.). The mixture which remained clear after 24 hr. under reflux was hydrolysed at 0° and made just acid. Hexaphenyldisilane (1·0 g., 7·8%) was separated; it had m. p. 365° after crystallisation from xylene. The organic layer gave triphenylsilanol, m. p. 150—151° (from ether–hexane) (6·0 g., 45%).

An identical experiment in which the excess of magnesium was left in the reaction mixture gave a dark solution containing much suspended material. Filtration and crystallisation from xylene gave hexaphenyldisilane, m. p. 365° (10 g., 75%).

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