Reactions of Organodigermanes

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Electrophilic attack by CX_3CO_2H (X = Cl or F) on Ge_2Ph_6 cleaves either 1 or 2 phenyl groups forming $Ge_2Ph_5(OCOCX_3)$ and $[GePh_2(OCOCX_3)]_2$ which are readily converted into the corresponding halides, Ge_2Ph_5X and $(GePh_2X)_2$. Both the diesters and dihalides are susceptible to hydrolysis with nucleophilic cleavage of the Ge–Ge bond. A mass spectroscopic study of these compounds is reported.

COMPOUNDS of the type Ge_2R_6 (R = alkyl or aryl) are thermally very stable[1] (Ge_2Ph_6 melts without decomposition at 354°) and are unreactive towards air and water. Strong nucleophiles such as lithium, lithium alkyls, and sodium in liquid ammonia cleave the Ge–Ge bond and there is evidence that reactions of this type are not totally selective in that some R–Ge bond cleavage occurs. Electrophilic attack by halogens or aluminium halides proceeds mainly by cleavage of the Ge–Ge bond but again R–Ge bond cleavage is evident. Redistribution reactions between Ge_2R_6 and $GeCl_4$ occur under mild conditions with substitution of one or two R groups by Cl yielding Ge_2R_5Cl and $(GeR_2Cl)_2$. There is no report of the reaction of Ge_2R_6 compounds with mineral acids, though permethylpolygermanes are said to react with HCl at 250°.

This work is concerned with the cleavage of phenyl groups from hexaphenyldigermane by substituted acetic acids and with the reactivity of the phenylgermanium esters, $Ge_2Ph_5(OCOCX_3)$ and $[GePh_2(OCOCX_3)]_2$. Earlier studies by Wittig and co-workers[2] demonstrated that, whereas Si_2Ph_6, Ge_2Ph_6, and $Ph_3GeSiPh_3$ are unaffected by acetic acid at 140° even in the presence of aluminium chloride, $Ph_3GeSnPh_3$ reacts with acetic acid yielding first $Ph_3GeSn(OAc)_3$ and finally $(AcO)_3GeSn(OAc)_3$. Substituted acetic acids are known to cleave one Ge–C bond in germanacyclanes and F_3CCO_2H converts tetraphenylgermane into $GePh_3(OCOCF_3)$.[1]

In the present work we have found that whereas hexaphenyldigermane is unreactive towards acetic acid or $ClCH_2CO_2H$ in boiling xylene, trichloro- and trifluoroacetic acids cleave either 1 or 2 phenyl groups according to the experimental conditions.

$$Ge_2Ph_6 \xrightarrow{X_3CCO_2H} Ge_2Ph_5(OCOCX_3) + [GePh_2(OCOCX_3)]_2$$

Both reactions proceed under mild conditions in high yield and without cleavage of the Ge–Ge bond.

The dependence of these cleavage reactions on acid strength makes it seem likely that electrophilic attack at the aromatic carbon atom of the Ph–Ge bond is the rate determining step rather than nucleophilic attack at the metal.[2] In support of this tetrabenzylgermane is unreactive towards trifluoroacetic acid under conditions where $GePh_4$ reacts. Moreover autoprotonation of the

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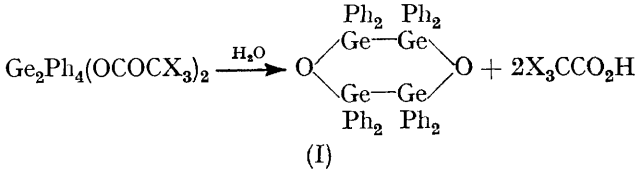
[1] F. Glockling, 'The Chemistry of Germanium,' Academic Press, 1970.

[2] E. Wiberg, E. Amberger, and J. Cambensi, *Z. anorg. Chem.*, 1967, **351**, 164.

acid must be important since hexaphenyldigermane is unaffected by HCl in boiling chloroform. In no case have we obtained evidence for the substitution of more than one phenyl group per Ge atom and this deactivation towards further electrophilic cleavage may be ascribed to protonation of the germyl ester groupings by excess acid, giving $\geqslant\mathrm{GeOC^{+}(OH)CX_3}$. The 1,2-digermanium esters are white crystalline solids, unaffected by moist air over several weeks; proof of structure comes from hydrolysis to the cyclic oxide (I). Their carbonyl stretching frequencies are considerably lower (60—80 cm^{-1}) than in the corresponding mono-esters, pointing to strong intramolecular interaction between adjacent ester groups. These esters provide a convenient route to other functionally substituted digermanes: reaction with $\mathrm{SiX_4}$ (X = Cl or Br) or strong mineral acids HX (X = F, Cl, Br, or I) in acetone produces the corresponding halides without cleavage of the Ge–Ge bond. This reaction, applied to $\mathrm{GePh_3(OCOCX_3)}$, is probably the best method of making $\mathrm{Ph_3GeX}$ free from the corresponding dihalide.



(I)

$$\mathrm{Ge_2Ph_4(OCOCX_3)_2} \xrightarrow{\mathrm{H_2O{-}Me_2CO}} \mathrm{(GePh_2O)_4 + (GePh_2H)_2O} \tag{1}$$

$$\mathrm{Ge_2Ph_4(OCOCX_3)_2} \xrightarrow{\mathrm{KI,\ H_2O{-}Me_2CO}} \mathrm{(GePh_2O)_3 + (GePh_2H)_2O} \tag{2}$$

$$\mathrm{Ge_2Ph_4(OCOCX_3)_2} \xrightarrow{\mathrm{H_2O{-}NaOH}} \mathrm{(GePh_2O)_3 + H_2} \tag{3}$$

Hexaphenyldigermane is inert to boiling 10% NaOH and to hydrochloric acid whereas the 1,2-diesters behave very differently towards aqueous acids and bases. Treatment with aqueous acetone for a short period at room temperature produces only the cyclic oxide (I) with no indication of Ge–Ge bond cleavage by the liberated acid. However refluxing with aqueous acetone does cleave the Ge–Ge bond [reaction (1)]. The same products are formed if an excess of $\mathrm{X_3CCO_2H}$ is added, but in the presence of iodide ion the cyclic trimeric oxide is produced [reaction (2)]. This tetramer–trimer relationship parallels that reported for the hydrolysis of $\mathrm{Ph_2GeCl_2}$.[1] Hydrolysis of the diesters by aqueous NaOH differed since the hydride $\mathrm{(GePh_2H)_2O}$ decomposes in alkaline solution to hydrogen and $\mathrm{(GePh_2O)_3}$ [reaction (3)]. The cyclic oxide (I) is cleaved by aqueous $\mathrm{X_3CCO_2H}$ and by aqueous base to give the products of reactions (1) and (3) respectively. Similarly the 1,2-dihalides, $\mathrm{(GePh_2X)_2}$ (X = F, Cl, Br, or I), are cleaved by aqueous base to yield the cyclic trimeric oxide although they are unaffected by aqueous hydrogen halides in refluxing acetone. These observations make it clear that substituting phenyl groups in hexaphenyldigermane by electronegative substituents (ester, halide, $\mathrm{Ge_2OGe_2}$) renders the germanium far more susceptible to nucleophilic attack.

Mass Spectra.—Supplementary Publication No. 20714 (10 pp., 1 microfiche) lists % ion abundances and metastable confirmed processes for $\mathrm{Ge_2Ph_4X_2}$ (X = F, Cl, Br, I, or H), $\mathrm{Ge_2Ph_5X}$ (X = F, Cl, or I), $\mathrm{Ge_2Ph_5(OCOCF_3)}$, $\mathrm{[GePh_2(OCOCX_3)]_2}$ (X = F or Cl), and $\mathrm{(GePh_2O)_3}$.*

Many of the fragmentation paths are similar to those reported for simpler related compounds.[3] Parent ions were observed in all cases except $\mathrm{[GePh_2(OCOCCl_3)]_2}$ and their abundances were greater for the monohalides $\mathrm{Ge_2Ph_5X}$ than the dihalides $\mathrm{Ge_2Ph_4X_2}$. Even electron ions were far more abundant than odd-electron ions and, for the substituted digermanes, $\mathrm{Ge_2}$-containing ions carried 1—7% of the total ion current. Processes of some interest include migration of phenyl, halide, and ester groups across the Ge–Ge bond, both in parent and fragment ions.

$$\mathrm{Ge_2Ph_4X_2^{+\cdot}} \longrightarrow \mathrm{GePh_3^{+} + GePhX_2\cdot}\ (\mathrm{X = F, Cl, or\ I})$$

$$\mathrm{Ge_2Ph_4X_2^{+\cdot}} \longrightarrow \mathrm{GePh_4^{+\cdot} + GeX_2}\ (\mathrm{X = F, Cl, or\ I})$$

$$\mathrm{Ge_2Ph_4X_2^{+\cdot}} \longrightarrow \mathrm{GePh_3^{+} + GePhX_2\cdot}\ (\mathrm{X = Br})$$

$$\mathrm{Ge_2Ph_4I^{+}} \longrightarrow \mathrm{GePh_3^{+} + GePhI}$$

$$\mathrm{Ge_2Ph_4(OCOCF_3)_2} \longrightarrow \mathrm{GePh_3^{+} + GePh(OCOCF_3)_2}$$

Similarly the ion $\mathrm{GePh_2F_2^{+\cdot}}$ in the spectrum of $\mathrm{Ge_2Ph_4F_2}$ is probably due to the process, $\mathrm{Ge_2Ph_4F_2^{+\cdot}} \longrightarrow \mathrm{GePh_2F_2^{+\cdot} + GePh_2}$, although no metastable peak was observed. Cleavage of the Ge–Ge bond without rearrangement of groups was also observed. In the

$$\mathrm{Ge_2Ph_4Cl_2^{+\cdot}} \longrightarrow \mathrm{GePh_2Cl^{+} + GePh_2Cl\cdot}$$

spectrum of $\mathrm{Ge_2Ph_5F}$ the low abundance ion, $\mathrm{GePh_2F_2^{+\cdot}}$ is probably due to an impurity. Spectra of the esters $\mathrm{[GePh_2(OCOCX_3)]_2}$ contain ions in which halide has been transferred to germanium with loss of $\mathrm{CO_2CX_2}$. Examples are: $\mathrm{Ge_2Ph_4X_2^{+\cdot}}$, $\mathrm{Ge_2Ph_4X^{+}}$, and $\mathrm{GePh_2X^{+}}$. The trichloroacetato-compound gave a high abundance of $\mathrm{CO_2^{+\cdot}}$ and $\mathrm{CCl_3^{+}}$ (4—5%) in contrast to the trifluoro-analogue. The cyclic trimeric oxide $\mathrm{(GePh_2O)_3}$ is of interest in that over 65% of the total ion current is carried by ions in which the $\mathrm{Ge_3O_3}$ skeleton remains and the molecular ion carried 14·4% of the total ion current. An unexpected metastable-confirmed process is the loss of water from the ion $\mathrm{Ge_3Ph_5O_3^{+}}$; elimination of O· from the parent ion and GeO from the fragment ion $\mathrm{Ge_3Ph_4O_3^{+\cdot}}$ were also metastable confirmed.

* For details of Supplementary Publications see Notice to Authors No. 7 *J. Chem. Soc.* (*A*). 1970, Index Issue.

[3] F. Glockling and J. R. C. Light, *J. Chem. Soc.* (*A*), 1968, 773.

EXPERIMENTAL

Spectra were recorded at 70 eV on an MS 902 mass spectrometer using a direct insertion probe with the source temperature in the range 150—250 °C.

All the compounds gave satisfactory C, H, and halogen analyses and produced molecular ions in their mass spectra except $[\mathrm{GePh_2(OCOCCl_3)}]_2$.

$\mathrm{Ge_2Ph_5(OCOCCl_3)}$ *and* $[\mathrm{GePh_2(OCOCCl_3)}]_2$.—Trichloroacetic acid (0·34 g) and $\mathrm{Ge_2Ph_6}$ (1·27 g) were refluxed in toluene (50 ml) for 24 h. Removal of toluene left $\mathrm{Ge_2Ph_5(OCOCCl_3)}$ as a white solid which was washed with hexane and crystallised from cyclohexane (0·8 g, 55%), ν(C=O), 1730 $\mathrm{cm^{-1}}$, m.p. 145 °C. The diester, $[\mathrm{GePh_2(OCOCCl_3)}]_2$ was similarly obtained using excess $\mathrm{CCl_3CO_2H}$ and refluxing for 2 days, (87%), ν(C=O), 1650 $\mathrm{cm^{-1}}$, m.p. 186—187 °C.

$\mathrm{Ge_2Ph_5(OCOCF_3)}$ *and* $[\mathrm{GePh_2(OCOCF_3)}]_2$.—Trifluoroacetic acid (7 ml), $\mathrm{Ge_2Ph_6}$ (5 g), and toluene (15 ml) were stirred for 24 h at 20°. Removal of excess acid and toluene by distillation gave, from benzene, first $\mathrm{Ge_2Ph_6}$ (0·7 g) and then $\mathrm{Ge_2Ph_5(OCOCF_3)}$ (4·5 g, 85%), ν(C=O), 1750 $\mathrm{cm^{-1}}$, m.p. 202—204 °C. The diester $[\mathrm{GePh_2(OCOCF_3}]_2$, ν(C=O), 1685 $\mathrm{cm^{-1}}$, m.p. 140 °C was formed quantitatively using excess $\mathrm{CF_3CO_2H}$ and refluxing for 4 h.

$\mathrm{Ge_2Ph_5X}$ (X = F, Cl, *or* I).—These were obtained in 80—90% yield from $\mathrm{Ge_2Ph_5OCOCX_3}$ in acetone and an excess of concentrated aqueous halogen acid. M.p.'s X = F, 138 °C; X = Cl, 152 °C; X = I, 225 °C.

$(\mathrm{GePh_2X})_2$ (X = F, Cl, Br, *or* I).—These were isolated in 80—90% yield from $(\mathrm{GePh_2OCOCX_3})_2$ in benzene and $\mathrm{SiCl_4}$ or $\mathrm{SiBr_4}$, or by using concentrated aqueous hydrogen halide in acetone. M.p.'s X = F, 92 °C; X = Cl, 135 °C; X = Br, 169 °C; X = I, 196 °C.

Hydrolysis of $[\mathrm{GePh_2(OCOCCl_3)}]_2$.—(a) The ester (1 g) was added to acetone (50 ml) and water (1 ml) and rapidly pumped to dryness yielding the oxide $(\mathrm{Ge_2Ph_4O})_2$ (0·7 g) [*M* (mass spec.), 940; ν(GeO) 850 $\mathrm{cm^{-1}}$].

(b) The ester (1·8 g) was refluxed for 2 days in acetone (250 ml), water (1 ml), and $\mathrm{CCl_3CO_2H}$ (10 g). Dilution with water gave a solid which, by extraction with hexane yielded $(\mathrm{GePh_2H})_2\mathrm{O}$, ν(GeH), 2040 $\mathrm{cm^{-1}}$. The hexane insoluble part consisted of $(\mathrm{GePh_2O})_4$ (0·5 g), m.p. 221 °C. This reaction, carried out in the presence of NaI (4·7 g) gave the trimer, $(\mathrm{GePh_2O})_3$ rather than the tetramer.

(c) The ester (1·8 g) in acetone (250 ml) was refluxed for 2 days with NaOH (2·0 g) and water (1 ml). Normal work-up gave the cyclic trimer, $(\mathrm{GePh_2O})_3$, (1·0 g, 92%), m.p. 147 °C. In a sealed evacuated system this reaction also yielded hydrogen. The same products were obtained by the base hydrolysis of $(\mathrm{GePh_2Cl})_2$.

Hydrolysis of $(\mathrm{Ge_2Ph_4O})_2$.—(a) The cyclic oxide (0·3 g) in acetone (150 ml) was refluxed with NaOH (2·0 g) in water (1 ml). Work-up gave the trimer $(\mathrm{GePh_2O})_3$ (0·3 g).

(b) The cyclic oxide (0·3 g) in acetone (150 ml) was refluxed with $\mathrm{CF_3CO_2H}$ (4 ml) and water (1 ml) for 2 days. Work-up gave $(\mathrm{GePh_2O})_4$ (0·1 g) and, from hexane, impure $(\mathrm{GePh_2H})_2\mathrm{O}$ (i.r. identification).

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