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NEW REARRANGEMENT OF TRIPHENYL(TRIPHENYLSILYLPEROXY)-GERMANE CATALYZED BY NUCLEOPHILES

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Summary

The peroxide $Ph_3GeOOSiPh_3$ rearranges in THF solution at ca. 20°C in the presence of fluoride ions or triethylamine to the germasiloxane, $Ph_2(PhO)GeOSiPh_3$, while thermal rearrangement of the same peroxide gives $Ph_3GeOSi(OPh)Ph_2$. The reaction of tris(trimethylsilylmethyl)stannyllithium (I) with one equivalent of the germasiloxane $Ph_2(PhO)GeOSiPh_3$ in THF yields $(Me_3SiCH_2)_3SnPh$, $(Ph_2GeO)_x$ and Ph_3SiOLi. Analogous products have been obtained in high yield in the reactions of I with the peroxides $Ph_3GeOOSiPh_3$ and $Ph_3GeOOSiMe_3$. It is assumed that the initial step of these reactions is rearrangement of the peroxides, catalyzed by $(Me_3SiCH_2)_3Sn$ anions, with the formation of the germasiloxanes $Ph_2(PhO)GeOSiR_3$ (R = Ph or Me). The mechanism of this catalytic rearrangement of unsymmetrical peroxides is discussed.

Introduction

The peroxide —O—O— group is the most labile fragment in organometallic peroxides. However, in the case of unsymmetrical organometallic peroxides the character of the nucleophilic cleavage is dependent on the nature of the starting nucleophile, steric effects of peroxide group substituents and other factors. For instance, depending on the nature of the attacking nucleophile trimethyl(t-butylperoxy)silane is cleaved at the O—O, Si—O or C—H bond (eq. 1—3). Heterol-

$$\mathrm{Me_3SiOOCMe_3}\left[\begin{array}{ll} \xrightarrow{\mathrm{R_3SnLi}} \mathrm{R_3SnOCMe_3 + Me_3SiOLi[1,2]} & (1)\\ \xrightarrow{\mathrm{CsF}} \mathrm{Me_3SiF + Me_3COOLi[3]} & (2)\\ \xrightarrow{\mathrm{R_3GeLi}} \mathrm{R_3GeH + [Me_3SiOOC(Me_2)CH_2Li][1]} & (3)\\ \qquad\qquad\qquad\qquad\qquad\downarrow & \\ \qquad\qquad\quad \mathrm{Me_3SiOOLi + Me_2C = CH_2} & \end{array}\right.$$

$(R = Me_3SiCH_2)$

ytic cleavage of the peroxide group does not occur in reactions 2 and 3.

Recently we observed another case of an anomalous reaction between tris(trimethylsilylmethyl)stannyllithium (I) and triphenyl(trimethylsilylperoxy)germane [1] (eq.4). It is interesting to note that tris(trimethylsilylmethyl)germyllithium (II), which is an isologue of compound I, reacts with the same peroxide under comparable conditions to give $(Me_3SiCH_2)_3GeOGePh_3$ and Me_3SiOLi (i.e. with nucleophilic attack by the $(Me_3SiCH_2)_3Ge$ anion on the peroxidic oxygen atom bonded to the Ph_3Ge group). In order to ascertain the unusual direction of reaction 4 we have studied in the present work the reactions of some nucleophiles with triphenyl(triphenylsilylperoxy)germane (III). This peroxide is known [4] to be stable under normal conditions. On heating in an inert solvent in the absence of oxygen it is isomerized with formation of $Ph_2(PhO)SiOGePh_3$ [5—7]. It has been established that during thermal isomerization only those phenyl groups attached to the silicon atom migrate.

$$Ph_3GeOOSiMe_3 + R_3SnLi \xrightarrow[20°C]{THF} R_3SnPh + Ph_2GeO + Me_3SiOLi \qquad (4)$$

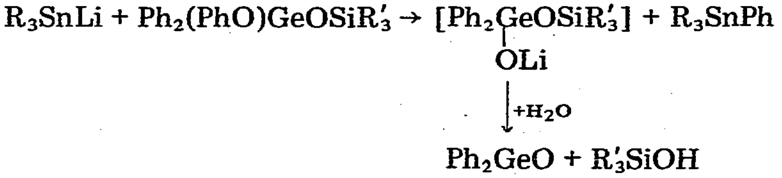
$(R = Me_3SiCH_2)$

Results and discussion

The peroxide III reacts with the germyllithium compound II in THF to give $(Me_3SiCH_2)_3GeOGePh_3$ and Ph_3SiOLi, i.e. the usual products of nucleophilic cleavage of the peroxide group by the $(Me_3SiCH_2)_3Ge$ anion. On the contrary the reaction of the stannyllithium compound I with the peroxide III in THF proceeds analogously to reaction 4. It affords tris(trimethylsilylmethyl)phenylstannane, diphenylgermanium oxide, $(Ph_2GeO)_x$ and lithium triphenylsiloxide. It seems reasonable to suggest that reactions of this type are complicated and can be described by Scheme 1.

SCHEME 1

$$Ph_3GeOOSiR'_3 \xrightarrow[THF, \sim 20°C]{R_3Sn^-} Ph_2(PhO)GeOSiR'_3 \qquad (5)$$



$$R_3SnLi + Ph_2(PhO)GeOSiR'_3 \rightarrow [Ph_2\underset{\displaystyle OLi}{\underset{|}{Ge}}OSiR'_3] + R_3SnPh$$
$$\Big\downarrow{\scriptstyle +H_2O}$$
$$Ph_2GeO + R'_3SiOH$$

(6)

$(R = Me_3SiCH_2;\ R' = Me \text{ or } Ph)$

The initial step of the reaction is probably a catalytic rearrangement of the starting peroxide catalyzed by $(Me_3SiCH_2)_3Sn$ anions (eq. 5). Then nucleophilic attack by the $(Me_3SiCH_2)_3Sn$ anion on the phenoxy group of the rearranged product takes place (eq. 6).

In accordance with Scheme 1 we have found that fluoride ions (the source of which is CsF) and Et_3N catalyzed the rearrangement of the peroxide III according to eq. 5. The yield of the rearrangement product is quantitative. In THF solution reaction 5 proceeds at room temperature, while thermal rearrangement of the peroxide III occurs under more drastic conditions ($\geqslant 110°$C) [5,7]. The catalytic rearrangement product, $Ph_2(PhO)GeOSiPh_3$ (IV), m.p. 110—112°C is different from the thermal rearrangement product, $Ph_3GeOSi(OPh)Ph_2$ (V), m.p. 126°C [5] in structure and properties. When compound V is being formed from the peroxide III, the migration of the phenyl group occurs exclusively from the silicon atom.

Hydrolysis of compound IV affords $(Ph_2GeO)_x$ (68.4%), phenol (72.7%) and triphenylsilanol (80.0%), while hydrolysis of V gives phenol and triphenylgermanol in quantitative yield.

We have found that the germasiloxane IV reacts with the stannyllithium compound I to form tris(trimethylsilylmethyl)phenylstannane, diphenylgermanium oxide and triphenylsilanol (i.e. in accordance with eq. 6). On the contrary, treatment of the germasiloxane V in THF with the lithium derivative I gives tris(trimethylsilylmethyl)phenylstannane, $(Ph_2SiO)_3$ and triphenylgermanol in high yield (eq. 7).

$$R_3SnLi + Ph_3GeOSi(OPh)Ph_2 \xrightarrow[\sim 20°C]{THF} \xrightarrow{H_3O^+} R_3SnPh + 1/3\ (Ph_2SiO)_3 + Ph_3GeOH \quad (7)$$

$(R = Me_3SiCH_2)$

The quantitative formation of IV from the peroxide III must involve a concerted process, which is catalyzed by nucleophilic coordination of $(Me_3SiCH_2)_3$-Sn and F anions or Et_3N on the germanium atom. The germanium atom is known [8,9] to be more electrophilic in comparison with the silicon atom. For instance, the interaction of the lithium derivatives RLi with the germasiloxanes $R_3SiOGeR'_3$ usually occurs by nucleophilic attack on the germanium atom by the R^- anion [1,8].

$$Ph_3GeOOSiPh_3 \xrightarrow{L:} Ph_2(PhO)GeOSiPh_3 \quad (8)$$

$(L: = F^-, (Me_3SiCH_2)_3Sn^- \text{ or } Et_3N:)$

Nucleophilic catalysis is of great significance in the reactions of organometallic compounds [10]. In our case the nucleophilic coordination of the nucleophile L with the germanium atom causes reduction of the effective electronegativity of this atom, and contributes to the polarization of the germanium—phenyl bond and a further concerted heterolytic bond redistribution.

In reactions with the peroxide III compounds I and II have different reactivities. Analogous examples were observed before, for instance, in the reactions of isostructural stannyl- and germyl-lithium compounds with ketones [11]. However, the reaction of triethyl(triphenylsilylperoxy)germane with compounds I and II readily proceeds in THF and can be described by eq. 9. It has been shown by GLC that these reactions are not accompanied by processes analogous to 5 and 6.

$$(Me_3SiCH_2)_3MLi + Et_3GeOOSiPh_3 \rightarrow (Me_3SiCH_2)_3MOGeEt_3 + Ph_3SiOLi \quad (9)$$

$(M = Ge, Sn)$

In the IR spectra of the compounds $(Me_3SiCH_2)_3GeOGePh_3$, $(Me_3SiCH_2)_3$-

SnPh, $(Me_3SiCH_2)_3GeOGeEt_3$ and $(Me_3SiCH_2)_3SnOGeEt_3$, the frequencies characteristic of Me_3SiCH_2M (M = Ge, Sn), Sn—Ph and Ge—Ph fragments are identical with those reported in ref. 1. The bands at 780—900 cm^{-1} correspond to groups Ge—O—Ge and Ge—O—Sn. Et_3Ge group vibrations in the region 400—1500 cm^{-1} are in agreement with those reported in ref. 13.

Experimental

All reactions were carried out in evacuated sealed ampoules following the technique described in ref. 12. The melting points were determined in evacuated sealed capillaries. IR spectra were recorded on a double-beam Zeiss—Jena Model UR-20 spectrometer.

Triphenyl(triphenylsilylperoxy)germane (III) was prepared by the literature method [4].

Reaction of tris(trimethylsilylmethyl)germyllithium (II) with the peroxide III

A solution of 1.68 g (4.9 mmol) of II in 12 ml of THF was added to a solution of 2.93 g (4.9 mmol) of the peroxide III in 10 ml of THF. The reaction was complete in 3—5 min at 20°C. The solvent was removed by recondensation in vacuo. The residue was extracted with hexane. The hexane solution was kept at —70°C for 3 h. The crystals which precipitated were crystallized twice from hexane at the same temperature to give 2.40 g (74.5%) of $(Me_3SiCH_2)_3GeOGePh_3$, m.p. 119—120°C (in agreement with ref. 1). A mixture of $(Me_3SiCH_2)_3GeOGePh_3$ with an authentic sample gave no melting point depression. Hydrolysis of the residue gave 1.06 g (77.9%) of triphenylsilanol, m.p. 150—152°C (lit. [14] m.p. 151—153°C). IR (cm^{-1}): ν(Si—Ph) 1120, ν(OH) 3680.

Reaction of tris(trimethylsilylmethyl)stannyllithium (I) with the peroxide III

To a solution of 2.74 g (4.6 mmol) of III in 10 ml of THF was added 1.78 g (4.6 mmol) of I in 10 ml of THF at room temperature. The mixture discoloured after 3—5 min. THF was replaced with hexane in the usual manner. The organic layer was kept at —70°C for 5—6 h. The crystalline product which precipitated was recrystallized three times from hexane at the same temperature to afford 1.97 g (93.8%) of tris(trimethylsilylmethyl)phenylstannane, m.p. 103—105°C (in agreement with ref. 1). Hydrolysis of the residue gave 0.96 g (79.0%) of diphenylgermanium oxide, m.p. 215—223°C (in agreement with ref. 15 for tetramer), and 0.94 g (74.0%) of triphenylsilanol, m.p. 151—152°C (mixed m.p.).

Catalytic rearrangement of triphenyl(triphenylsilylperoxy)germane (III)

(a). A suspension of 0.35 g (2.3 mmol) of CsF in 5 ml of THF was added to 4.00 g (6.72 mmol) of the peroxide III in 10 ml of THF. After completion of the slightly-exothermal reaction the mixture was shaken at 20°C for 3 h. The organic layer was decanted from CsF and THF was replaced with hexane in the usual manner. The crystalline product precipitated is almost insoluble in hexane. The product was washed several times with hexane and dried in vacuo. 3.85 g (96.3%) of $Ph_2(PhO)GeOSiPh_3$ (IV) was obtained, m.p. 110—112°C. (Found: C, 72.24; H, 5.21; Ge, 12.45; Si, 4.59. $C_{36}H_{30}GeO_2Si$ calcd.: C, 72.63; H, 5.08; Ge, 12.19; Si, 4.72%.) IR (cm^{-1}): ν(Si—O—Ge) ~1000, ν(Ph—O—Ge) ~860 [6], ν(Si—Ph)

1110, ν(Ge—Ph) 1100 [16], absent (—O—O—).

(b). To a solution of 2.60 g (4.36 mmol) of peroxide III in 10 ml of THF was added a solution of 0.15 g (1.5 mmol) of triethylamine in 3 ml of THF at room temperature. The reaction mixture was worked up as in the above experiment to give 2.44 g (93.9%) of IV, m.p. 110—112°C (mixed m.p.). The IR spectrum of this compound is identical with that given for IV in the above experiment.

Hydrolysis of $Ph_2)PhO)GeOSiPh_3$ (IV)

2.80 g of compound IV was dissolved in the mixture of 20 ml of chloroform and 1 ml of ethanol. To the solution obtained was added 4 ml of concentrated hydrochloric acid (excess). The organic layer was separated, dried over K_2CO_3 and some of the solvent was removed in vacuo. The mixture was decanted from the precipitate of $(Ph_2GeO)_4$ (0.78 g, 68.4%), m.p. 218—223°C (mixed m.p.). GLC analysis of the reaction mixture showed the presence of 0.32 g (72.7%) of phenol (GLC analysis was carried out on a Tsvet-1 chromatograph with a heat conductivity detector using a 50 × 0.4 cm column packed with Thermol 3 (15%) on Schimalite B, with helium as the carrier gas). Then the solvent was removed under reduced pressure. To the residue was added 10 ml of petroleum ether. On slight heating of the mixture phenol was completely dissolved in ether, the solution was decanted from the precipitate of Ph_3SiOH. The product was washed twice with petroleum ether and dried. 1.04 g (80.0%) of triphenylsilanol was obtained, m.p. 150—152°C. Mixed melting with an authentic sample of Ph_3SiOH gave no depression in the melting point.

Reaction of I with compound IV

A solution of 2.36 g (6.1 mmol) of I in 10 ml of THF was added to a solution of 3.63 g (6.1 mmol) of IV in 10 ml of THF. The mixture discoloured in 3—5 min at 20°C. After replacing THF with hexane the usual work-up afforded 2.04 g (73.1%) of tris(trimethylsilylmethyl)phenylstannane, m.p. 104—105°C. A mixture of $(Me_3SiCH_2)_3SnPh$ with an authentic sample gave no melting point depression. Hydrolysis of the residue gave 1.32 g (78.3%) of triphenylsilanol, m.p. 151—152°C (mixed m.p.) and 0.96 g (64.9%) of diphenylgermanium oxide, m.p. 218—223°C (in agreement with ref. 15).

Reaction of I with the thermal rearrangement product of the peroxide III, $Ph_3GeOSi(OPh)Ph_2$ (V)

To a solution of 2.46 g (4.1 mmol) of compound V in 10 ml of THF was added a solution of 1.60 g (4.1 mmol) of I in 10 ml of THF. After 3—5 min at ca. 20°C the mixture was completely discoloured. The reaction mixture on usual work-up gave 1.45 g (76.7%) of $(Me_3SiCH_2)_3SnPh$, m.p. 104—106°C (mixed m.p.). Hydrolysis of the residue gave 1.06 g (79.7%) of triphenylgermanol, m.p. 128—130°C (lit. [17] m.p. 127—131°C) and 0.59 g (71.9%) of hexaphenylcyclotrisiloxane, m.p. 187—189°C (in agreement with ref. 18).

Triethyl(triphenylsilylperoxy)germane (VI)

To a solution of 4.00 g (13.7 mmol) of Ph_3SiOOH in 200 ml of ether was added 7.1 g (29.6 mmol) of triethylgermanium bromide, and the solution was cooled to 0°C. Then dry ammonia was passed through the reaction mixture until ammonium bromide was completely precipitated. After filtration and removal of ether under reduced pressure, the residue was recrystallized twice from hexane to give 3.40 g (55.1%) of VI, m.p. 40—41°C. (Found: C, 63.25; H, 6.81; (Ge + Si), 21.94%; Mol.wt. (cryoscopy in benzene) 440. $C_{24}H_{30}GeO_2Si$ calcd.: C, 63.89; H, 6.70; (Ge + Si), 22.31%; Mol.wt. 451.)

Reaction of I with $Et_3GeOOSiPh_3$ (VI)

A solution of 1.50 g (3.9 mmol) of I in 10 ml of THF was added to a solution of 1.75 g (3.9 mmol) of VI in 5 ml of THF. The reaction was complete in 3—5 min at 20°C. THF was replaced with hexane in the usual manner. 1.77 g (82.3%) of $(Me_3SiCH_2)_3SnOGeEt_3$ was isolated from the hexane solution, b.p. 105—106°C/ 0.5 Torr, n_D^{20} 1.5120. (Found: C, 39.54; H, 8.95; Ge, 13.04; Si, 15.12; Sn, 21.31. $C_{18}H_{48}GeOSi_3Sn$ calcd.: C, 38.88; H, 8.70; Ge, 13.05; Si, 15.15; Sn, 21.34%.) After hydrolysis of the residue 0.86 g (80.4%) of triphenylsilanol was obtained, m.p. 149—151°C. Mixed melting with an authentic sample of Ph_3SiOH gave no depression in the melting point.

Reaction of II with peroxide VI

Following the above procedure, 2.31 g (5.1 mmol) of VI in 5 ml of THF on treatment with a solution of 1.75 g (5.1 mmol) of II afforded 2.14 g (81.7%) of $(Me_3SiCH_2)_3GeOGeEt_3$, b.p. 95—96°C/0.5 Torr, n_D^{20} 1.4930. (Found: C, 43.08; H, 9.45; Ge, 28.23; Si, 15.96. $C_{18}H_{48}Ge_2OSi_3$ calcd.: C, 42.39; H, 9.49; Ge, 28.46; Si, 16.52%.) Hydrolysis of the residue gave 1.17 g (82.4%) of triphenylsilanol, m.p. 150—152°C (mixed m.p.).

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