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REACTIONS OF COMPOUNDS CONTAINING Sn—Li AND Ge—Li BONDS WITH ORGANIC AND ORGANOMETALLIC PEROXIDES

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Summary

The reactions of tris(trimethylsilylmethyl)stannyllithium, tris(trimethylsilylmethyl)germyllithium and triethylgermyllithium with di-t-butyl peroxide, bis(trimethylsilyl)peroxide, trimethyl(t-butylperoxy)silane, triphenyl(t-butylperoxy)germane, bis(triphenylgermyl) peroxide, triphenyl(trimethylsilylperoxy)germane, benzoyl peroxide and dicyclohexyl peroxydicarbonate were investigated. The reactions proceed under mild conditions with nucleophilic attack by the R_3M anion ($R = Et$, Me_3SiCH_2, $M = Ge, Sn$) on one of the peroxide oxygen atoms. In the case of unsymmetrical organometallic peroxides the character of nucleophilic cleavage is dependent on the nature of the starting nucleophile, steric effects of peroxide group substituents and other factors.

Introduction

In spite of the great extent of organolithium chemistry [1] the reactions of organolithium compounds with peroxides have been insufficiently studied [2]. They involve the heterolysis of a peroxide group and depend essentially on the nature of organic groups in both organometallic compound and peroxide [3-6]. For example, alkyllithium compounds react with dialkyl peroxides very easily by an S_N2 process to form ethers and the corresponding lithium alkoxides:

$$RLi + R'OOR' \rightarrow R'OLi + ROR'$$

The reactions of aryllithium compounds with various dialkyl peroxides proceed with the formation of ethers together with diaryls (10-30%) as by-products [3,4].

Only few examples of the reactions of organolithium compounds with diacyl and organometallic peroxides are known [7,8]. No reactions of organosilyllithium and the related compounds R_3MLi ($M = Si, Ge, Sn, Pb$) with peroxides have been studied [9]. However, these reactions are interesting since R_3MLi compounds are weaker nucleophiles than RLi and their side-reactions should be less pronounced.

The present paper is concerned with reactions of tris(trimethylsilylmethyl)stannyllithium, its germanium analogue, and triethylgermyllithium with some organic and organometallic peroxides.

Results and discussion

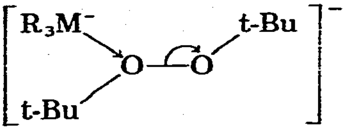
By analogy with tris(trimethylsilylmethyl)stannyllithium (I) [10] the previously unknown tris(trimethylsilylmethyl)germyllithium (II) has been obtained according to eqn. 1.

$$GeCl_4 \xrightarrow{RMgCl} R_4Ge \xrightarrow{Br_2} R_3GeBr \xrightarrow{LiAlH_4} R_3GeH \xrightarrow{(C_2H_5)_2Hg} (R_3Ge)_2Hg \xrightarrow{Li} R_3GeLi \qquad (1)$$

$(R = Me_3SiCH_2)$

We have found that compounds I and II react with di-t-butyl peroxide in tetrahydrofuran (THF) under mild conditions by nucleophilic attack by the R_3M anion (M = Ge, Sn) on the peroxide oxygen and heterolysis of the peroxide group.

$R_3MLi + t\text{-}BuOO\text{-}t\text{-}Bu \rightarrow$



$Li^+ \rightarrow R_3MO\text{-}t\text{-}Bu + t\text{-}BuO^-Li^+$ (2)

$(R = Me_3SiCH_2,\ M = Ge, Sn)$

The yield of lithium t-butoxide and R_3MO-t-Bu compounds is high. However, the analogous reaction with triethylgermyllithium gives a small yield of Et_3GeO-t-Bu (11%), together with lithium t-butoxide (71%) and hexaethyldigermane (64%). The formation of latter product can be explained by the reaction of t-butoxy(triethyl)germane with starting triethylgermyllithium (eqn. 3). Similar reactions, giving the compounds with metal—metal bonds, have been studied in detail [11].

$$Et_3GeO\text{-}t\text{-}Bu + Et_3GeLi \rightarrow Et_3GeGeEt_3 + t\text{-}BuOLi \qquad (3)$$

It is known [8] that bis(trimethylsilyl) peroxide is more reactive towards the nucleophilic agents than is di-t-butyl peroxide. The main pathway in the reactions of this peroxide with compounds I and II leads to lithium trimethylsiloxide and $(Me_3SiCH_2)_3MOSiMe_3$ compounds (M = Sn, Ge) via an S_N2 mechanism (eqn. 4). The first compound could be isolated as hexamethyldisiloxane.

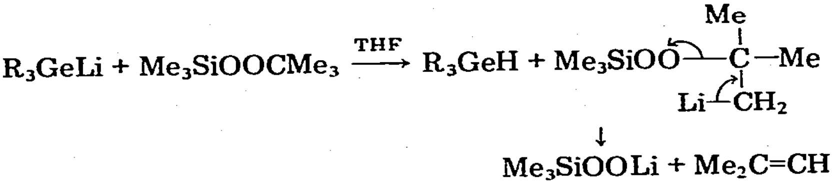
$$\begin{tikzcd}
R_3MLi + Me_3SiOOSiMe_3 \arrow[r, "(a)"] & R_3MOSiMe_3 + Me_3SiOLi \arrow[d, "(b)"', "+ R_3MLi"] \\
& R_3MMR_3 + Me_3SiOLi
\end{tikzcd} \qquad (4)$$

$(R = Me_3SiCH_2 \text{ or } Et;\ M = Sn \text{ or } Ge)$

In addition, the $(Me_3SiCH_2)_3M$ anion attacks the $(Me_3SiCH_2)_3MOSiMe_3$ compounds formed to give hexakis(trimethylsilylmethyl)-distannane (III) or -digermane (IV) in ca. 10% yield. III and IV were also obtained from the reactions of tris(trimethylsilylmethyl)stannyllithium with $(Me_3SiCH_2)_3SnOSiMe_3$ or tris(trimethylsilylmethyl)germyllithium with $(Me_3SiCH_2)_3GeOSiMe_3$. The formation of III and IV in reaction 4b (instead of compounds with Sn—Si and Ge—Si bonds) indicates that in $(Me_3SiCH_2)_3MOSiMe_3$ compounds (M = Sn, Ge) the tin and germanium atoms are more electrophilic than the silicon atom. These results lead to the conclusion that the steric requirements of the alkyl groups bonded to Sn—O—Si and Ge—O—Si linkages have little effect on the nature of the products obtained.

The reaction of bis(trimethylsilyl) peroxide with triethylgermyllithium occurs analogously, but the rate of step 4b is probably comparable to that of 4a. Even when the reagent ratio was 1/1, only hexaethyldigermane, lithium trimethylsiloxide and unreacted peroxide (50%) were isolated.

Treatment of trimethyl(t-butylperoxy)silane in THF with the stannyllithium compound I at room temperature gives $(Me_3SiCH_2)_3SnO$-t-Bu and Me_3SiOLi [12], a result which may be interpreted in terms of a nucleophilic attack by the $(Me_3SiCH_2)_3Sn$ anion on the peroxidic oxygen atom bonded to t-butyl group. Surprisingly, the similar reaction of compound II with the same peroxide in THF gives $(Me_3SiCH_2)_3GeH$ (76%), isobutylene (90%) and lithium trimethylsilyl peroxide $Me_3SiOOLi$ (84%). The last product and trimethylchlorosilane gave quantitatively bis(trimethylsilyl)peroxide. The reaction apparently proceeds via the formation of the lithiated intermediate which decomposes by heterolytic process (eqn. 5).



$$\mathrm{R_3GeLi + Me_3SiOOCMe_3 \xrightarrow{THF} R_3GeH + Me_3SiOO{-}\overset{Me}{\underset{Li{-}CH_2}{C}}{-}Me \;\longrightarrow\; Me_3SiOOLi + Me_2C{=}CH_2} \qquad (5)$$

$(R = Me_3SiCH_2)$

A considerable difference between the route of nucleophilic cleavage of the unsymmetrical organometallic peroxides was also observed in the case of triphenyl(t-butylperoxy)germane. Reaction of compound I with an equimolar amount of this peroxide in THF at room temperature affords $(Me_3SiCH_2)_3SnO$-t-Bu (78%) and lithium triphenylgermoxide (73%) (eqn. 6). The reaction of germyllithium compound II with the same peroxide under comparable conditions can be represented by eqn. 7.

$$R_3SnLi + Ph_3GeOO\text{-t-Bu} \rightarrow R_3SnO\text{-t-Bu} + Ph_3GeOLi \qquad (6)$$

$$R_3GeLi + Ph_3GeOO\text{-t-Bu} \rightarrow R_3GeOGePh_3 + \text{t-BuOLi} \qquad (7)$$

$(R = Me_3SiCH_2)$

A still greater difference is observed in reactions of triphenyl(trimethylsilylperoxy)germane with compounds I and II under comparable conditions. The reaction of II with the peroxide is similar to eqn. 7 (eqn. 8), while compound I affords the unexpected product, $(Me_3SiCH_2)_3SnPh$ (eqn. 9). In order to ascertain the mechanism of formation of tris(trimethylsilylmethyl)phenylstannane and diphenylgermanium oxide reaction 9 should be studied in more detail. It is interesting to note that the reaction of I with bis(triphenylgermyl) peroxide occurs with heterolysis of the peroxide group, eqn. 10, similar to eqn. 4a. In this case no formation of $(Me_3SiCH_2)_3SnPh$ is observed. It may be assumed that in the case of unsymmetrical organometallic peroxides the character of nucleophilic cleavage is determined essentially by the nature of nucleophile, and steric and polar effects of the peroxide group substituents.

$$\underset{}{R_3GeLi} + \underset{(II)}{Ph_3GeOOSiMe_3} \xrightarrow[20^\circ C]{THF} R_3GeOGePh_3 + Me_3SiOLi \tag{8}$$

$(R = Me_3SiCH_2)$

$$R_3SnLi + Ph_3GeOOSiMe_3 \xrightarrow[20^\circ C]{THF} R_3SnPh + Ph_2GeO + Me_3SiOLi \tag{9}$$

$(R = Me_3SiCH_2)$

$$\underset{(I)}{R_3SnLi} + Ph_3GeOOGePh_3 \xrightarrow[20^\circ C]{THF} R_3SnOGePh_3 + Ph_3GeOLi \tag{10}$$

$(R = Me_3SiCH_2)$

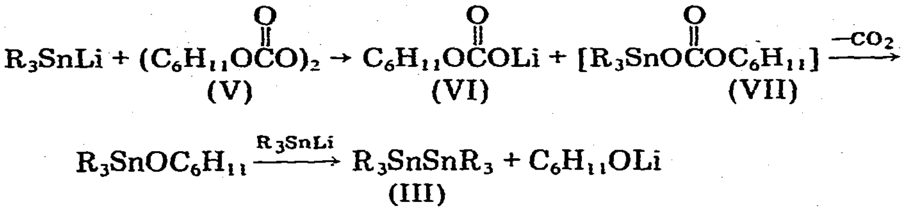
It has been reported [7] that the reaction of phenyllithium with benzoyl peroxide in ether yielded a complex mixture from which benzoic acid and triphenylcarbinol were isolated. It was interesting to find out whether the nature of the nucleophile controls the course of this reaction. It could be expected that in the case of $(Me_3SiCH_2)_3SnLi$ (I), which is a weaker nucleophile than phenyllithium, the side-reactions should be less pronounced. We have found that compound I and benzoyl peroxide in THF afford hexakis(trimethylsilylmethyl)distannane (III) (71%) and lithium benzoate (69%) (eqn. 11).

$$\begin{tikzcd}
R_3SnLi + (PhCOO)_2 \arrow[r, "(a)"] & R_3SnOCOPh + PhCOOLi \arrow[d, "(b)"', "+R_3SnLi"] \\
 & \underset{(III)}{R_3SnSnR_3} + PhCOOLi
\end{tikzcd} \tag{11}$$

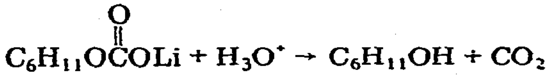
$(R = Me_3SiCH_2)$

In agreement with this scheme, it has been found that the reaction of stannyllithium I with $(Me_3SiCH_2)_3SnOCOPh$ (which has been synthesized via other routes) gives distannane III and lithium benzoate in 75 and 77% yield respectively.

Dicyclohexyl peroxydicarbonate (V) reacts with I in THF at room temperature to form carbon dioxide, distannane III, lithium cyclohexoxide and lithium cyclohexyl carbonate (VI). The reaction probably proceeds via the intermediate $(Me_3SiCH_2)_3SnOC(O)OC_6H_{11}$ (VII) which spontaneously decarboxylates to give $(Me_3SiCH_2)_3SnOC_6H_{11}$. The latter is converted to distannane III and lithium cyclohexoxide by reaction with second equivalent of stannyllithium (I) (eqns. 12 and 12a). In agreement with this scheme, 50% of carbon dioxide evolves directly upon mixing the reagents in THF. The germanium analogue of VII, $Et_3GeOC(O)OC_6H_{11}$, is also unstable and decomposes into CO_2 and $Et_3GeOC_6H_{11}$ [13]. The other 50% of carbon dioxide evolves at the acid hydrolysis of the reaction mixture (eqn. 12a).



$$\begin{gathered}R_3SnLi + (C_6H_{11}O\overset{O}{\overset{\|}{C}}O)_2 \rightarrow C_6H_{11}O\overset{O}{\overset{\|}{C}}OLi + [R_3SnO\overset{O}{\overset{\|}{C}}OC_6H_{11}] \xrightarrow{-CO_2} \\ \qquad\quad (V) \qquad\qquad\qquad\quad (VI) \qquad\qquad\qquad\qquad (VII) \\ R_3SnOC_6H_{11} \xrightarrow{R_3SnLi} R_3SnSnR_3 + C_6H_{11}OLi \\ (III)\end{gathered} \qquad (12)$$



$$C_6H_{11}O\overset{O}{\overset{\|}{C}}OLi + H_3O^+ \rightarrow C_6H_{11}OH + CO_2 \qquad (12a)$$

$(R = Me_3SiCH_2)$

We have also found that a reaction between I and t-butyl perbenzoate in THF at 20°C involves two concomitant processes (eqns. 13 and 13a).

$$R_3SnLi + PhC(O)OO\text{-}t\text{-}Bu \begin{cases} \rightarrow R_3SnO\text{-}t\text{-}Bu + PhCOOLi & (13) \\ \rightarrow R_3SnOCOPh + t\text{-}BuOLi & (13a) \end{cases}$$

$(R = Me_3SiCH_2)$

The main products of the reaction are R_3SnO-t-Bu (43%), lithium benzoate (84%) and lithium t-butoxide (77%), together with $R_3SnOCOPh$, which is not isolated from the reaction mixture, as it is quickly converted into distannane III (49% yield) (see eqn. 11b). Attempts to prepare distannane III, starting from R_3SnO-t-Bu and I were unsuccessful.

Thus, the reactions with acyl peroxides discussed above occur also with heterolysis of the peroxide group. Initially formed $R_3SnOCOPh$ or $R_3SnOC_6H_{11}$ (but not R_3SnO-t-Bu) then readily react with I, giving R_3SnSnR_3 in sufficiently high yield.

The IR spectra of the compounds $(Me_3SiCH_2)_3MOSiMe_3$, $(Me_3SiCH_2)_3$-MO-t-Bu (M = Ge, Sn), $(Me_3SiCH_2)_3SnPh$ obtained in this study exhibit absorption bands at 1250, 1020 (1060), 840, ≈700 and 600 cm^{-1}, characteristic of Me_3SiCH_2M fragments (M = Ge, Sn). The bands at 960-1000 cm^{-1} correspond to groups Sn—O—C, Sn—O—Si, Ge—O—C and Ge—O—Si. Sn—Ph and Ge—Ph vibrations are observed at 1080-1100 cm^{-1} [15].

Experimental

All reactions were carried out in evacuated sealed ampoules following the technique described in ref. 14. The melting points were determined in evacuated sealed capillaries. GLC analyses of gaseous and volatile products were carried out on a Tsvet-101 chromatograph with a heat conductivity detector using

200 × 0.4 cm column packed with Reoplex 400 (15%) on Chromosorb W, with helium as the carrier gas. IR spectra were recorded on a double-beam Zeiss-Jena Model UR-20 spectrometer.

Bis(trimethylsilyl)peroxide, bis(triphenylgermyl)peroxide, trimethyl(t-butylperoxy)silane, triphenyl(t-butylperoxy)germane and triphenyl(trimethylsilylperoxy)germane were prepared by published methods [16-19].

Tetrakis(trimethylsilylmethyl)germane

Grignard reagent was prepared under argon from 20.5 g (0.84 mol) of magnesium, 100 g (0.82 mol) of chloromethyltrimethylsilane and 600 ml of ether. The ether was evaporated and 500 ml of dry benzene was added. To the reaction mixture 21.8 g (0.1 mol) of germanium tetrachloride was added with stirring and refluxing (30 min), then mixture was refluxed for 9 h. After cooling, the reaction mixture was hydrolyzed with water and dilute acetic acid. The organic layer was dried over $CaCl_2$ and the solvent evaporated. Vacuum distillation of the residue gave the desired product (34.5 g, 80.4%), b.p. 93-95°C/1.5 Torr, n_D^{20} 1.4730. (Found: C, 45.21; H, 10.49; Ge, 16.79; Si, 26.25. $C_{16}H_{44}GeSi_4$ calcd.: C, 45.60; H, 10.52; Ge, 17.22; Si, 26.66%.)

Tris(trimethylsilylmethyl)bromogermane

A mixture of 29.5 g (70 mmol) of tetrakis(trimethylsilylmethyl)germane, 11.2 g (70 mmol) of bromine and 27.0 g of ethyl bromide was heated for 100 h at 70°C with stirring. Fractionation of the reaction mixture afforded 27.5 g (94.8%) of the desired product, b.p. 100-102°C/1.5 Torr, n_D^{20} 1.4870. (Found: Br, 19.58. $C_{12}H_{33}BrGeSi_3$ calcd.: Br, 19.29%.)

Tris(trimethylsilylmethyl)germane

A solution of 27.0 g (65.2 mmol) of $(Me_3SiCH_2)_3GeBr$ in 50 ml of ether was added dropwise under argon with vigorous stirring to a suspension of 3.60 g (94.9 mmol) of $LiAlH_4$ in 200 ml of ether. The mixture was refluxed with stirring for 20 h, then cooled and hydrolyzed with water and HCl. The organic layer was separated, dried over $CaCl_2$ and the solvent evaporated. By distillation of the residual liquid in vacuo 18.7 g (85.4%) of tris(trimethylsilylmethyl)germane was obtained, b.p. 80-81°C/1 Torr, n_D^{20} 1.4619. (Found: C, 43.17; H, 10.23; G, 21.51; Si, 24.96. $C_{12}H_{34}GeSi_3$ calcd.: C, 42.99; H, 10.22; Ge, 21.65; Si, 25.13%.)

Bis[tris(trimethylsilylmethyl)germyl]mercury

A mixture of 1.35 g (5.2 mmol) of freshly distilled diethylmercury and 3.50 g (10.4 mmol) of $(Me_3SiCH_2)_3GeH$ was heated at 80°C for 5 h when 230 ml (100%) of ethane evolved. The crystalline pale-yellow product obtained was dissolved in 12 ml of hexane. The solution was decanted from mercury (traces) and kept at −70°C for 2 h. The crystals which precipitated were crystallized twice from hexane at the same temperature to give 3.93 g (89.0%) of the desired mercurial, m.p. 132-134°C. (Found: C, 32.86; H, 7.51; Ge, 16.82; Hg, 22.76; Si, 19.06. $C_{24}H_{66}Ge_2HgSi_6$ calcd.: C, 33.17; H, 7.65; Ge, 16.71; Hg, 23.08; Si, 19.39%.)

Tris(trimethylsilylmethyl)germyllithium (II)

To 0.70 g (100.9 mmol) of lithium, in the form of small pieces of thin foil, in 20 ml of THF, frozen at liquid nitrogen temperature, was added 4.0 g (4.6 mmol) of $[(Me_3SiCH_2)_3Ge]_2Hg$. The mixture was shaken at 20°C for 8 h. The resulting dark-brown solution was decanted from the metallic mercury (0.83 g, 90.2%) and excess lithium. The solution obtained (compound II in THF) was used in future reactions.

Reaction of $(Me_3SiCH_2)_3SnLi$ (I) with di-t-butyl peroxide

A solution of 2.12 g (5.5 mmol) of compound I in 20 ml of THF was added to a solution of 0.80 g (5.5 mmol) of di-t-butyl peroxide in 2 ml of THF. The mixture was heated at 65°C for 7 h. The solvent was removed by recondensation in vacuo. The residue was extracted with hexane. Distillation of the extract gave 1.78 g (71.8%) of $(Me_3SiCH_2)_3SnO$-t-Bu, b.p. 98-100°C/1 Torr, n_D^{20} 1.4705. (Found: C, 42.32; H, 9.38; Si, 18.49; Sn, 26.06. $C_{16}H_{42}OSi_3Sn$ calcd.: C, 42.38; H, 9.34; Si, 18.58; Sn, 26.17%.) The residue was hydrolyzed. GLC analysis of the organic phase showed the presence of t-butyl alcohol (0.30 g, 74.4%).

Reaction of tris(trimethylsilylmethyl)germyllithium (II) with di-t-butyl peroxide

A solution of 2.42 g (7.1 mmol) of II in 20 ml of THF was added to a solution of 1.10 g (7.5 mmol) of di-t-butyl peroxide in 4 ml of THF. Reaction was complete in 3-5 min at 20°C. THF was replaced with hexane in the usual manner. 2.28 g (67.9%) of $(Me_3SiCH_2)_3GeO$-t-Bu was isolated from hexane solution, b.p. 70-71°C/1 Torr, n_D^{20} 1.4635. (Found: C, 46.49; H, 10.25; Ge, 18.37; Si, 21.45. $C_{16}H_{42}GeOSi_3$ calcd.: C, 47.18; H, 10.39; Ge, 17.82; Si, 20.68%.) GLC analysis of the hydrolysis products revealed the presence of 0.42 g (79.2%) of t-butyl alcohol. The reaction of Et_3GeLi (III) with di-t-butyl peroxide and those of compounds I-III with bis(trimethylsilyl)peroxide are presented in Table 1.

TABLE 1

REACTIONS OF COMPOUNDS I-III WITH DI-t-BUTYL PEROXIDE AND BIS(TRIMETHYLSILYL)-PEROXIDE IN THF

Starting reagents g (mmol)	Temperature (°C)	Reaction time (min)	Reaction products	Yield (%)	B.p. (°C/Torr)	n_D^{20}
III, 2.30 (13.8)	20	3-5	$Et_3GeGeEt_3$	63.6	88-90/2	1.4940
t-BuOOBu-t, 1.01 (6.9)			Et_3GeO-t-Bu	11.3		
			t-BuOH[a]	70.6		
I, 2.82 (7.3)	20	3-5	$(Me_3SiCH_2)_3SnOSiMe_3$[b]	67.8	79-81/1.5	1.4660
$Me_3SiOOSiMe_3$, 1.30 (7.3)			$(Me_3SiCH_2)_6Sn_2$	10.0	m.p. 106-108	
			$Me_3SiOSiMe_3$[a]	86.2		
II, 2.82 (8.3)	20	3-5	$(Me_3SiCH_2)_3GeOSiMe_3$[c]	80.0	72-73/1.5	1.4580
$Me_3SiOOSiMe_3$, 1.48 (8.3)			$(Me_3SiCH_2)_6Ge_2$	9.4	m.p. 132-134	
			$Me_3SiOSiMe_3$[a]	83.1		
III, 2.40 (14.4)	20	3-5	$Et_3GeGeEt_3$	73.0	74-76/1	1.4920
$Me_3SiOOSiMe_3$, 1.28 (7.2)			$Me_3SiOSiMe_3$[a]	81.1		

[a] Isolated after hydrolysis of t-BuOLi and Me_3SiOLi. [b] Found: C, 38.58: H, 8.90: Si, 23.95: Sn, 25.30. $C_{15}H_{42}OSi_3Sn$ calcd.: C, 38.37: H, 9.01: Si, 23.93: Sn, 25.28%. [c] Found: C, 42.80: H, 10.23: Ge, 17.21: Si, 26.44. $C_{15}H_{42}GeOSi_3$ calcd.: C, 42.55: H, 10.00: Ge, 17.24: Si, 26.53.

Reaction of compound I with trimethyl(t-butylperoxy)silane

A solution of 2.88 g (7.4 mmol) of I in 20 ml of THF was added to a solution of 1.21 g (7.5 mmol) of Me_3SiOO-t-Bu in 4 ml of THF. The specific colour of the stannyllithium compound disappeared after standing at 20°C for 3-5 min. The usual work-up afforded 2.48 g (73.8%) of $(Me_3SiCH_2)_3SnO$-t-Bu, b.p. 98-100°C/1 Torr, n_D^{20} 1.4702, and 0.42 g (70.0%) of hexamethyldisiloxane (GLC analysis).

Reaction of compound II with trimethyl(t-butylperoxy)silane

A solution of 2.82 g (8.3 mmol) of II in 20 ml of THF was added to a solution of 1.34 g (8.3 mmol) of Me_3SiOO-t-Bu in 3 ml of THF. Reaction was complete in 3-5 min at 20°C, after which 166 ml (89.7%) of isobutylene had evolved (GLC). The reaction mixture on usual work-up gave 2.10 g (76.0%) of $(Me_3SiCH_2)_3GeH$, b.p. 78-80°C/1 Torr, n_D^{20} 1.4610. The residue was treated with a solution of trimethylchlorosilane (0.90 g, 8.3 mmol) in 2 ml of hexane and left overnight at room temperature. Fractionation afforded 1.22 g (83.6%) of bis(trimethylsilyl) peroxide, b.p. 36°C/30 Torr, n_D^{20} 1.3975 (lit. [16] b.p. 36°C/30 Torr n_D^{20} 1.3970). This peroxide was also identified by GLC and IR. In addition, 0.32 g (94.1%) of LiCl was obtained.

Reaction of I with triphenyl(t-butylperoxy)germane

A solution of 2.91 g (7.5 mmol) of I in 20 ml of THF was added to 2.94 g (7.5 mmol) of Ph_3GeOO-t-Bu in 4 ml of THF. At 20°C the reaction was complete after 3-5 min. The reaction mixture was worked up as usual to give 2.56 g (77.8%) of $(Me_3SiCH_2)_3SnO$-t-Bu, b.p. 99-102°C/1 Torr, n_D^{20} 1.4708 and 1.84 g (73.0%) of triphenylgermanol, m.p. 128-130°C (lit. [20] m.p. 127-131°C).

Reaction of II with triphenyl(t-butylperoxy)germane

To a solution of 3.43 g (8.7 mmol) of Ph_3GeOO-t-Bu in 4 ml of THF was added a solution of 2.98 g (8.7 mmol) of II in 20 ml of THF at room temperature. The mixture was discoloured after 3-5 min. After replacing THF with hexane the usual work-up afforded 3.90 g (68.4%) of $(Me_3SiCH_2)_3GeOGePh_3$, m.p. 119-121°C (three times from hexane at −70°C). (Found: C, 55.09; H, 7.53; Ge, 22.23; Si, 12.90. $C_{30}H_{48}Ge_2OSi_3$ calcd.: C, 55.08; H, 7.40; Ge, 22.19; Si, 12.88%.) GLC analysis of the hydrolysis products showed the presence of t-butyl alcohol (0.48 g, 75.0%).

Reaction of compound I with triphenyl(trimethylsilylperoxy)germane

A solution of 2.40 g (6.2 mmol) of I in 20 ml of THF was added to 2.54 g (6.2 mmol) of $Ph_3GeOOSiMe_3$ in 4 ml of THF. After 3-5 min at ca. 20°C the mixture was completely discoloured. 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 give 1.92 g (67.7%) of tris(trimethylsilylmethyl)phenylstannane, m.p. 104-106°C. (Found: C, 47.46; H, 8.08; Si, 17.98; Sn, 25.34. $C_{18}H_{38}Si_3Sn$ calcd.: C, 47.26; H, 8.37; Si, 18.42; Sn, 25.95%.) Hydrolysis of the residue gave 0.92 g (61.3%) of diphenylgermanium oxide, m.p. 218-223°C (in agreement with ref. 21), and 0.42 g (84.0%) of hexamethyldisiloxane (GLC analysis).

Reaction of II with triphenyl(trimethylsilylperoxy)germane

Following the above procedure, 3.56 g (8.7 mmol) of $Ph_3GeOOSiMe_3$ in 5 ml of THF on treatment with a solution of 2.96 g (8.7 mmol) of II afforded 4.30 g (75.7%) of $(Me_3SiCH_2)_3GeOGePh_3$, m.p. 118-120°C. Mixed melting with an authentic sample of $(Me_3SiCH_2)_3GeOGePh_3$ gave no depression in the melting point. GLC analysis of the hydrolysis products showed the presence of hexamethyldisiloxane (0.58 g, 82.9%).

Reaction of I with bis(triphenylgermyl) peroxide

A solution of 2.40 g (6.2 mmol) of I in 16 ml of THF was gradually added to 4.00 g (6.2 mmol) of $Ph_3GeOOGePh_3$ in 5 ml of THF. The mixture was discoloured in 3-5 min at room temperature.

After replacing THF with hexane the usual work-up afforded 3.36 g (77.4%) of $(Me_3SiCH_2)_3SnOGePh_3$, m.p. 105-107°C (three times from hexane). (Found: C, 52.20; H, 6.90; Ge, 9.87; Si, 11.70; Sn, 16.69. $C_{30}H_{48}GeOSi_3Sn$ calcd.: C, 51.46; H, 6.91; Ge, 10.37; Si, 12.03; Sn, 16.95%.) Hydrolysis of the residue gave 1.48 g (74.0%) of triphenylgermanol, m.p. 129-131°C (mixed m.p.).

Reaction of I with $(Me_3SiCH_2)_3SnOSiMe_3$

A solution of 2.90 g (7.4 mmol) of I in 20 ml of THF was added to a solution of 3.52 g (7.4 mmol) of $(Me_3SiCH_2)_3SnOSiMe_3$ in 10 ml of THF. The mixture was heated for 12 h at 75°C. THF was replaced with hexane in the usual manner and the reaction mixture was then hydrolyzed with oxygen-free water. The organic layer was separated, dried over $CaCl_2$ and the volatiles were removed by recondensation in vacuo. Fractionation of the residue gave 3.26 g (57.0%) of $(Me_3SiCH_2)_3SnH$, b.p. 80-82°C/1 Torr, n_D^{20} 1.4752 (lit. [10] b.p. 81-83°C/1 Torr, n_D^{20} 1.4750) [both unreacted $(Me_3SiCH_2)_3SnLi$ and $(Me_3SiCH_2)_3SnOSiMe_3$ gave on hydrolysis $(Me_3SiCH_2)_3SnH$] and 2.04 g (35.8%) of hexakis(trimethylsilylmethyl)distannane, b.p. 155-157°C/1 Torr, m.p. 108-110°C (in agreement with ref. 10). GLC analysis of the volatiles revealed the presence of 0.54 g (88.5%) of hexamethyldisiloxane.

Reaction of II with $(Me_3SiCH_2)_3GeOSiMe_3$

A solution of 2.66 g (7.8 mmol) of II in 20 ml of THF was added to a solution of 3.30 g (7.8 mmol) of $(Me_3SiCH_2)_3GeOSiMe_3$ in 10 ml of THF. The mixture was heated for 12 h at 75°C. THF was replaced with hexane and the reaction mixture hydrolyzed with oxygen-free water. The usual work-up gave 3.40 g (65.0%) of tris(trimethylsilylmethyl)germane, b.p. 79-81°C/1 Torr, n_D^{20} 1.4615 [formed in the hydrolysis reaction of both unreacted $(Me_3SiCH_2)_3GeLi$ and $(Me_3SiCH_2)_3GeOSiMe_3$] and 1.56 g (30.0%) of hexakis(trimethylsilylmethyl)digermane, m.p. 132-134°C. (Found: C, 43.28; H, 9.93; Ge, 21.51; Si, 24.93. $C_{24}H_{66}Ge_2Si_6$ calcd.: C, 43.12; H, 9.95; Ge, 21.72; Si, 25.21%.) GLC analysis of the volatiles showed the presence of hexamethyldisiloxane (0.53 g, 84.1%).

Reaction of I with benzoyl peroxide

A solution of 3.21 g (8.3 mmol) of I in 20 ml of THF was added to a solution of 1.00 g (4.1 mmol) of benzoyl peroxide in 5 ml of THF. The reaction was complete at room temperature after 3-5 min. THF was replaced with hexane as usual.

Distillation of the organic layer afforded 2.22 g (70.7%) of hexakis(trimethylsilylmethyl)distannane, b.p. 155-156°C/1 Torr, m.p. 106-108°C (mixed m.p.). After treatment of the residue with dilute hydrochloric acid, 0.71 g (68.6%) of benzoic acid was obtained, m.p. 119-121°C (mixed m.p.).

Reaction of I with tris(trimethylsilylmethyl)tin benzoate

To a solution of 2.60 g (5.2 mmol) of $(Me_3SiCH_2)_3SnOCOPh$ in 4 ml of THF was added a solution of 2.02 g (5.2 mmol) of I in 20 ml of THF. The reaction was completed after 3-5 min at 20°C. Work-up in the usual fashion afforded 2.96 g (75.1%) of hexakis(trimethylsilylmethyl)distannane, b.p. 156-157°C/1 Torr, m.p. 107-108°C (mixed m.p.). After acid hydrolysis of the residue 0.48 (77.4%) of benzoic acid was obtained, m.p. 118-120°C (mixed m.p.).

Reaction of I with dicyclohexyl peroxydicarbonate

A solution of 3.96 g (10.2 mmol) of I in 20 ml of THF was added to a solution of 1.46 g (5.1 mmol) of $(C_6H_{11}OCOO)_2$ in 6 ml of THF. After standing at 20°C for 3-5 min the colour disappeared and 110 ml (48%) of CO_2 was evolved. THF was replaced with hexane as usual and then the mixture was centrifuged. 2.66 g (68.6%) of hexakis(trimethylsilylmethyl)distannane was obtained from the hexane solution, b.p. 156-158°C/1 Torr, m.p. 107-109°C. The residue was hydrolyzed to give 110 ml (48%) of CO_2 and 0.72 g (71.0%) of cyclohexanol (GLC analysis).

Reaction of I with t-butyl perbenzoate

A solution of 2.76 g (7.1 mmol) of I in 20 ml of THF was added to 1.38 g (7.1 mmol) of PhC(O)OO-t-Bu in 4 ml of THF. After 30 min at 20°C the mixture was completely discoloured. Fractionation of the organic layer in vacuo afforded 1.40 g (43.2%) of $(Me_3SiCH_2)_3SnO$-t-Bu, b.p. 99-101°C/1 Torr, n_D^{20} 1.4710 and 1.32 g (48.9%) of distannane, b.p. 156-158°C/1 Torr, m.p. 108-110°C (mixed m.p.). Hydrolysis of the residue gave 0.54 g (84.4%) of benzoic acid, m.p. 118-120°C and 0.10 g (76.9%) of t-butyl alcohol (GLC analysis).

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