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THE PREPARATION AND PROPERTIES OF α-TIN KETONES

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SUMMARY

Acyltin compounds were prepared by the addition of triphenyltinlithium to acid chlorides at −70°. Their chemical properties resembled closely those of other Group IV acyl compounds.

The $n \rightarrow \pi^*$ carbonyl group absorption was similar to that of the silicon and germanium analogs.

The origin of the observed bathochromic shifts is discussed.

INTRODUCTION

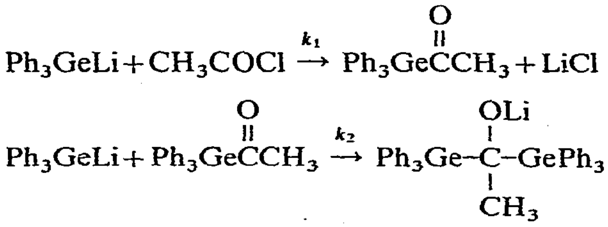
In the past ten years many ketones with the general formula R_3MCOR', M = C, Si or Ge, have been reported[1-8]. These ketones have aroused considerable interest due to the large bathochromic shifts in the position of the $n \rightarrow \pi^*$ transition of the non-bonding electrons of the carbonyl oxygen in the germanium and silicon containing ketones relative to that of their carbon analogs.

West has rationalized these shifts on the basis of d_π-p_π bonding involving overlap of the *d*-orbitals of the metal with the π- and π*-orbitals of the carbonyl group[9]. The energy of the π- and π*-orbitals is lowered while the energy of the *n*-orbital is largely unaffected. Therefore the $n \rightarrow \pi^*$ transition occurs at lower energy.

Agolini, Klemenko, Csizmadia and Yates on the base of semi-empirical LCAO-MO calculations have predicted the magnitude of the observed shifts without invoking *d*-orbital participation and have shown that the effect of including *d*-orbitals in the calculations is negligible[10]. They ascribe the observed shifts primarily to the inductive effect of the metal which results in a higher energy of the *n*-orbital without changing the energy of the π*-orbital. The result is a decrease in the energy of the $n \rightarrow \pi^*$ transition.

Since only carbon, silicon and germanium ketones had been studied it seemed of interest to prepare α-tin ketones in an effort to gain additional information on the effects involved.

A number of synthetic routes have been used to prepare α-metal ketones[1,4,8]. The easiest involves the addition of the readily available triphenylmetallithium to an acid chloride. The ketone thus formed can add a second mole of organolithium to give an alcoholate. Since k_2 is generally much larger than k_1 the yields of ketones are generally low. However, in cases where k_2 is small ,such as with (*p*-methoxybenzoyl)-triphenylgermane, excellent yields of ketone have been reported by this route[4].



$$Ph_3GeLi+CH_3COCl \xrightarrow{k_1} Ph_3Ge\overset{O}{\overset{\|}{C}}CH_3+LiCl$$

$$Ph_3GeLi+Ph_3Ge\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{k_2} Ph_3Ge\text{–}\underset{CH_3}{\underset{|}{\overset{OLi}{\overset{|}{C}}}}\text{–}GePh_3$$

As it has been reported that triphenyltinlithium fails to add to carbon dioxide or ketones[11] it might be predicted that k_2 would be small for an α-tin ketone.

In previous reports of the reaction of triphenyltinlithium with acid chlorides[12,13], no carbonyl containing products were isolated. However, it was reported that when triphenyltinsodium was added to benzoyl chloride that the resultant solution was yellow[13]. An unsuccessful attempt was made to isolate the yellow compound, and no structure for it was suggested.

RESULTS AND DISCUSSION

The α-tin ketones were readily prepared by the addition of triphenyltinlithium to acid chlorides at −70°. Thus acetyl chloride gave acetyltriphenyltin, (I)[6], benzoyl chloride gave benzoyltriphenyltin, (II), and pivalyl choride gave pivalyltriphenyltin, (III).

The germanium analog of (I), acetyltriphenylgermane, was prepared in low yield by the addition of triphenylgermyllithium to acetyl chloride at −80°. It was formed in better yield by the oxidation of 1-(triphenylgermyl)ethanol prepared by the addition of triphenylgermyllithium to acetaldehyde[6].

The germanium and silicon analogs of (III) were prepared in good yields by the addition of the respective organolithium compounds to pivalyl chloride. Presumably the bulky tert-butyl group slows down the rate of reaction of the ketone relative to that for the acid chloride.

The other silyl and germyl ketones have been described previously[1,7].

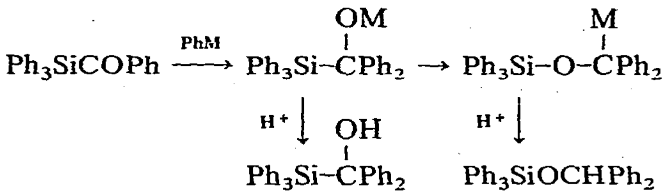
Reactions

The smooth reduction of acylsilanes to the corresponding carbinol by lithium aluminium hydride is well known[1,14,15]. Similarly acetyltriphenylgermane and acetyltriphenyltin were readily reduced by lithium aluminium hydride.

$$Ph_3GeCOCH_3 \xrightarrow[2.\ H^+]{1.\ LiAlH_4} Ph_3GeCHOHCH_3$$

$$Ph_3SnCOCH_3 \xrightarrow[2.\ H^+]{1.\ LiAlH_4} Ph_3SnCHOHCH_3$$

The addition of phenylmagnesium bromide or phenyllithium to benzoyltriphenylsilane followed a complex pattern. If the Grignard reagent was added rapidly and the reaction mixture worked up immediately the expected alcohol was isolated. When the lithium reagent was used the rearrangement product was isolated[16]. If the reaction was not worked up rapidly complex mixtures of products were isolated[16].

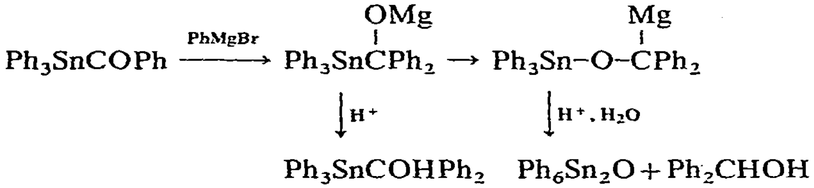


$$\begin{array}{lcc} Ph_3SiCOPh \xrightarrow{PhM} & Ph_3Si{-}\overset{OM}{\overset{|}{C}}Ph_2 & \longrightarrow Ph_3Si{-}O{-}\overset{M}{\overset{|}{C}}Ph_2 \\ & {\scriptstyle H^+}\downarrow & {\scriptstyle H^+}\downarrow \\ & Ph_3Si{-}\overset{OH}{\overset{|}{C}}Ph_2 & Ph_3SiOCHPh_2 \end{array}$$

Similarly when phenylmagnesium bromide was added to benzoyltriphenylgermane followed by immediate work-up the expected carbinol, (triphenylgermyl)diphenylmethanol was isolated. However, when the reaction mixture was refluxed overnight a complex mixture of products was formed.

$$Ph_3GeCOPh \xrightarrow[2.\,H^+]{1.\,PhMgBr} Ph_3GeC(OH)Ph_2$$

When phenylmagnesium bromide was added to benzoyltriphenyltin the alcohol was formed in low yield. The major products were hexaphenyltin oxide and benzhydrol.



$$\begin{array}{lcc} Ph_3SnCOPh \xrightarrow{PhMgBr} & Ph_3Sn\overset{OMg}{\overset{|}{C}}Ph_2 & \longrightarrow Ph_3Sn{-}O{-}\overset{Mg}{\overset{|}{C}}Ph_2 \\ & \downarrow{\scriptstyle H^+} & \downarrow{\scriptstyle H^+,\,H_2O} \\ & Ph_3SnCOHPh_2 & Ph_6Sn_2O + Ph_2CHOH \end{array}$$

The photochemical oxidation of aliphatic acylsilanes to esters is known[17]. Thus it was found that acetyltriphenylsilane upon exposure to air and ultraviolet radiation slowly gives triphenylsilylacetate[16]. Acetyltriphenyltin was also oxidized

$$Ph_3SiCOCH_3 \xrightarrow[h\nu]{O_2} Ph_3SiOCOCH_3$$

to the corresponding acetate. Pivalyltriphenyltin followed a similar course, however, in addition to triphenyltin pivalate, hexaphenylditin oxide and pivalic anhydride were formed. The origin of the difference between the acetyl- and pivalyltin compounds may be related to the observation that the triphenyltin acetate came out of solution as it was formed while the triphenyltin pivalate was soluble.

Benzoylsilanes are relatively inert toward photochemical oxidation[16] but are readily cleaved in the presence of light and moisture[18].

$$PhCHO \xleftarrow[h\nu]{H_2O} Ph_3SiCOPh \overset{O_2}{\underset{h\nu}{\not\longrightarrow}} Ph_3SiOCOPh$$

Benzoyltriphenyltin, (II), was similarly relatively insensitive to photochemical oxidation but readily hydrolyzed in the presence of moisture and light to give benzaldehyde.

$$PhCHO \xleftarrow[h\nu]{H_2O} \underset{(II)}{Ph_3SnCOPh} \overset{O_2}{\underset{h\nu}{\not\longrightarrow}} Ph_3SnOCOPh$$

The benzoyltriphenyltin, (II), was sufficiently thermally stable to be distilled at 210°(0.1 mm). However, when heated to 125–150° for an hour in the presence of air it was converted into an infusable, light yellow solid, presumably a tin oxide. The pivalyltriphenyltin decomposed at its melting point (90–94°).

Thus, although the chemical behaviour of the acyltin compounds was not extensively investigated, the reactions studied appeared to proceed similarly to analogous reactions in silicon and germanium compounds.

Spectral results

The position of the infrared carbonyl group absorption and of the $n \rightarrow \pi^*$ transition for the compounds prepared above and for a number of model compounds is shown in Table 1.

TABLE 1

IR AND UV CARBONYL GROUP ABSORPTION OF ACYLSILICON, -GERMANIUM AND -TIN COMPOUNDS

Compound	$\nu(CO)$[a]	λ_{max}[b]	
	(cm^{-1})	($m\mu$)	eV
Ph_3CCOCH_3	1710	302	4.11
$Ph_3SiCOCH_3$	1644	376[c]	3.30
$Ph_3GeCOCH_3$	1669	365[c]	3.40
$Ph_3SnCOCH_3$	1670	375[c]	3.31
$Ph_3SiCOCMe_3$	1628	377	3.29
$Ph_3GeCOCMe_3$	1652	363	3.42
$Ph_3SnCOCMe_3$	1655	376	3.30
Ph_3CCOPh	1692	338	3.67
$Ph_3SiCOPh$	1618	424[c]	2.92
$Ph_3GeCOPh$	1628	418[c]	2.96
$Ph_3SnCOPh$	1627	435	2.85

[a] In CCl_4. [b] In heptane. [c] Most intense peak of multiplet see refs. 1 and 6.

The interpretation of these results is complicated by a lack of agreement on the values of the electronegativity of silicon, germanium and tin. The two orders of electronegativity generally reported are $C \gg Si > Ge \simeq Sn$[19] and $C \gg Ge > Si \simeq Sn$[20]. The ability of silicon, germanium and tin to accept electrons into their vacant *d*-orbitals leads to the formation of either d_σ or d_π type bonds. Studies have shown that the ease of formation of d_σ bonds, with their accompanying increase in the coordination number of the metal, decreases $Sn > Ge > Si$[21]. The formation of d_π–p_π bonds, which are not accompanied by a formal change in the coordination number of the metal, is reported to decrease $Si > Ge > Sn$ in most cases[21].

A recent X-ray diffraction study of the crystal structure of acetyltriphenylgermane[22] has shown that d_π–p_π bonding is absent and therefore it seems reasonable to assume that d_π–p_π bonding is also absent in the acyltin compounds.

Thus the observed shifts in the position of the $n \rightarrow \pi^*$ transition of the acyltin and acylgermanium compounds relative to the carbon ketones must be due primarily to the inductive effect of the metal.

The observed shift in the position of the $n \rightarrow \pi^*$ transition of the acylsilanes must also be due primarily to the inductive effect of the silicon.

However, regardless of the relative importance of other factors it should be apparent that the better the matching of energy of the *d*- and of the π^*-orbitals the more important d_π–p_π bonding will be. Since the energy of the π^* level in a benzoyl group, PhCO-, is lower than that in an acetyl group, CH_3CO-, d_π–p_π bonding should be more important in aliphatic ketones than in aromatic ones.

If we examine the ultraviolet spectra results in Table 1 it can be observed that the position of the $n \rightarrow \pi^*$ absorption of all the germanium ketones occurs at approximately 0.1 eV higher energy than the tin ketones. The $n \rightarrow \pi^*$ absorption of the two aliphatic silyl ketones occurs at 0.01 eV lower energy than the tin ketones while the benzoylsilane occurs at 0.07 eV higher energy than the benzoyltin compound.

These results are consistent with the interpretation that the primary cause of the observed shift is the inductive effect of the metal. They also indicate that at least in the case of the aliphatic silyl ketones, where the matching in energy of the 3*d*- and π^*-orbitals is best that there may be a small additional effect attributable to d_π–p_π bonding.

In conclusion it should be mentioned that Chan and Rochow[23] have recently reported a study of the $n \rightarrow \pi^*$ absorption in *N*-substituted ketimines, $R_2C{=}N{-}MR'_3$, M = C, Si, Ge or Sn. Their results are similar to those reported in this paper and in previous papers on α-metal ketones and indicate that whatever the nature of the interaction of the metal atom that it is not peculiar to the carbonyl group.

EXPERIMENTAL

General

All reactions were carried out under an atmosphere of dry nitrogen. Those involving tin compounds were performed in the dark. Melting points are uncorrected. Elemental analysis were by Galbraith Laboratories, Inc., Knoxville, Tennessee or by Mrs. D. Roberts, Department of Chemistry, University of Alberta, Edmonton. IR, UV, NMR and mass spectra were determined on Perkin–Elmer model 721, Perkin–Elmer model 202, Varian Associates model A56-60A and Metropolitan–Vickers MS-9 spectrometers, respectively.

Acetyltriphenyltin

A solution of triphenyltinlithium was prepared from 38.6 g (0.1 mole) of triphenylchlorotin and 2.75 g (0.4 g-atom) of lithium in 200 ml of THF. It was cooled to −70° and then added to 7.1 ml (0.1 mole) of acetyl chloride in 200 ml of THF similarly cooled to −70°. The resultant mixture was allowed to warm to room temperature. The volatile material was removed under reduced pressure and then pentane was added. The mixture was filtered and the filtrate was concentrated under reduced pressure to obtain 34.2 g (88%) of acetyltriphenyltin, (I), as a waxy solid.

Exposure of (I) to air and light in either solution or as a solid rapidly gave triphenyltin acetate. All attempts to purify (I) always gave products contaminated by triphenyltin acetate.

1-(*Triphenylstannyl*)*ethanol*

A solution of 4.0 g (0.01 mole) of acetyltriphenyltin in 50 ml of THF was added to 0.4 g (0.01 mole) of lithium aluminium hydride in 50 ml of THF. The mixture was stirred for 1 h and then added to wet ethyl ether followed by dilute hydrochloric acid. The ether layer was washed with water, dried with sodium sulfate and concentrated under reduced pressure. The resultant pasty solid was recrystallized from pentane to obtain 2.9 g (72%) of 1-(triphenylstannyl)ethanol, m.p. 93–95°. (Found: C, 60.5; H, 5.08. $C_{20}H_{20}OSn$ calcd.: C, 60.8; H, 5.10%.)

The NMR spectrum (CCl_4) consisted of a multiplet from τ 2.3–2.9, a quartet τ 5.42 (J 7.5 cps) a doublet τ 8.38 (J 7.5 cps) and a singlet τ 8.58 with relative areas of 13:1:3:1, respectively.

On standing in air (IV) decomposed. Seyferth has previously noted instability of an α-tin carbinol[24].

Pivalyltriphenyltin

A solution of triphenyltinlithium was prepared from 30 g (0.08 mole) of triphenylchlorotin and 3 g (0.4 g-atom) of lithium in 100 ml of THF. It was cooled to −70° and then added to 9.8 g (0.082 mole) of pivalyl chloride in 100 ml of THF cooled to −70°. The mixture was allowed to warm to room temperature and then was stirred for 3 h. The solvent was removed under reduced pressure and the residue extracted with mixtures of benzene and heptane. Recrystallization from heptane gave 22 g (63%) of pivalyltriphenyltin, m.p. 90–94° (decompn.). (Found: C, 62.5; H, 5.43. $C_{23}H_{24}OSn$ calcd.: C, 63.5; H, 5.56%.)

The NMR spectrum (CCl_4) consisted of a multiplet from τ 2.4 to 2.9 and a singlet at τ 8.96 with relative areas of approximately 2:1.

When a carbon tetrachloride solution of the ketone was exposed to air and light hexaphenylditin oxide rapidly began to precipitate from the solution. On examination of the IR and NMR spectra of the resultant carbon tetrachloride solution indicated that it contained a mixture of pivalic anhydride and triphenyltin pivalate.

Triphenyltin pivalate

Silver pivalate was prepared by the addition of an excess of a saturated solution of silver nitrate to a concentrated solution of ammonium pivalate. The resultant precipitate was washed several times with water, dried and used without further purification.

A mixture of 2.1 g (0.01 mole) of silver pivalate and 3.9 g (0.01 mole) of triphenylchlorotin in 30 ml of benzene was stirred for 48 h. The solid was filtered off and the filtrate evaporated under reduced pressure. The resultant solid was recrystallized many times from a variety of solvent mixtures to obtain 2.6 g (57%) of triphenyltin pivalate m.p. 112–115°. (Found: C, 60.8; H, 5.41. $C_{23}H_{24}O_2Sn$ calcd.: C, 61.2; H, 5.36%.)

The NMR spectrum (CCl_4) consisted of a multiplet from τ 2.25 to 2.9 and a singlet at τ 8.83 with relative areas of 5 to 3, respectively.

Benzoyltriphenyltin

A solution of triphenyltinlithium was prepared from 60 g (0.16 mole) of triphenylchlorotin, and 6 g (0.87 g-atom) of lithium in 300 ml of THF. It was cooled to −70° and then added to 20 ml (0.17 mole) of benzoyl chloride in 50 ml of THF cooled to −70°. The mixture was allowed to warm to room temperature and then worked up as above.

The resultant yellow oil was distilled to obtain 24 g (33 %) of benzoyltriphenyltin, (II), b.p. 210°(0.1 mm). Crystallization gave a solid, m.p. 214–217°. (Found: C, 66.0; H, 4.53. $C_{25}H_{20}OSn$ calcd.: C, 66.0; H, 4.43 %.)

The mass spectrum was in agreement with the proposed structure showing in addition to a weak molecular ion *m/e* 456 (0.7 %) $(C_6H_5)_3SnCOC_6H_5^{+}$; strong fragment patterns at *m/e* 77 (28 %) $C_6H_5^{+}$; 105 (22 %) $C_6H_5CO^{+}$; 120 (45 %) Sn^{+}; 154 (21 %) $(C_6H_5)_2^{+}$; 197 (54 %) $C_6H_5Sn^{+}$; 274 (23 %) $(C_6H_5)_2Sn^{+}$; 309 (31 %) $SnC_{15}H_9^{+}$; 351 (100 %) $(C_6H_5)_3Sn^{+}$.

Samples of (II) in wet ether, when exposed to light, rapidly decolorized and developed a strong odor of benzaldehyde. The benzaldehyde was isolated as its 2,4-dinitrophenylhydrazone, m.p. 235–237°. When oxygen was bubbled through a solution of (II) irradiated with a low pressure UV source no triphenyltin benzoate was isolated. The benzoic acid isolated probably came from the oxidation of the benzaldehyde formed.

Reaction of benzoyltriphenylgermane with phenylmagnesium bromide

The Grignard reagent prepared from 1.0 g (0.0064 mole) of bromobenzene and 0.17 g (0.007 g-atom) of magnesium in 15 ml of ether was added to 2.5 g (0.0061 mole) of benzoyltriphenylgermane in 10 ml of ether at 0°. The mixture was stirred for 5 min and was then added to a saturated solution of ammonium chloride. The ether layer was separated, washed with water, dried with sodium sulfate and concentrated under reduced pressure. The resultant pasty solid was recrystallized from heptane/benzene to obtain 1.7 g (57 %) of (triphenylgermyl)diphenylmethanol, m.p. 152–155° identical in all respects to an authentic sample[1].

When a similar reaction mixture was refluxed for 12 h and then worked up as above a complex mixture of products was formed. No (triphenylgermyl)diphenylmethanol was detected by TLC.

Reaction of benzoyltriphenyltin with phenylmagnesium bromide

The Grignard reagent prepared from 1.0 g (0.0064 mole) of bromobenzene and 0.17 g (0.007 g-atom) of magnesium in 20 ml of ether was added to 2.2 g (0.0048 mole) of benzoyltriphenyltin in 10 ml of ether at 0°. The mixture was stirred for 5 min and was then worked up as above. Recrystallization of the residue from mixtures of heptane and chloroform gave 0.3 g (16 %) of tetraphenyltin, m.p. 227° and 0.22 g (9 %) of (triphenylstannyl)diphenylmethanol m.p. 256–259°. (Found: C, 69.3; H, 5.03. $C_{31}H_{26}OSn$ calcd.: C, 69.8; H, 4.92 %.) In addition 0.8 g (47 %) of hexaphenylditin oxide, m.p. 120°, and 0.38 g (43 %) of benzhydrol m.p. 67–68°, were isolated by chromatography on silica gel eluted with heptane and benzene.

1-(*Triphenylgermyl*)*ethanol*

(*a*) A solution of triphenylgermyllithium was prepared from 7.5 g (0.022 mole) of triphenylbromogermane and 0.5 g (0.075 g-atom) of lithium in 25 ml of THF. It was cooled to −70° and then added to a solution of 1.2 ml (0.021 mole) of acetaldehyde in 20 ml of THF at −70°. The reaction mixture was allowed to warm to room temperature and then worked up with ethyl ether and dilute hydrochloric acid. Recrystallization of the oil obtained by evaporation of the ether layer, from ethanol gave 4.1 g (59%) of 1-(triphenylgermyl)ethanol, m.p. 107–108°. (Found: C, 69.1; H, 5.79. $C_{20}H_{20}GeO$ calcd.: C, 68.8; H, 5.78%.)

The NMR spectrum (CCl_4) consisted of a multiplet from τ 2.4–2.8, a quartet τ 5.55 (J 7.5 cps), a doublet τ 8.52 (J 7.5 cps) and a singlet at τ 8.48 with approximate areas of 17 : 1 : 3 : 1, respectively.

(*b*) A solution of 40 mg (0.0001 mole) of acetyltriphenylgermane in 10 ml of THF was added to 4 mg (0.0001 mole) of lithium aluminium hydride in 10 ml of THF. After stirring for 1 h the mixture was worked up with wet ether and dilute hydrochloric acid. The resultant solid when recrystallized from ethanol gave 28 mg (70%) of 1-(triphenylgermyl)ethanol, m.p. 105–108°, identified by comparison with a sample of the authentic carbinol described above.

Acetyltriphenylgermane

(*a*) To a solution of 3.5 g (0.01 mole) of 1-triphenylgermylethanol in 200 ml of acetone 6 ml (0.01 mole) of a 1.7 *M* solution of chromium trioxide in 2.5 *M* sulfuric acid was added. After stirring for 5 min the green solution was added to ethyl ether and water. The ether layer was washed with water, dried with sodium sulfate and concentrated under reduced pressure. The resultant oil was recrystallized from ethanol to obtain 0.8 g (23%) of acetyltriphenylgermane, m.p. 121.5–123°. (Found: C, 69.3; H, 5.39. $C_{20}H_{18}GeO$ calcd.: C, 69.2; H, 5.23%.) In addition 1.9 g (61%) of hexaphenyldigermoxane, m.p. 180–182° was isolated.

(*b*) A solution of triphenylgermyllithium prepared from 8.5 g (0.022 mole) of triphenylbromogermane and 0.5 g (0.075 g-atom) of lithium in 25 ml of THF was cooled to −80°. It was then rapidly added to 1.8 ml (0.026 mole) of acetyl chloride in 20 ml of THF also cooled to −80°. After stirring for 2 h at −80° the reaction mixture was allowed to warm to room temperature and then worked up in the usual manner with ethyl ether and dilute hydrochloric acid. Recrystallization of the product from ethanol gave 4.4 g (61%), of 1,1-bis(triphenylgermyl)ethanol, m.p. 195–200°[4].

Chromatography of the mother liquors on silica gel eluted with heptane gave 0.09 g (1.2%) of acetyltriphenylgermane m.p. 119–123°.

Pivalyltriphenylsilane

A solution of triphenylsilyllithium was prepared from 9 g (0.03 mole) of triphenylchlorosilane and 0.9 g (0.13 g-atom) of lithium in 60 ml of THF. It was cooled to −70° and then it was added to 10.8 g (0.09 mole) of pivalyl chloride in 100 ml of THF at −70°. The reaction mixture was allowed to warm to room temperature and then stirred for 4 h. Work-up with ethyl ether and dilute hydrochloric acid followed by recrystallization from ethanol gave 7.2 g (70%) of pivalyltriphenylsilane, m.p. 103–106°. (Found: C, 80.0; H, 7.05. $C_{23}H_{24}OSi$ calcd.: C, 80.2; H, 7.02%.)

Pivalyltriphenylgermane

Addition of a solution of triphenylgermyllithium prepared from 3.8 g (0.01 mole) of triphenylbromogermane and 0.4 g (0.057 g-atom) of lithium in 20 ml of THF to 3.6 g (0.03 mole) of pivalyl chloride in the same manner as the previous experiment gave 2.4 g (62%) of pivalyltriphenylgermane, m.p. 103–105°. (Found: C, 70.9; H, 6.27. $C_{23}H_{24}GeO$ calcd.: C, 71.0; H, 6.27%.)

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