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REACTIONS OF TRIETHYLGERMYLLITHIUM WITH *N*,*N*-DIALKYLATED CARBOXAMIDES

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Summary

The reactions of triethylgermyllithium with *N*,*N*-dialkylated carboxamides have been investigated. *N*,*N*-Dimethylacetamide, *N*,*N*-dimethylpivalamide, *N*,*N*-diethyltrifluoroacetamide and *N*,*N*-diethylbenzamide act on triethylgermyllithium, which is made from bis(triethylgermyl)mercury and lithium in hexane, to release the corresponding acyltriethylgermanes as the principal product. The regioselectivity of the present reactions was found to depend markedly on the reaction conditions and the nature of the acyl fragment of amides. Thus, triethylgermyllithium reacts with *N*,*N*-dimethylacetamide as metallating agent to give lithium *N*,*N*-dimethylacetamide, if the reaction is carried out in tetrahydrofuran solution. Mechanistic interpretations of these results are discussed.

Introduction

In 1966 we reported the first synthesis of triethylsilyllithium by treatment of bis(triethylsilyl)mercury with metallic lithium [1–3]. Analogous reactions with other silylmercurials have been investigated [4–12]. The same method has been used to prepare triethylgermylmetal compounds, Et_3GeM, where M = Na, K, Rb, and Cs [13]. An important advantage of this general method is that the trialkylsilyl- and trialkylgermyl-alkali metal compounds can be obtained not only in polar solvents such as diethyl ether, tetrahydrofuran (THF) and hexamethylphosphoramide (HMPA) but also in hexane, which has no specific solvating power. The chemistry of silyl- and germylmetallic reagents represents an ever-expanding topic of investigation that has received a great deal of attention in recent years [14]. In particular, the ^{1}H NMR frequencies for Et_3GeM, where M = Li, Na, K, Cs, in benzene become more separated as the size of alkali metal increases. Separation of the ion pair could be accomplished by addition of HMPA to the benzene solution [15]. We have also observed that triethylgermylpotassium acted as a one-electron transfer reagent in the

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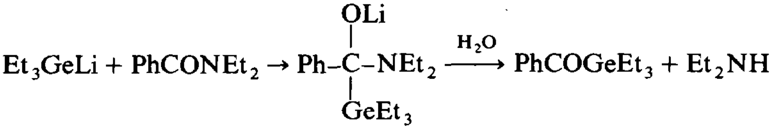
presence of HMPA to produce radical anions from fluorene, naphthalene, biphenyl and benzophenone by ESR spectrometry [16]. Later, one-electron transfer processes were observed during the reactions of triethylgermyl anions with aryl halides and also with naphthalene [17].

Of interest is the finding [18] that the unsolvated triethylsilyllithium readily reacts with HMPA, dimethoxyethane (DME) and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) in hexane solution to form 1 : 1 adducts which we have isolated as colorless pyrophoric solids. Later work [12] showed that unsolvated hexameric trimethylsilyllithium $(Me_3SiLi)_6$ reacted with TMEDA in cyclopentane to yield the crystalline complex $(Me_3SiLi)_2 \cdot (TMEDA)_3$. Moreover, the latter complex reacts with hydrocarbons such as benzene and toluene to afford phenyltrimethylsilane and benzyltrimethylsilane, respectively, along with lithium hydride [12]. This reaction is quite similar to that reported several years ago between unsolvated triethylsilylpotassium and benzene, which gave phenyltriethylsilane and potassium hydride in very high yield [19].

In this paper, we report a comprehensive study of the reaction of triethylgermyllithium with a variety of *N,N*-dialkylamides. A preliminary report of this work has already appeared [20].

Results and discussion

The reaction between equimolar amounts of triethylgermyllithium and *N,N*-diethylbenzamide in hexane gives, after hydrolysis, the expected benzoyltriethylgermane and diethylamine in high yields



$$Et_3GeLi + PhCONEt_2 \rightarrow Ph\text{-}\underset{GeEt_3}{\overset{OLi}{C}}\text{-}NEt_2 \xrightarrow{H_2O} PhCOGeEt_3 + Et_2NH$$

An analogous route is postulated for the reactions of *N,N*-dialkylcarboxamides with organolithium reagents [21,22]. We have found that under comparable conditions the reaction of *N,N*-diethylbenzamide with triethylsilyllithium proceeds in a rather unusual fashion giving triethylsilanol (39%) together with smaller quantities of $Et_3Si(Ph)CHNEt_2$ (I) (23%) and 1,2-bis(diethylamino)-1,2-diphenylethylene (II) (14%). The latter is present as a mixture of *Z* and *E* isomers (2 : 1). No formation of benzoyltriethylsilane was observed.

Several years ago, Gilman and Gaj reported that keeping a solution of triphenylsilyllithium and *N,N*-dimethylbenzamide in THF produced, after hydrolysis, triphenylsilanol and $Ph_3Si(Ph)CHNMe_2$ [23]. The mechanism of this reductive triphenylsilylation possibly involves three consecutive steps: (i) normal addition of Ph_3SiLi to the amide carbonyl, (ii) migration of the silyl group from carbon to negatively charged oxygen * and (iii) cleavage of the resulting intermediate by a second molecule of the silyllithium reagent [24,25]. This mechanism may also operate in our case. Consequently, the product I seems to result from the interaction of inter-

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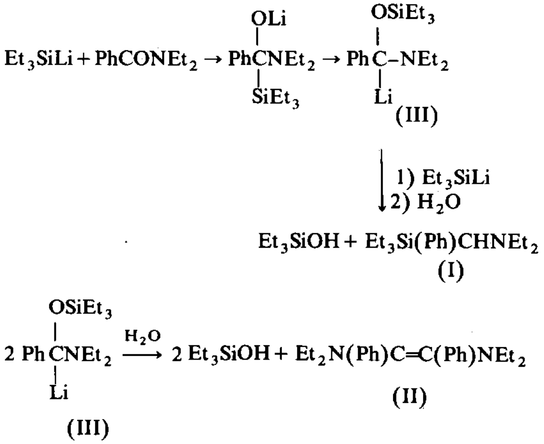
* This type of R_3Si group migration from carbon to oxygen has been well established in Brook's extensive studies [26].

mediate III with triethylsilyllithium. The mechanism of formation of the product II is uncertain (Scheme 1).

SCHEME 1



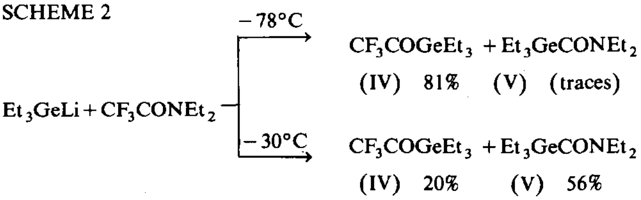
$$Et_3SiLi + PhCONEt_2 \rightarrow Ph\underset{SiEt_3}{\overset{OLi}{C}}NEt_2 \rightarrow Ph\underset{Li}{\overset{OSiEt_3}{C}}\text{-}NEt_2 \ (III)$$

$$\xrightarrow{1)\ Et_3SiLi\ \ 2)\ H_2O} Et_3SiOH + Et_3Si(Ph)CHNEt_2 \ (I)$$

$$2\ Ph\underset{Li}{\overset{OSiEt_3}{C}}NEt_2 \ (III) \xrightarrow{H_2O} 2\ Et_3SiOH + Et_2N(Ph)C{=}C(Ph)NEt_2 \ (II)$$

Treatment of *N*,*N*-diethyltrifluoroacetamide with 1 equivalent of Et_3GeLi in hexane at −78°C (followed by work up with water) afforded trifluoroacetyl-(triethyl)germane (IV) as main product (81%), and only traces of product V were detected. However, the course of this reaction is highly temperature dependent. When the same reaction was repeated at −30°C, the amide V was isolated in 58% yield (Scheme 2). It is of interest that the *N*,*N*-diethylamide of triethylgermanecarboxylic acid (V) is unknown.

SCHEME 2



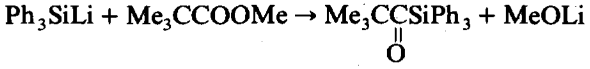
$$Et_3GeLi + CF_3CONEt_2 \xrightarrow{-78°C} CF_3COGeEt_3 \ (IV)\ 81\% + Et_3GeCONEt_2 \ (V)\ (traces)$$

$$Et_3GeLi + CF_3CONEt_2 \xrightarrow{-30°C} CF_3COGeEt_3 \ (IV)\ 20\% + Et_3GeCONEt_2 \ (V)\ 56\%$$

It is well-recognized that organolithium compounds also react regioselectively with fluorinated *N*,*N*-dialkylamides at −78°C to give the corresponding ketones in high yield [27].

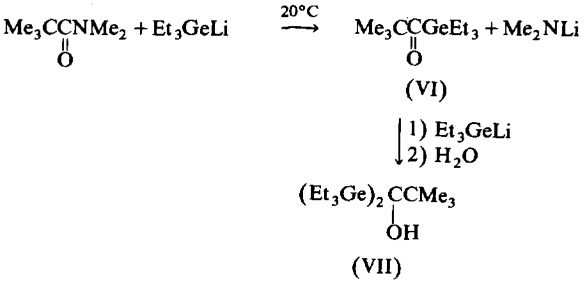
The reaction of equimolar quantities of *N*,*N*-dimethylpivalamide and triethylgermyllithium in hexane at −78 or −20°C proceeds very slowly. Similar treatment of *N*,*N*-dimethylpivalamide at room temperature, followed by hydrolysis gives mainly pivaloyltriethylgermane (VI) (30%) together with a 24% yield of 1,1-bis(triethylgermyl)-2,2-dimethylpropan-1-ol (VII). The low yield of the ketone VI and the presence of the alcohol VII can be explained reasonably by Scheme 3.

The initial step leading up to the formation of VI finds direct analogy in the work of Peddle [28] on the reaction of triphenylsilyllithium with methyl pivalate:



$$Ph_3SiLi + Me_3CCOOMe \rightarrow Me_3C\underset{\|\atop O}{C}SiPh_3 + MeOLi$$

SCHEME 3



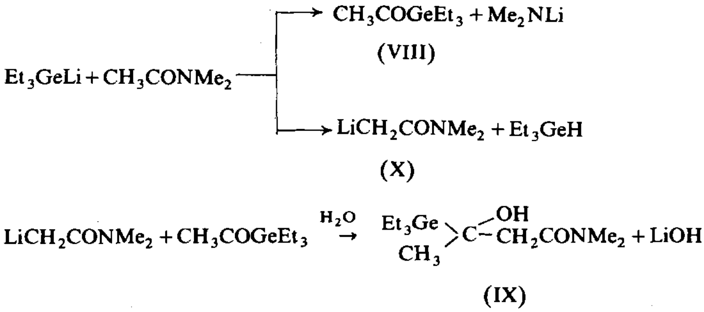
$$\mathrm{Me_3C\underset{\underset{O}{\|}}{C}NMe_2 + Et_3GeLi \xrightarrow{20°C} Me_3C\underset{\underset{O}{\|}}{C}GeEt_3 + Me_2NLi}\ \mathrm{(VI)}$$

$$\mathrm{(VI)} \xrightarrow{\mathrm{1)\ Et_3GeLi;\ 2)\ H_2O}} \mathrm{(Et_3Ge)_2\underset{\underset{OH}{|}}{C}CMe_3}\ \mathrm{(VII)}$$

The product VI thus formed adds a second molecule of germyllithium to give, after hydrolysis, the alcohol VII. The analog of VI, pivaloyltriphenylgermane, was prepared in good yield by addition of triphenylgermyllithium to pivaloyl chloride at −70°C [29a].

Treatment of triethylgermyllithium with one equivalent of *N*,*N*-dimethylacetamide in hexane at room temperature gives the expected acylgermane (VIII) and product IX (see Scheme 4). The reaction probably proceeds along two concomitant paths: one is the formation of VIII and the other is deprotonation of the starting acetamide by Et_3GeLi to produce lithium *N*,*N*-dimethylacetamide (X). The latter is able to add to VIII to give the *β*-hydroxy amide IX.

SCHEME 4



$$\mathrm{Et_3GeLi + CH_3CONMe_2 \longrightarrow CH_3COGeEt_3 + Me_2NLi}\ \mathrm{(VIII)}$$

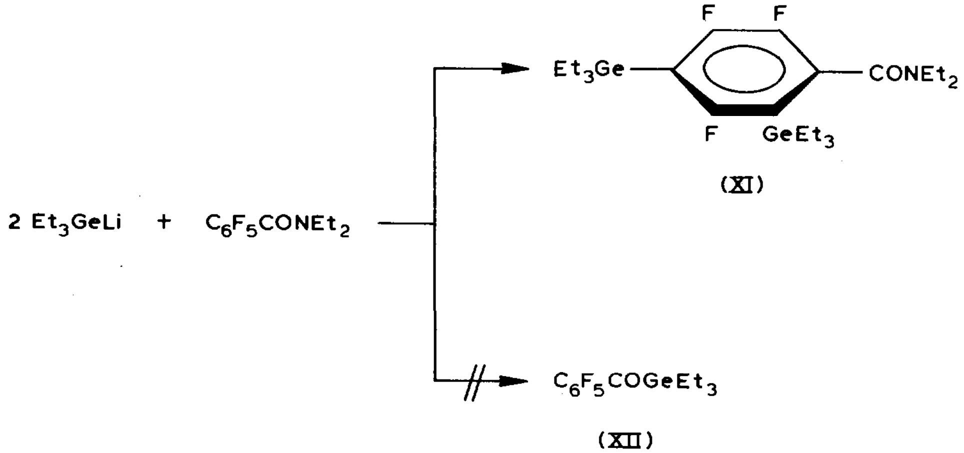
$$\mathrm{Et_3GeLi + CH_3CONMe_2 \longrightarrow LiCH_2CONMe_2 + Et_3GeH}\ \mathrm{(X)}$$

$$\mathrm{LiCH_2CONMe_2 + CH_3COGeEt_3 \xrightarrow{H_2O} \overset{Et_3Ge}{\underset{CH_3}{}}\!\!>\!C\overset{OH}{<}CH_2CONMe_2 + LiOH}\ \mathrm{(IX)}$$

This assumption is supported by the fact that triethylgermyllithium and *N*,*N*-dimethylacetamide in THF at −78°C give the expected lithium *N*,*N*-dimethylacetamide X. The ambident anion X was efficiently trapped with trimethylchlorosilane to provide *N*,*N*-dimethyl-2-trimethylsilylacetamide. The product obtained was comparable in all physical properties to an authentic sample [29b]. Moreover, the interaction of acetyltriethylgermane (VIII) with the anion X (generated in THF at −78°C as described above) results in a high yield of the amide alcohol IX.

The structure assigned to IX is based on elemental analysis and spectral data. The appearance of the IR absorption at 3400 cm^{-1} and the ^1H NMR singlet at 4.74 ppm indicate the presence of the alcohol function. Moreover, the ^1H NMR spectrum shows separate signals for the two CH_3 groups attached to nitrogen, indicative of restricted rotation around the N–CO bond [30]. The CH_2CO group protons give a spectrum of AB type due to the neighbouring asymmetrical carbon atom.

An attempt to convert *N*,*N*-diethylpentafluorobenzamide into pentafluoroben-



(XI)

(XII)

zoyl(triethyl)germane with triethylgermyllithium gave, in our hands, a high yield (83%) of amide XI and none of the required product XII.

It is worthwhile to note that the similar reaction of phenyllithium with isopropyl pentafluorobenzoate in diethyl ether gave a mixture from which 2,6-$Ph_2C_6F_3COOPr$-i was isolated [31].

Pentafluorobenzoyl(triethyl)germane (XII) was prepared, however, in moderate yield (54%) by the reaction of pentafluorobenzoyl chloride with triethylgermyllithium in the presence of one equivalent of copper(I) iodide. Our attempts to prepare this compound by the same reaction in the absence of copper(I) iodide were unsuccesful. Hexaethyldigermane, triethylchlorogermane and pentafluorobenzene were found to be major constituents of the reaction mixture.

$C_6F_5COCl + Et_3GeLi/CuI$ complex → $C_6F_5COGeEt_3$

Copper(I) iodide was earlier used with good results in combination with triphenylsilyllithium [32], dimethylphenylsilyllithium [33–38], trimethylsilyllithium [35] trimethylstannyllithium [35–43] and tributylstannyllithium [44].

Seeking a convenient alternative, we have found that benzoyl chloride reacts readily with a germylcopper reagent formed from triethylgermyllithium and copper(I) iodide to give benzoyltriethylgermane in reasonable yield. Analogously, trivinylgermyllithium * and copper(I) iodide in the ratio 1 : 1 react with benzoyl chloride at −30°C to give benzoyltrivinylgermane.

The 1,4-addition reaction of organolithium reagents to α,β-unsaturated amides has received sporadic attention [46–50]. It is interesting to note [47], however, that α,β-unsaturated amides with sterically protected carbonyl groups react with organolithium compounds to give the 1,2-addition products [cf. 46]. No products resulting from the addition at the carbonyl group were found [47]. We have reported in a preliminary communication [51] that triethylgermyllithium reacts readily with *N,N*-diethylcrotonamide at −60°C to give the conjugate addition product, i.e. *N,N*-diethyl-3-triethylgermylbutanamide (XIII). Analogously, *N,N*-dimethylcinnamamide yielded exclusively *N,N*-dimethyl-3-phenyl-3-triethylgermylpropanamide (XIV) on condensation with Et_3GeLi.

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* For the preparation of this reagent, see ref. 45.

Experimental

All reactions were carried out in evacuated sealed ampoules or under dry argon following the technique described in ref. 52. All solvents (pure grade commercial products) were dried and distilled over sodium ketyl immediately before use. THF was dried in the same way then refluxed over $LiAlH_4$ and finally distilled under vacuum directly into the reaction vessel. GLC analyses were obtained with a Chrom 4 using 6 ft × 0.25 in stainless steel columns packed with 15% Polymethylsiloxan 1000 on Chromaton N-AW. The chromatograph was fitted with a thermal conductivity detector. IR spectra were recorded with a UR-20 spectrophotometer. ^1H NMR spectra were obtained on a Tesla BS 487 C (80 MHz) instrument. Chemical shifts were reported as downfield positive with respect to $SiMe_4$. Mass spectra were measured on a Varian Mat 212 spectrometer and calibrated with perfluorokerosene.

Benzoyltriethylgermane

A mixture of 2.7 g (0.015 mol) of *N,N*-diethylbenzamide, 3.4 g (0.02 mol) of triethylgermyllithium and 30 ml of hexane was stirred at room temperature. After 4 h, the reaction was terminated by the addition of a saturated ammonium chloride solution (1.5 ml). The organic layer was decanted, dried over anhydrous magnesium sulfate and fractionally distilled to give 3.5 g (88%) of benzoyltriethylgermane, b.p. 86–87°C (7×10^{-2} mmHg), n_D^{20} 1.5318 IR (cm^{-1}): ν(C=O) 1630 [cf. 53].

Reaction of triethylsilyllithium with N,N-diethylbenzamide

A solution of 4.8 g (0.039 mol) of triethylsilyllithium and 7.0 g (0.039 mol) of *N,N*-diethylbenzamide in 60 ml of hexane was kept with (magnetic) stirring in a sealed glass ampoule at room temperature for 3 h. The volatiles products were analyzed by GLC, after the usual hydrolytic work-up. Triethylsilanol 3.2 g (39%) was identified. The distillation afforded 1.7 g (23%) of *N,N*-diethyl-α-(triethylsilyl)-benzylamine (I), b.p. 78–80°C (7×10^{-2} mmHg), together with high-boiling fraction. Preparative GLC produced an analytical sample of I as a colorless oil, n_D^{20} 1.5105. (Found: C, 73.65; H, 11.19; N, 5.05; Si, 10.11, $C_{17}H_{31}NSi$ calcd.: C, 73.57; H, 11.26; N, 5.05; Si, 10.11%).

NMR spectrum (CCl_4) (δ, ppm): 3.50 (s, 1 H, CH). 2.56 (m, 6 H, CH_2), 0.83 (m, 18 H, CH_3 and SiC_2H_5); mass spectrum *m/e* 271 (M^+). The high-boiling fractions from three similar experiments were combined and fractionally redistilled, amounting 3.4 g (14%) of *Z* and *E* isomers (2:1) of 1,2-bis(diethylamino)-1,2-diphenylethylene (II), b.p. 116–118°C ($7 \cdot 10^{-2}$mmHg), n_D^{20} 1.5701.(Found: C, 81.11; H, 9.24; N, 7.98; $C_{22}H_{30}N_2$ calcd.: C, 81.94; H, 9.38; N, 8.69%). IR (cm^{-1}): ν (C=C) 1546. NMR spectrum (CCl_4) (δ, ppm) for (*Z*)-II: 7.15 (m, 10 H, C_6H_5), 2.45 (q, 8 H, CH_2), 0.83 (t, 12 H, CH_3); for (*E*)-II: 7.15 (m, 10 H, C_6H_5), 2.95 (q, 8 H, CH_2), 0.83 (t, 12 H, CH_3). Mass spectrum *m/e* 322 (M^+).

Trifluoroacetyltriethylgermane (IV)

To a solution of 3.3 g (0.02 mol) of triethylgermyllithium in 20 ml of hexane, frozen at liquid nitrogen temperature, was added 2.8 g (0.017 mol) of *N,N*-diethyltrifluoroacetamide. The mixture was shaken at −78°C for 3 h, and was then worked up as above. After removal of the solvent in vacuo, distillation of the residue gave 4.5 g (81%) of IV, b.p. 58–59°C (30 mmHg), n_D^{20} 1.4091. (Found: C, 37.74; H, 6.08;

F, 21.83; Ge, 27.92. $C_8H_{15}F_3GeO$ calcd.: C, 37.42; H, 5.89; F, 22.19; Ge, 28.27%). IR (cm^{-1}): ν(C=O) 1684.

The crude reaction mixture obtained after work up was examined by GLC. Only traces of product V were found.

N,N-Diethylamide of triethylgermanecarboxylic acid (V)

A mixture of triethylgermyllithium (6.2 g, 0.037 mol) and *N,N*-diethyltrifluoroacetamide (5.4 g, 0.032 mol) in hexane (30 ml) was stirred at −30°C for 4 h. The usual hydrolytic work up and evaporation of the solvent under reduced pressure gave a crude oily product shown by GLC to contain 74% amide V and 26% trifluoroacetyltriethylgermane (IV). The crude products from two similar experiments were combined and fractionally distilled to give 9.6 g (56%) of the amide V, b.p. 68–70°C (8×10^{-2} mmHg), n_D^{20} 1.4776. (Found: C, 51.07; H, 9.63; Ge, 28.04; N, 5.16. $C_{11}H_{25}GeNO$ calcd.: C, 50.83; H, 9.70; Ge, 27.93; N, 5.39%). IR (cm^{-1}): ν(C=O) 1585. NMR spectrum (CCl_4) (δ, ppm): 2.40 (m, 10 H, NC_2H_5), 0.70 (m, 15 H, GeC_2H_5). Distillation gave 3.1 g (20%) of trifluoroacetyltriethylgermane (IV), b.p. 59°C (30 mmHg), n_D^{20} 1.4090.

Reaction of triethylgermyllithium with N,N-dimethylpivalamide

To a solution of 6.4 g (0.038 mol) of triethylgermyllithium in hexane (60 ml) was added 3.8 g (0.029 mol) of *N,N*-dimethylpivalamide at room temperature. The mixture was stirred for 4 h and was then worked up as above. After removal of the solvent in vacuo, distillation of the residue gave 2.2 g (30%) of VI, b.p. 49–51°C (6×10^{-2} mmHg), n_D^{20} 1.4581. (Found: C, 53.78; H, 10.08; Ge, 29.21. $C_{11}H_{24}GeO$ calcd.: C, 53.95; H, 9.88; Ge, 29.64%). IR (cm^{-1}): ν (C=O) 1640. In addition, 2.4 g (24%) of 1,1-bis(triethylgermyl)-2,2-dimethylpropan-1-ol (VII), b.p. 102–103°C (6×10^{-2} mmHg), n_D^{20} 1.5061 was isolated. (Found: C, 50.09; H, 9.49; Ge, 39.32. $C_{17}H_{40}GeO$ calcd.: C, 50.33; H, 9.94; Ge, 39.79%). IR (cm^{-1}): ν(O–H) 3470.

Reaction of triethylgermyllithium with N,N-dimethylacetamide

A mixture of 6.6 g (0.040 mol) of triethylgermyllithium and 3.4 g (0.039 mol) of *N,N*-dimethylacetamide in hexane was stirred at −20°C for 1.5 h. The mixture was allowed to warm to 20°C over 2 h, quenched with 10% NH_4Cl, dried over $MgSO_4$ and the solvent evaporated off. The residue was distilled to give 4.1 g (50%) of acetyltriethylgermane (VIII), b.p. 65°C (8 mmHg), n_D^{20} 1.4583. (Found: C, 47.57; H, 8.93; Ge, 35.64. $C_8H_{18}GeO$ calcd: C, 47.50; H, 8.97; Ge, 35.88%). IR (cm^{-1}): ν(C=O) 1657. NMR spectrum (CCl_4) (δ, ppm): 2.07 (s, 3 H, CH_3); 0.86 (m, 15 H, GeC_2H_5).

In addition, 2.0 g (18%) of IX, b.p. 95°C (8×10^{-2} mmHg), n_D^{20} 1.4906 was isolated. (Found: C, 49.66; H, 9.25; Ge, 25.21; N, 4.57. $C_{12}H_{27}GeNO_2$ calcd.: C, 49.71; H, 9.39; Ge, 25.04; N, 4.83%). IR (cm^{-1}): ν (C=O) 1630, (O–H) 3400. NMR spectrum (CCl_4) (δ, ppm): 2.32 (d, 2 H, CH_2 $^2J \simeq 16$ Hz), 2.20 (d, 2 H, CH_2 $^2J \simeq 16$ Hz), 2.85 (s, 3 H, N–CH_3), 2.78 (s, 3 H, N–CH_3), 1.12 (s, 3 H, C–CH_3), 0.85 (m, 15 H, Ge–C_2H_5).

N,N-Dimethyltrimethylsilylacetamide

N,N-Dimethylacetamide (3.4 g, 0.039 mol) was added to a solution of 8.1 g (0.041 mol) of triethylgermylpotassium in benzene (60 ml) with stirring. Stirring was continued for 1.5 h at room temperature. Chlorotrimethylsilane (8.6 g, 0.117 mol) was added to the mixture. After completion of the addition, stirring was continued for a further 1 h. The resulting solid was removed by filtration. The solvent was removed in vacuo. The resulting oil (5.1 g, 79%) was distilled under reduced pressure. The principal fraction, b.p. 55–56°C (2 mmHg), n_D^{20} 1.4515, was *N,N*-dimethyltrimethylsilylacetamide (lit. [29b] b.p. 80–81°C (7 mmHg), n_D^{20} 1.4510). NMR spectrum (CCl_4) (δ, ppm): 2.87 (s, 3 H, NCH_3), 2.73 (s, 3 H, N–CH_3), 1.30 (s, 2 H, $SiCH_2$), 0.07 (s, 9 H, $SiCH_3$).

N,N-Dimethylpropionamide

A stirred solution of *N,N*-dimethylacetamide (3.5 g, 0.04 mol) in THF (30 ml) was cooled to −20°C and treated with triethylgermyllithium (6.7 g, 0.04 mol) in THF (30 ml). The mixture was stirred at −20°C for 1 h and methyl iodide (5.0 ml, 0.08 mol) was injected. The reaction mixture was stirred at room temperature for 1 h, filtered through Celite to remove inorganic salts and processed in the normal manner to give 3.5 g (87%) of *N,N*-dimethylpropionamide which was shown to be identical (boiling point, n_D^{20}, GLC, IR, NMR) to an authentic sample.

N,N-Diethyl-2,4-bis(triethylgermyl)-3,5,6-trifluorobenzamide (XI)

N,N-Diethylpentafluorobenzamide (10.2 g, 0.038 mol) was treated with triethylgermyllithium (6.2 g, 0.037 mol) in hexane solution (60 ml) at −40°C. The mixture was stirred for 3 h. The standard work up gave 8.0 g (74%) of the amide XI, b.p. 135–136°C (7×10^{-2} mmHg), n_D^{20} 1.5122. (Found: C, 50.81; H, 7.73; F, 10.33; Ge, 26.29; N, 2.14. $C_{23}H_{40}F_3GeNO$ calcd.: C, 50.34; H, 7.35; F, 10.80; Ge, 26.46; N, 2.55%). IR (cm^{-1}): ν(C=O) 1630. ^{19}F NMR spectrum (δ, ppm): 146.9 (q, F(3), $^3J_{3,5} \simeq 25$ Hz, $^5J_{3,6} \simeq 18$ Hz), 121.6 (d, F(5), $^3J_{5,3} \simeq 25$ Hz), 85.2 (d, F(6), $^5J_{6,3} \simeq 18$ Hz) *.

Pentafluorobenzoyltriethylgermane (XII)

A mixture of 3.2 g (0.019 mol) of triethylgermyllithium and 3.7 g (0.019 mol) of copper(I) iodide in THF (30 ml) was stirred at −30°C for 30 min, and then treated with 5.8 g (0.025 mol) of pentafluorobenzoyl chloride. The mixture was stirred for an additional 1 h at room temperature. Hexane (10 ml) was added gradually, and the precipitate was filtered off. The resulting solution was evaporated to a yellow oil. The latter was distilled to give 3.6 g (54%) of XII, b.p. 55–56°C (7×10^{-2} mmHg), n_D^{20} 1.4678. (Found: C, 43.56; H, 4.05; F, 26.37; Ge, 20.41. $C_{13}H_{15}F_5GeO$ calcd.: C, 44.00; H, 4.26; F, 26.77; Ge, 20.46%). IR (cm^{-1}): ν (C=O) 1652.

Benzoyltrivinylgermane

A mixture of 3.2 g (0.02 mol) of trivinylgermyllithium and 3.8 g of copper(I) iodide in THF (30 ml) was stirred at −30°C for 30 min and then treated with 3.1 g (0.022 mol) of benzoyl chloride. The mixture was stirred for an additional 1 h at −30°C. The same work up as above gave 3.1 g (60%) of benzoyltrivinylgermane as an oil, b.p. 85–86°C (6×10^{-2} mmHg), n_D^{20} 1.5606. (Found: C, 59.86; H, 5.44; Ge, 28.07. $C_{13}H_{14}GeO$ calcd.: C, 60.32; H, 5.45; Ge, 28.04%). Mass spectrum (*m/e*) 258 (M^+).

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* ^{19}F NMR spectra was recorded on a Varian A-60 with C_6F_6 as the internal standard.

N,N-Diethyl-3-triethylgermylbutanamide (XIII)

A solution of 2.8 g (0.020 mol) of *N,N*-diethylcrotonamide in 10 ml of hexane was cooled to −60°C and solution of 3.3 g (0.020 mol) of triethylgermyllithium in 20 ml hexane was added dropwise. The mixture was stirred for 3 h at −60°C. The reaction was quenched with 5 ml of methanol, and washed with a saturated solution of NH_4Cl. Drying ($MgSO_4$) and evaporation of the solvent gave an oil which was distilled to give XIII: 3.7 g 62% yield; b.p. 79–80°C (6×10^{-2} mmHg). n_D^{20} 1.4783. (Found: C, 55.58; H, 10.26; Ge, 24.16; N, 4.56. $C_{14}H_{31}GeNO$ calcd.: C, 55.68; H, 10.35; Ge, 24.04; N, 4.64%). IR (cm^{-1}): ν (C=O) 1663. NMR spectrum ($CDCl_3$) (δ, ppm): 3.36 (q, 2 H, $N-CH_2$, $^2J \simeq 7.0$ Hz), 3.33 (q, 4 H, $N-CH_2$, $^2J \simeq 7.0$ Hz), 2.33 (d, 4 H, $C-CH_2$, $^2J \simeq 6.0$ Hz), 2.35 (d, 2 H, $C-CH_2$, $^2J \simeq 6.0$ Hz), 1.68 (m, 1 H, CH), 1.21 (d, 3 H, CH_3), 1.00 (t, 6 H, CH_3), 0.90 (m, 15 H, GeC_2H_5).

N,N-Dimethyl-3-phenyl-3-triethylgermylpropanamide (XIV)

A solution of 3.4 g (0.020 mol) of triethylgermyllithium in 30 ml dry hexane was cooled at −60°C and treated with 3.2 g (0.018 mol) of *N,N*-dimethylcinnamamide diluted with 10 ml of hexane. The mixture was stirred for 3 h and then allowed to reach room temperature. The reaction mixture was worked up as above to give 4.6 g (76%) of the amide XIV, b.p. 124–125°C (7×10^{-2} mmHg), n_D^{20} 1.5372. (Found: C, 60.62; H, 8.45; Ge, 22.01; N, 4.16. $C_{17}H_{29}GeNO$ calcd.: C, 60.92; H, 8.42; Ge, 21.64; N, 4.18%). IR (cm^{-1}): ν(C=O) 1660. NMR spectrum ($CDCl_3$) (δ, ppm): 7.00 (m, 5 H, C_6H_5); 2.76 (s, 3 H, NCH_3); 2.77 (s, 3 H, NCH_3); 2.60–2.90 (m, 3 H, $CHCH_2$); 0.95 (m, 15 H, GeC_2H_5).

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