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SYNTHESIS AND COPPER-CATALYZED REACTIONS OF α-METALATED DIAZOCARBONYL COMPOUNDS

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Summary

Monogermylated ketenes, $R(Et_3Ge)C{=}C{=}O$, have been prepared by the Wolff rearrangement of carbenoids, $Et_3Ge\ddot{C}COR$, generated by the copper-catalyzed decomposition of the corresponding α-(triethylgermyl)diazo ketones in hexane. In contrast, triethylsilyldiazoacetone decomposes over copper by another reaction scheme to give, unexpectedly 1,1-diethyl-3,5-dimethyl-2-oxa-1-sila-3-cyclopentene. The copper-catalyzed interaction of $Et_3MC(N_2)COOEt$ ($M = Si$, Ge, Sn) with bis(triethylsilyl)- or bis(triethylgermyl)-mercury results in high yield of the corresponding bimetalated ketenes, $Et_3M(Et_3M')C{=}C{=}O$, where M and M' are Si, Ge or Sn. The first step in this interaction probably involves the insertion of the carbenoid, $Et_3M\ddot{C}CO_2Et$, into the Group IV element—mercury bond. The general procedure for the preparation of α-metalated diazocarbonyl compounds via readily available bis(triethylsilyl)- and bis(triethylgermyl)-mercury is described.

Introduction

In recent years, besides continued developments in normal carbene chemistry [1—3], there have been increasing reports and interest in α-metalated carbenes. Such reactive species have mainly been generated from α-metallodiazo compounds.

However, depending on the choice of conditions for the generation reaction, either carbenes or carbenoids can be prepared from precursors. Comparison of the chemical properties of normal carbenes and the appropriate carbenoids has already been carried out [1,3]. Copper-catalyzed decomposition of alkyl diazoacetates to carbenoids is well known. Copper carbenoids react with a greater degree of selectivity towards olefins than the corresponding free carbenes [3b,11]. Moreover, carbalkoxycarbenoids are a less reactive species than the free carbenes, :$CHCO_2R$, generated by the photolysis or thermolysis of aliphatic diazo compounds [1]. It is possible that α-metallated carbenes and the corresponding carbenoids differ in reactivity. However, literature on the reactivity of α-metalated carbenoids is very scarce.

We wish to report here a general method for the synthesis of trialkylsilyl- and trialkylgermyl-diazocarbonyl compounds. In addition, some copper-catalyzed reactions of these diazo compounds are described.

Results and discussion

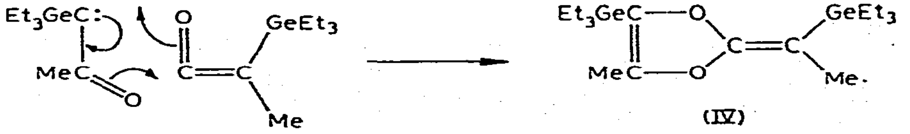
We have already found * that germylated carbenoids II generated by the copper-catalyzed thermolysis of α-(triethylgermyl)diazoketones (I) in hexane at 80—90°C, rearrange to monogermylated ketenes (III) according to eqn. 1.

$$\underset{\text{(I)}}{Et_3GeC(N_2)COR} \xrightarrow[-N_2]{Cu} \underset{\text{(II)}}{Et_3Ge\ddot{C}COR} \dashrightarrow \underset{\text{(III)}}{R(Et_3Ge)C{=}C{=}O} \qquad (1)$$

$$R = Me, Et, Ph$$

For example, the best method for the preparation of $Ph(Et_3Ge)C{=}C{=}O$ is the copper-catalyzed decomposition of α-(triethylgermyl)diazoacetophenone (prepared in situ via reaction 7 in THF). The data for the ketenes III are presented in Table 1. The structure of the ketenes was assigned on the basis of the infrared band at 2100 cm^{-1}. Moreover, the structure of methyl(triethylgermyl)ketene has been confirmed by the reaction with methanol to lead to methyl α-(triethylgermyl)propionate.

It should be noted that copper catalysis normally suppresses the Wolff rearrangement of ketocarbenes generated by diazoketone decomposition [2,6], but some exceptions have been found [5] including reaction 1. The ketenes III were found to be reasonably stable with respect to dimerization. However, in the case of triethylgermyldiazoacetone, along with methyl(triethylgermyl)ketene, substituted 2-methylene-1,3-dioxol (IV) is formed in 20—30% yield. This seems to result from 1,3-cycloaddition of the ketocarbenoid II (R = Me) to the corresponding ketene III.



(IV)

(2)

The formation of heterocycles of type IV (e.g. 1,4-dioxa-2,3-benzofulvalene [10]) by a similar reaction was observed during the thermolysis of some α-diazoketones (for example, 2-diazo-1-oxo-1,2-dihydronaphthalene [7] and *o*-quinone diazides [8—10]).

The structure of IV is based on elemental analysis, molecular weight, and spectral data. The IR spectrum contains frequencies corresponding to the Et_3Ge

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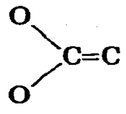
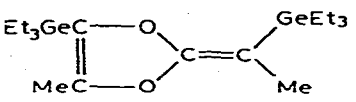
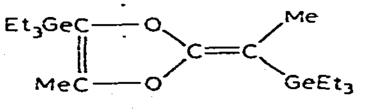
* Short communication, see ref. 4.

moiety (580 and 700 cm^{-1}). IR absorption bands characteristic of the  grouping are seen at 1250 and 1690 cm^{-1} (cf. ref. 8) and there is a band assigned to the C=C group in the cycle at 1625 cm^{-1}. Additional information about the structure was obtained from the NMR spectrum. A multiplet at ca. 1 ppm was assigned to the protons of the Et_3Ge moiety. Two singlets at 1.59 and 1.61 ppm were assigned to the methyl protons of the $Ge-C-CH_3$ group and two singlets at 1.90 and 1.95 were assigned to the methyl protons of the $O-C-CH_3$ group. This could imply that compound IV is present as a mixture of *E* and *Z* isomers in solution.

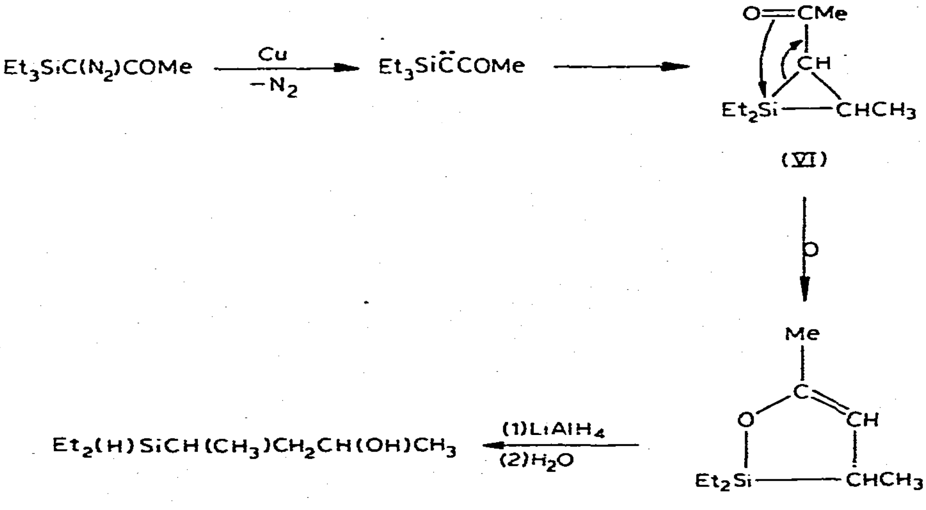


Z-isomer



E-isomer

It should be noted that triethylsilyldiazoacetone decomposes over copper in hexane by another reaction scheme to give, unexpectedly 1,1-diethyl-3,5-dimethyl-2-oxa-1-sila-4-cyclopentene (V). No methyl(triethylsilyl)ketene was detected in the reaction mixture (GLC). Thus very little, if any, Wolff rearrangement occurs in this reaction. The mechanism of the formation of V is thought to involve initial formation of acetyl(triethylsilyl)carbenoid and its subsequent intramolecular 1,3-insertion into the α-C—H bond of the $SiCH_2CH_3$ group to form intermediate silacyclopropane (VI); VI then rearranges to give compound V.



(3)

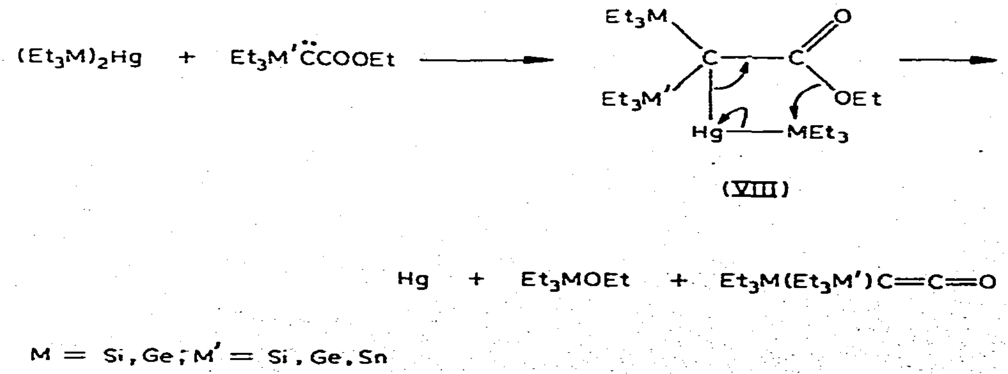
Reaction 3 is confirmed by the following facts. Recently Ando et al. postulated the formation of silacyclopropane by the intramolecular 1,3-insertion of the silylcarbene generated in the thermolysis of phenyl(trimethylsilyl)diazomethane [12]. It is also known [11] that certain copper carbenoids can and do insert inter- and intra-molecularly into C—H bonds.

In the IR spectrum of V there was one band at 3030 cm^{-1} due to a =CH stretching vibration, another at 1650 cm^{-1} attributed to a C=C stretching frequency and two strong Si—O—C stretching frequencies at 1150 and 1008 cm^{-1}. This spectrum is very similar to that previously reported for the appropriate heterocycle, 1,1-dimethyl-2-oxa-1-sila-3-cyclohexene [13]. The NMR data are also in agreement with the structure of V (see experimental section). Moreover, treatment of V with lithium aluminum hydride in ether at 30°C gave (after hydrolysis) a mixture of (1-methyl-4-hydroxybutyl)diethylsilane (VII) and the corresponding ketone in a 90/10 ratio. Satge et al. [14] described similar behaviour for 1,1-dimethyl-2-oxa-1-silacyclopentanes. Treatment of these compounds with $LiAlH_4$ caused scission of the Si—O bond to give silyl-substituted alcohols containing a Si—H bond. Finally, the route for the formation of the mixture of VII and the corresponding ketone was confirmed by a separate experiment in which a sample of 1-phenyl-1-(trimethylsiloxy)ethylene was treated with $LiAlH_4$. This reaction also occurs via reductive scission of the Si—O—C=C grouping in the silyl enol ether

$$\underset{Ph}{Me_3SiOC}{=}CH_2 \xrightarrow{LiAlH_4} \xrightarrow{H_2O} Me_3SiH + PhCH(OH)Me + PhCOMe \qquad (4)$$

Seyferth et al. [15,16] showed that dihalocarbenes generated by thermolysis of phenyl(trihalomethyl)mercurials react with bis(trimethylsilyl)- or bis(trimethylgermyl)-mercury to give complex mixtures of products. These reactions proceed via dihalocarbene insertion into the Si—Hg (Ge—Hg) bond followed by another CX_2 insertion into the newly formed Hg—C bond.

We have already found * that a similar type of reaction between bis(triethylsilyl)- or bis(triethylgermyl)-mercury and carbenoids of the type $Et_3M\ddot{C}COOEt$ (generated via copper-catalyzed thermolysis of appropriate diazo esters) proceeds according to equation 5. In this case the carbenoid attacks preferentially, if not exclusively, the Hg—Si (or Hg—Ge) bond to give VIII as a transient intermediate.



(5)

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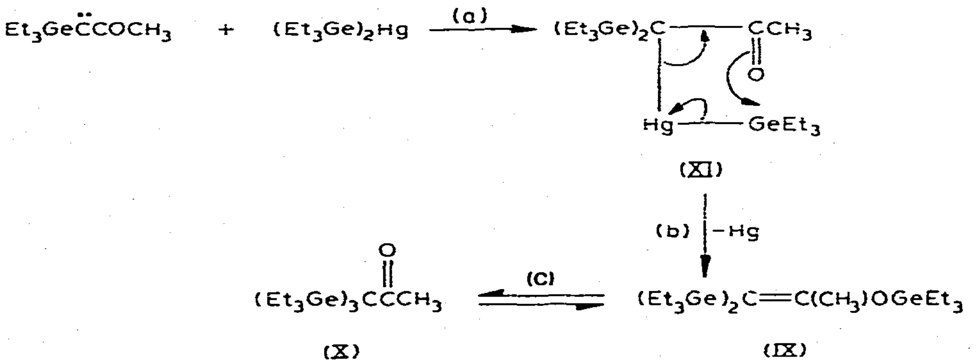
* Short communications, see refs. 17 and 18.

These findings clearly indicate that reaction 5 may open a new route to the preparation of bimetalated ketenes. It is well known [19—22] that bis(triethylgermyl)mercury reacts with mercurials of the type $Hg(CX_2COOEt)_2$, where X = H, Cl, F, etc., under mild conditions, to give metallic mercury and the corresponding Et_3GeCX_2COOEt derivative. The reaction proceeds through the formation of $Et_3GeHgCX_2COOEt$ as an unstable intermediate. The exchange reaction between $(Et_3Si)_2Hg$ and $Hg(CX_2COOEt)_2$ proceeds analogously and also involves two consecutive steps, (i) the formation of an asymmetric mercurial, $Et_3SiHgCX_2COOEt$, and (ii) its demercuration. Thus, reaction 5 is the first example where demercuration of $Et_3GeHgCX_2COOEt$ and related compounds (X = Et_3Si or Et_3Ge) is accompanied by cleavage of the carbethoxy group *.

In the presence of metallic copper, triethylgermyldiazoacetone reacts with an equimolar amount of bis(triethylgermyl)mercury in hexane at 80—90°C to give nitrogen, mercury, and 1,1-bis(triethylgermyl)-2-(triethylgermoxy)-1-propene (IX), together with a very small amount of 1,1,1-tris(triethylgermyl)acetone (X). The latter is a keto form of compounds IX. In this case the formation of compounds IX and X is also compatible only with insertion of generated acetyl(triethylgermyl)carbenoid into the Ge—Hg bond of the mercurial. The formation of an intermediate XI is followed by its demercuration (eq. 6).



(6)

Reaction 6c is probably reversible (cf. ref. 23), but the equilibrium is strongly shifted to the right. Moreover, it may be assumed that the demercuration of intermediate XI proceeds via initial formation of the triethylgermoxy isomer IX (i.e. via the reaction depicted in eqn. 6b). The structure of the reaction products IX and X has been established from the IR spectrum which contains absorption bands at 1200 and 1560 cm^{-1} corresponding to stretching vibrations of the C=C bond in the $Ge_2C{=}C{-}O$ grouping. Furthermore, the spectrum displays a very weak band at 1670 cm^{-1} characteristic of the carbonyl group of ketone X.

It is well known that exchange reactions between compounds containing Si—Hg—Si or Ge—Hg—Ge groupings and various mercurials are a potential source of new types of organometallic compounds [24]. The interaction of bis(triethylsilyl)- or bis(triethylgermyl)-mercury with mercurials of the type HgX_2 (where X is an electron-accepting diazocarbonyl radical) in THF results in a high yield

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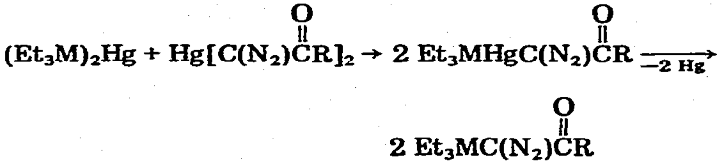
* See Note added in proof on p. 164.

of the corresponding α-(triethylsilyl)- or α-(triethylgermyl)-diazocarbonyl compounds. The reactions proceed via intermediate unsymmetrical mercurials which are thermally unstable (eq. 7).



$$(Et_3M)_2Hg + Hg[C(N_2)\overset{\overset{O}{\|}}{C}R]_2 \rightarrow 2\ Et_3MHgC(N_2)\overset{\overset{O}{\|}}{C}R \xrightarrow[-2\ Hg]{} 2\ Et_3MC(N_2)\overset{\overset{O}{\|}}{C}R \qquad (7)$$

M = Si, Ge; R = Me, Et, Ph, OMe, OEt

Experimental data for the $Et_3MC(N_2)COR$ compounds prepared are summarized in Table 1.

TABLE 1

PROPERTIES AND ANALYTICAL DATA OF THE COMPOUNDS STUDIED

Compound	Yield (%)	B.p. (°C/mmHg)	n_D^{20}	Analysis (found (calcd.) (%))		
				C	H	M
$Me(Et_3Ge)C=C=O$	65	78—80/12	1.4657	50.44 (50.31)	8.56 (8.43)	33.81 (33.78)
$Et(Et_3Ge)C=C=O$	71	75—78/10	1.4668	52.25 (52.48)	8.52 (8.81)	31.67 (31.72)
$Ph(Et_3Ge)C=C=O$	53	95—97/1	1.5354	60.51 (60.73)	7.25 (7.28)	26.33 (26.22)
$(Et_3Si)_2C=C=O$	68	85—86/1	1.4722	61.84 (62.14)	11.38 (11.17)	19.88 (20.75)
$Et_3Si(Et_3Ge)C=C=O$	82	86—88/1	1.4812	53.47 (53.38)	10.01 (9.60)	31.67 (31.98)
$(Et_3Ge)_2C=C=O$	73	89—90/1	1.4932	47.40 (47.42)	8.45 (8.41)	40.24 (40.23)
$Et_3Ge(Et_3Sn)C=C=O$	73	110—111/1	1.5076	41.37 (41.45)	7.42 (7.45)	46.84 (47.15)
$Et_3SiC(N_2)COMe$	48	58—60/1	1.4745	53.91 (54.50)	9.48 (9.15)	14.51 (14.16)
$Et_3SiC(N_2)CO_2Me$	78	63—64/2	1.4652	50.32 (50.41)	8.81 (8.46)	13.02 (13.11)
$Et_3SiC(N_2)CO_2Et$	78	65—66/1	1.4698	52.48 (52.61)	8.72 (8.83)	12.12 (12.30)
$MePh_2SiC(N_2)CO_2Et$	80	M.p. 133—135°C		65.84 (65.78)	5.90 (5.84)	9.36 (9.05)
$Et_3GeC(N_2)COMe$	82	60—62/1	1.4968	44.53 (44.52)	7.71 (7.43)	29.99 (29.88)
$Et_3GeC(N_2)COEt$	73	70—72/1	1.4962	46.84 (46.76)	7.81 (7.85)	28.06 (28.26)
$Et_3GeC(N_2)CO_2Me$	85	70—71/1	1.4889	41.91 (41.77)	6.79 (6.97)	29.02 (28.68)
$Et_3GeC(N_2)CO_2Et$	85	73—74/1	1.4845	43.97 (44.01)	7.36 (7.39)	26.87 (26.64)
$(Me_3CCH_2)_2SnC(N_2)COMe$ [a]	95	M.p. 180°C (dec.)		52.03 (52.06)	9.01 (8.74)	—
$(Me_3CCH_2)_3SnC(N_2)CO_2Et$ [a]	92	140—141/1	1.4916	50.61 (50.13)	8.33 (8.41)	26.11 (25.84)

[a] Prepared via reaction 7 from $[(Me_3CCH_2)_3Sn]_2Hg$ and the corresponding mercury bis-diazo(carbonyl) compounds.

Experimental

Infrared spectra were obtained on a UR-20 spectrophotometer. NMR spectra were recorded on a Tesla BS 487 C (80 MHz) instrument with tetramethylsilane as internal standard. All reactions were carried in evacuated sealed ampules or under dry argon following the technique described in ref. 25.

Copper-catalyzed thermolysis of triethylgermyldiazoacetone

A mixture of 2.43 g (0.01 mol) of $Et_3GeC(N_2)COCH_3$, 0.5 g of freshly precipitated copper and 20 ml of hexane was maintained at 90–100°C for 6 h; 220 ml (ca. 100%) of nitrogen was evolved. The organic layer was fractionally distilled to give 1.39 g (65%) of methyl(triethylgermyl)ketene (see Table 1). IR (cm^{-1}): $\nu(C{=}C{=}O)$ 2100. NMR spectrum (CCl_4) (δ, ppm): 0.8–1.0 (15 H, m), 1.6 (3H, s). In addition, 0.65 g (30%) of IV was obtained, b.p. 137–139°C/1 mmHg, n_D^{20} 1.4992. (Found: C, 49.98; H, 8.37; Ge, 33.43; mol. wt. (cryoscopic in benzene) 421. $C_{18}H_{36}Ge_2O_2$ calcd.: C, 50.31; H, 8.43; Ge, 33.78%; mol. wt. 430. IR (cm^{-1}): $\nu(Et_3Ge)$ 580, 700, ν(C=C in cycle) 1650, $\nu(\genfrac{}{}{0pt}{}{O}{O}\!>\!C{=}C)$ 1250, 1690. NMR spectrum (CCl_4) (δ, ppm): 0.8–1.0 (30H, m), 1.59 and 1.61 (3H, s, $CH_3{-}C{-}Ge$), 1.90 and 1.95 (3H, s, $CH_3{-}C{-}O$).

Ethyl(triethylgermyl)ketene

A mixture of 3.51 g (0.012 mol) of $Et_3GeC(N_2)COEt$, 0.5 g of copper and 20 ml of hexane was heated at 90–100°C for 6 h. The usual work-up gave 270 ml (ca. 97%) of nitrogen and 2.21 g (71%) of the desired product (see Table 1). IR (cm^{-1}): $\nu(C{=}C{=}O)$ 2100, NMR spectrum (CCl_4) (δ, ppm): 0.8–1.0 (15H, m), 1.13, J 6 Hz (3H, t) and 1.95, J 6 Hz (2H, q).

Phenyl(triethylgermyl)ketene

Bis(triethylgermyl)mercury (4.57 g, 0.009 mol) was added to a previously degassed solution of $Hg[C(N_2)CPh]_2$ (4.32 g, 0.009 mol) in 40 ml of hexane in an evacuated ampule. The mixture was kept at room temperature for 48 h. The organic layer was decanted from the metallic mercury (3.49 g, ca. 100%) and was maintained at 80–90°C for 5 h over freshly precipitated copper. The usual work-up gave 350 ml (ca. 100%) of nitrogen and 2.61 g (53% based on $(Et_3Ge)_2Hg$) of phenyl(triethylgermyl)ketene (see Table 1); IR (cm^{-1}): $\nu(C{=}C{=}O)$ 2100. NMR spectrum (CCl_4) (δ, ppm): 1.05 (15H, s), 7.01 (5H, m).

Copper-catalyzed thermolysis of triethylsilyldiazoacetone

A solution of 4.01 g (0.02 mol) of $Et_3SiC(N_2)COCH_3$ in 40 ml of hexane was maintained over copper at 80–90°C for 5 h; 450 ml (ca. 100%) of nitrogen was evolved. The organic layer was fractionally distilled to give 2.20 g (64%) of compound V, b.p. 46–47°C/7 mmHg, n_D^{20} 1.4470. (Found: C, 63.38; H, 10.66; Si, 16.38; mol. wt. (cryoscopic in benzene) 176. $C_9H_{18}OSi$ calcd.: C, 63.47; H, 10.65; Si, 16.49%; mol. wt. 170. IR (cm^{-1}): $\nu({=}CH)$ 3030, $\nu(C{=}C{-}O)$ 1648, 1150, $\nu(Si{-}O{-}C)$ 1008. NMR spectrum (CCl_4) (δ, ppm): 0.77–0.98

(10H, m), 1.07, ^3J 3.5 Hz (3H, d, CH_3—C—Si), 1.72, ^4J 1 Hz, ^5J 0.9 Hz (3H, q, CH_3—C—O), 4.57 (1H, m, HC=C).

Reduction of compound V with $LiAlH_4$

A solution of 2.06 g (0.012 mol) of V in 10 ml of ether was added to a suspension of 1 g of $LiAlH_4$ in 10 ml of ether. The mixture was heated at 30°C for 3 h and hydrolyzed. The organic layer was separated and dried (Na_2SO_4). Fractionation of the reaction mixture gave 0.92 g (46%) of carbinol VII, b.p. 50—52°C/1 mmHg, n_D^{20} 1.4494. (Found: C, 61.98; H, 12.38; $H_{activ.}$, 0.58 (Tserevitinov test); Si, 16.10. $C_9H_{22}OSi$ calcd.: C, 61.99; H, 12.38; $H_{activ.}$, 0.58; Si, 16.11%). IR (cm^{-1}); ν(OH) 3400, ν(Si—H) 2110. NMR spectrum (CCl_4) (δ, ppm): 0.64—1.00 (14H, m, $Et_2SiCHCH_3$), 1.13, ^3J 6.3 Hz (3H, d, CH_3C—O), 1.41 (2H, m, CH_2), 2.85 (1H, s, OH), 3.55 (1H, m, Si—H), 3.84, ^3J 6.3 Hz (1H, q, CH—O). In addition, the IR spectrum has a very weak band in the carbonyl region at 1735 cm^{-1} and the NMR spectrum displays a 2.02 ppm signal (s, $COCH_3$) that shows the presence of the ketone, $Et_2(H)SiCH(CH_3)CH_2COCH_3$.

Reduction of $Ph(Me_3SiO)C{=}CH_2$ with $LiAlH_4$

A solution of 9.51 g (0.49 mol) of 1-phenyl-1-(trimethylsiloxy)ethylene in 300 ml of ether was added to a suspension of 10 g of $LiAlH_4$ in 100 ml of ether. The mixture was kept at 30°C for 3 h and hydrolyzed. The organic layer was dried over Na_2SO_4 and the solvent evaporated. By distillation of the residual liquid in vacuo 4.97 (83%) of a mixture of α-phenylethanol and acetophenone was obtained in the ratio 44/56, b.p. 83—88°C/12 mmHg. (Found: $H_{activ.}$, 0.37. $C_8H_{10}O$ calcd.: $H_{activ.}$ 0.83% (Tserevitinov test). IR (cm^{-1}): ν(C=O) 1690, ν(OH) 3450. NMR (CCl_4) (δ, ppm): 1.33, ^3J 6.5 Hz (3H, d, O—C—CH_3), 2.37 (3H, s, $COCH_3$), 3.87 (1H, s, OH), 4.65, ^3J 6.5 Hz (1H, q, O—CH), 7.13 (6H, m, C_6H_5).

In addition, GLC analysis of the volatile products revealed the presence of Me_3SiH (2.46 g, 67%).

Triethylsilyl(triethylgermyl)ketene

A mixture of 2.83 g (0.012 mol) of $Et_3SiC(N_2)COOEt$, 6.31 g (0.012 mol) of bis(triethylgermyl)mercury and 10 ml of hexane was maintained at 80—90°C for 12 h in the presence of 1 g of freshly precipitated copper; 290 ml (ca. 100%) of nitrogen was evolved. Metallic mercury (2.44 g, 99%) was precipitated and the organic layer decanted from the mixture of metals. The organic layer was fractionated to obtain the desired product (3.18 g, 82%), b.p. 86—88°C/1 mmHg, n_D^{20} 1.4812. (Found: C, 53.47; H, 10.01; (Si + Ge), 31.67. $C_{14}H_{30}GeOSi$ calcd.: C, 53.38; H, 9.60; (Si + Ge), 31.98%). IR (cm^{-1}): ν(C=C=O) 2100. 2.10 g (80%) of ethoxytriethylgermane was also obtained, b.p. 165°C, n_D^{20} 1.4374. Et_3GeOEt was also detected by GLC. The other compounds of this type were obtained in a similar way (see Table 1).

Reaction of triethylgermyldiazoacetone with $(Et_3Ge)_2Hg$

5.21 g (0.01 mol) of $(Et_3Ge)_2Hg$ was added to a mixture of 2.43 g (0.01 mol) of $Et_3GeC(N_2)COCH_3$, 1 g of copper and 10 ml of hexane. At 80—90°C the reaction was completed after 3 h. Metallic mercury (1.85 g, 93%) was precipitated and nitrogen (220 ml, ca. 100%) evolved. The organic layer was worked up as

TABLE 2

IR AND ^{1}H NMR SPECTRA OF α-METALATED DIAZOCARBONYL COMPOUNDS

Compound	ν(C=O) (cm^{-1})	ν(CN$_2$) (cm^{-1})	δ(R$_3$M) (ppm)	δ(CH$_2$) (ppm)	δ(CH$_3$) (ppm)	*J*(C$_2$H$_5$) (*Hz*)
$Et_3SiC(N_2)CO_2Me$	1680	2080	0,65–0,94 m		3,66 s	
$Et_3SiC(N_2)CO_2Et$	1680	2080	0,65–0,94 m	4,01 q	1,20 t	7,0
$Et_3SiC(N_2)COMe$	1650	2060	0,65–0,94		2,15 s	
$Et_3GeC(N_2)CO_2Me$	1680	2080	1,03 s		3,66 s	
$Et_3GeC(N_2)CO_2Et$	1680	2080	1,03 s	4,02 q	1,30 t	7,0
$Et_3GeC(N_2)COMe$	1640	2060	1,02s		2,17 s	
$Et_3GeC(N_2)COEt$	1640	2060	1,03 s	2,51 q	1,03 t	6,0
$(Me_3CCH_2)_3SnC(N_2)CO_2Et$ [a]	1680	2080	1,05 s, 1,33 s	4,15 q	1,20 t	7,0
$(Me_3CCH_2)_3SnC(N_2)COMe$ [a]	1663, 1632	2080, 2050	1,05 s, 1,33 s		2,20 s	

[a] Prepared via reaction 7 from $[(Me_3CCH_2)_3Sn]_2Hg$ and corresponding mercury bis-diazo-carbonyl compounds.

usual to give 4.15 g (78%) of IX containing traces of X, b.p. 158—159°C/1 mmHg; n_D^{20} 1.5110. (Found: C, 47.18; H, 9.05. $C_{21}H_{48}Ge_3O$ calcd.: C, 47.20; H, 9.06%). IR (cm^{-1}): ν(Ge—C) 575, 700, ν(Ge_2C=C—O) 1200, 1560, ν(C=O) 1670 (a very weak absorption band).

Triethylgermyldiazoacetone

5.20 g (0.01 mol) of bis(triethylgermyl)mercury was added to a solution of 3.67 g (0.01 mol) of $Hg[C(N_2)COCH_3]_2$ in 30 ml of THF. A weak exothermal reaction occurred resulting in the precipitation of metallic mercury (3.99 g, ca. 100%). Upon completing the exothermal reaction, the reaction mixture was allowed to stand at room temperature for 2—3 h. The organic layer was decanted from mercury and fractionally distilled to give 3.98 g (82%) of the desired product.

The other compounds of this type were obtained in a similar way. The results are summarized in Tables 1 and 2.

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* *Note added in proof:* The ketene $(Me_3Si)_2C{=}C{=}O$ is thought to be formed by similar heterolytic decomposition of lithium ester enolate [26].

$$(Me_3Si)_2C(Li)CO_2Bu\text{-}t \xrightarrow[25^\circ C,\ 30\ min]{THF} (Me_3Si)_2C{=}C{=}O + t\text{-}BuOLi$$

The ability to isolate the bimetalated ketenes $(Et_3M)(Et_3M')C{=}C{=}O$ rather than esters $(Et_3M)_2$-$(Et_3M')CCO_2Et$ in reaction 5 is clearly due to steric factors (i.e. bulky substituents can prevent association of counter ions at the demercuration stage).