SILYL- AND GERMYLMERCURIALS IN ORGANIC SYNTHESIS. A NEW ROUTE TO *O*-SILYLATED AND *O*-GERMYLATED ENOLATES *

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Summary

The exchange reaction of α-mercurated ketones with bis(triethylsilyl)- (I) and bis(triethylgermyl)mercury (II) leads to the formation of the corresponding triethylsilyl and triethylgermyl enol ethers. *O*-Silylated and *O*-germylated enolates derived from ketones and aldehydes can be also prepared by treating mercurials I and II with appropriate α-bromo-carbonyl compounds. This new pathway also represents the best available method for preparing bromo-containing triethylsilyl and triethylgermyl enol ethers. NMR and IR spectral characteristic useful in the identification and characterization of these and related compounds are summarized.

Introduction

Silyl-, germyl-, and stannyl-mercurials are widely used in organic synthesis [1,2]. From this point of view, the exchange reactions between $(R_3M)_2Hg$ (M = Si, Ge, Sn) and mercurials of the type HgX_2 of interest. These reactions usually lead to unsymmetrical compounds R_3M—HgX or their demercurated products [3,4].

$$(R_3M)_2Hg + HgX_2 \xrightarrow{a} 2\ R_3M-HgX \xrightarrow{b} 2\ R_3MX + 2\ Hg \qquad (1)$$

For example, the interaction of bis(triethylsilyl)mercury (I) with $Hg[C(N_2)COOEt]_2$ proceeds according to eq. 1a, b to give metallic mercury and ethyl triethylsilyldiazoacetate [5,6]. The compound $[(Me_3SiCH_2)_3Sn]_2Hg$ reacts similarly with HgX_2, when X is CH_2COOMe, $PhC\equiv C$, or $Co(CO)_4$ [4]. In

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* Dedicated to Professor G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

contrast, the reaction of bis(triethylgermyl)mercury (II) with fluorinated dialkylmercurials, HgR_2^f ($R_2^f = CF_3$, CH_2CF_3, CF_2CF_3 etc.) proceeds via formation of the corresponding fluoroalkyl(triethylgermyl)mercurials, Et_3GeHgR^f (i.e., via the reaction depicted in eq. 1a) [7].

The formation of the fluoroalkyl germyl-mercury compounds was interpreted in terms of a four-centre mechanism of the type previously proposed for the exchange reactions between $(CH_3)_2Hg$ and $(CD_3)_2Hg$ [8a] or $(Me_3Si)_2Hg$ * and $(Me_3Si)_2Hg$ [8b].

A similar mechanism would account for the interaction of optically active bis(methyl-1-napthylphenylgermyl) mercury with $Hg(CH_2COOMe)_2$. The reaction proceeds according to eq. 1a, b and yields a product which retains the configuration at germanium [9].

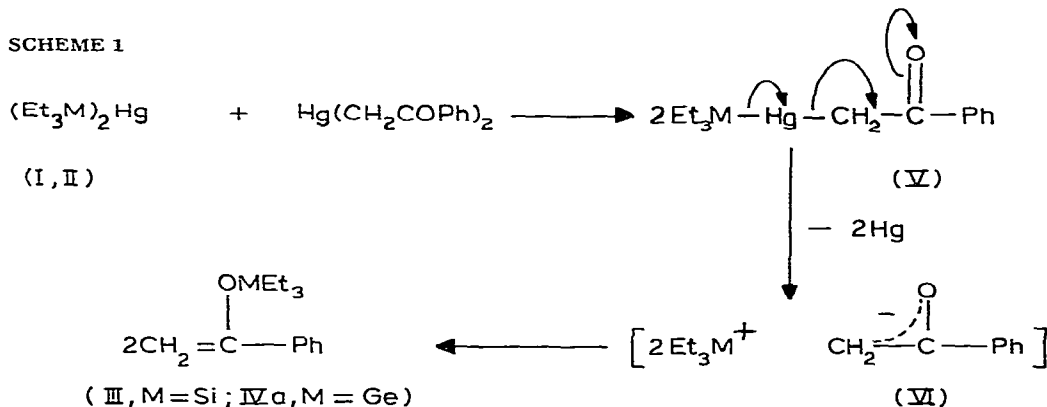$$(-)-(R_3Ge^*)_2Hg + Hg(CH_2COOMe)_2 \rightarrow 2\ Hg + 2\ (+)-R_3Ge^*CH_2COOMe \qquad (2)$$

$$R_3Ge^* = Me(1-C_{10}H_7)PhGe$$
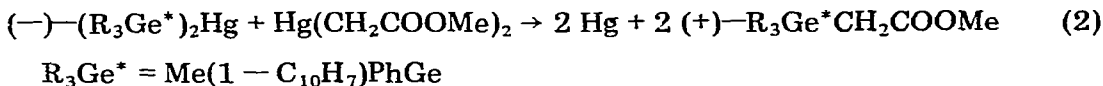
It is possible that demercuration of intermediate $R_3M—HgX$ involves the formation of ion pairs $R_3MHg^+X^-$ and/or $R_3M^+X^-$ [10]. In accord with this conclusion, addition of $(Et_3Si)_2Hg$ to an acetone solution of $Hg[C(N_2)COMe]_2$ causes a formation of metallic mercury and α-triethylsilyldiazoacetone together with unexpected diacetone alcohol [10d]. The most likely possibility is that exchange occurred to give, initially, intermediate $Et_3SiHgC(N_2)COMe$ which was subsequently demercurated to the ion pair. The anion $^-C(N_2)SOMe$ generated catalyzes the aldol-type condensation of acetone to give diacetone alcohol.

The reactions of mercurials I and II with α-mercurated ketones and α-bromo-ketones have now been investigated to ascertain whether silyl and germyl enol ethers can be prepared.

Results and discussion

The exchange reaction of α-mercurybisacetophenone with mercurials I and II in THF at 65°C results in a high yield of triethylsilyl enol ether (III) and its germanium analogue (IVa), respectively. Since the starting α-mercurated ketone has no enolic form [11] it may be assumed that reaction occurred with the initial formation of an unsymmetrical silyl- or germylmercury intermediate (V) containing a σ,π-conjugated bond system [12]. Further demercuration of intermediate V leads to ambident anions (VI). Subsequent recombination of the ion pairs gives III or IVa (Scheme 1).

SCHEME 1

An alternative reaction scheme which involves demercuration of intermediate V (M = Si) to lead to α-triethylsilylacetophenone, Et$_3$SiCH$_2$COPh, is less probable. According to Lutsenko, Baukov et al. [13], the above ketosilane is quite stable and undergoes rearrangement to siloxyalkene III under severe conditions (160°C). It has been established [14] that the rearrangement Me$_2$SiCH$_2$COPh → Me$_3$SiOC(Ph)=CH$_2$ occurs via an associative mechanism which involves a five-coordinate silicon intermediate. In the case of the reaction with compound II, along with the appropriate germyl enol IVa, α-triethylgermylacetophenone (IVb) is formed in a ratio of 86 : 14. Moreover, we have found (see below) that the O-isomer IVa slowly isomerizes to the C-isomer IVb at room temperature. This reaction is probably reversible (i.e IVa ⇌ IVb). A similar germanotropic equilibrium for the reversible isomarization of trimethylgermylated acetophenone and acetone has been reported by Lutsenko and his coworkers [15,16]. In both cases the equilibrium is strongly shifted to the C-isomer.

The reaction of equimolar quantities of α-mercurybiscyclohexanone and mercurial I or II under the same conditions yields metallic mercury and 1-triethylsiloxy-1-cyclohexene (VII) or 1-triethylgermoxy-1-cyclohexene (VIII), respectively. The results obtained are in agreement with the mechanism depicted in Scheme 1. The mechanism of the formation of VII and VIII is thought to involve initial formation of the ambident anion. This anion offers two potential sites for association with the counter-ion (e.g. Et$_3$Si$^+$). However, no formation of C-silylated or C-germylated isomers could be detected, which demonstrated the selectivity of this reaction.

Several methods are available for the synthesis of compound VII. One of them is based on the reaction of chlorotriethylsilane with an ambident enolate anion of cyclohexanone [17].

It is known [18] that mercurybisacetoacetic ester has the mercury atom bonded to the central carbon atoms of both ethyl acetoacetate groupings. However, the exchange reactions of this compound with I and II in THF lead to the ethyl ester of β-triethylsiloxycrotonic acid (IX) and its germanium analogue (X), respectively. The formation of the observed products could be rationalized by the mechanism shown in eq. 3, including decomposition of unsymmetrical mercurials to a silyl (or germyl) cation and ambident anion (XI), followed by simultaneous association of the counter-ions (cf. Scheme 1).

It should be noted that the O-silylated product IX was previously prepared by the reaction of chlorotriethylsilane with sodium acetoacetic ester [19]. In this reaction the ambident anion XI derived from proton abstraction also offers three potential sites for electrophilic attack. The structure and reactivity of enolate anion XI has been discussed previously [20,21].

According to ^{1}H NMR data (Table 2) products IX and X are mixtures of cis and trans isomers. For IX, the assignment of signals to cis and trans isomers is
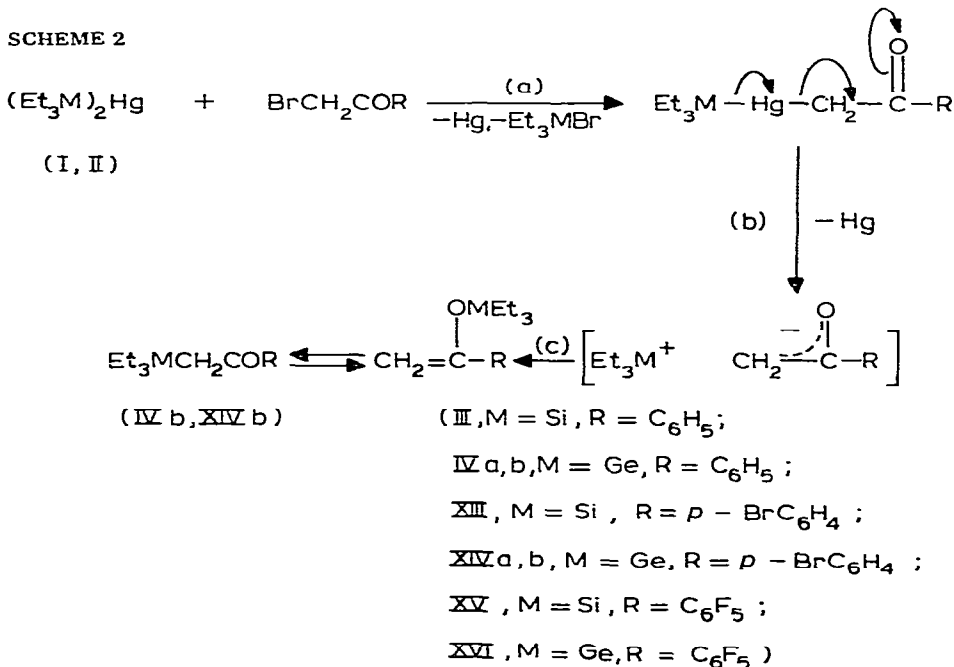
carried out by comparison of the measured chemical shifts of the vinyl proton with the value calculated using an additive scheme [22]. The assignment corresponds to that [23] for $R_3Si^*OC(Me)=CHCO_2Et$ where $R_3Si^* = Me(1—C_{10}H_7)$-PhSi. For *cis* and *trans* isomers of X the order of assignment of $CH_3C=C$ and $C=CH$ proton signals is in agreement with and argues against the order found for product IX, respectively. With association of the counter-ions (cf. eq. 3) one cannot but take into account the alternative structure $MeC(O)CH=C(OEt)$-$OSiEt_3$ (XII). However, this structure may be excluded from consideration since the calculated vinyl proton shifts for *trans* and *cis* isomer of XII (4.25 and 4.08 ppm, respectively) differ by only 0.9 ppm from the measured values.

As may be seen from the data presented in Table 1, α-bromocarbonyl compounds derived from enolizable ketones and aldehydes react with mercurials I or II, giving the corresponding silyl or germyl enol ethers in high yields [24,25]. For example, α-bromoacetophenone reacts with I under mild conditions to give enol ether III along with metallic mercury and bromotriethylsilane. However, a similar reaction of α-bromoacetophenone with mercurial II affords both *O*- and *C*-germylated products, IVa and IVb, in a ratio of 20 : 80. The fact that the mixture predominantly contains the thermodynamically more stable isomer IVb is not surprising. This may be explained by the presence in the reaction mixture of bromotriethylgermane which catalyzes the process of reversible isomerization IVa ⇌ IVb (cf. [15,16]).

Thus, the results (Table 1) may be best explained by Scheme 2.

SCHEME 2

$$(Et_3M)_2Hg \quad + \quad BrCH_2COR \xrightarrow[-Hg,-Et_3MBr]{(a)} Et_3M—Hg—CH_2—C—R$$

(I, II)

$$(b) \quad \Big| \quad -Hg$$

$$Et_3MCH_2COR \leftrightharpoons CH_2=\overset{OMEt_3}{\underset{|}{C}}-R \xleftarrow{(c)} \Big[Et_3M^+ \quad CH_2=\overset{O}{\underset{}{C}}-R\Big]$$

(IV b, XIV b)   (III, M = Si, R = C_6H_5;

   IV a,b, M = Ge, R = C_6H_5;

   XIII, M = Si, R = $p — BrC_6H_4$;

   XIV a,b, M = Ge, R = $p — BrC_6H_4$;

   XV, M = Si, R = C_6F_5;

   XVI, M = Ge, R = C_6F_5)

The mechanism of the formation of silyl and germyl enol ethers is thought to involve initial formation of unsymmetrical silyl- or germylmercurials via a four-centre exchange reaction [step a]. This step is similar to that postulated for thermal reaction of $(Me_3Si)_2Hg$ with arylhalides [26,27], pentafluorobromo-

TABLE 1

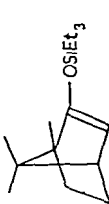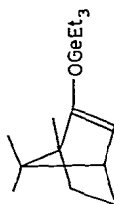ANALYTICAL AND OTHER DATA FOR SILYL AND GERMYL ENOL ETHERS AND RELATED COMPOUNDS

Compound	Method [h]	Yield (%)	B.p. (°C) (mmHg)	n_D^{20}	Analysis, found (calcd.) (%)		
					C	H	Si/Ge
$Et_3SiOC(Ph)=CH_2$ [a] (III)	1	67	87–89 (2)	1.5065			
	2	83	81–83 (1)	1.6075			
$Et_3GeOC(Ph)=CH_2$ (IVa) } Et_3GeCH_2COPh (IVb)	1	79	105–106 (1–2)	1.5270	60.02 (60.28)	7.93 (7.96)	25.55 (26.02)
Et_3SiO⟶ (VII)	1	74	97–99 (12)	1.4630	67.81 (67.85)	10.96 (11.39)	12.92 (13.22)
Et_3GeO⟶ (VIII)	1	72	70–71 (1)	1.4770	55.96 (56.10)	9.42 (9.41)	27.97 (28.25)
$Et_3SiOC(Me)=CHCO_2Et$ (IX)	1	83	76–78 (1.5)	1.4580	58.88 (58.97)	9.99 (9.90)	11.20 (11.48)
$Et_3GeOC(Me)=CHCO_2Et$ (X)	1	77	84–85 (1.5)	1.4760	50.18 (49.89)	8.33 (8.37)	25.20 (25.13)
$Et_3SiOC(C_6H_4Br\text{-}p)=CH_2$ (XIII)	2	50	92–94 (2.8×10^{-2})	1.5315	53.94 (53.67)	6.49 (6.76)	8.90 (8.96)
$Et_3GeOC(C_6H_4Br\text{-}p)=CH_2$ (XIVa) } $Et_3GeCH_2COC_6H_4Br\text{-}p$ (XIVb)	2	77	107–108 (2.1×10^{-2})	1.5628	46.65 (46.99)	5.89 (5.92)	20.22 (20.29)
$Et_3SiOC(C_6F_5)=CH_2$ (XV)	2	86	71–72 (1)	1.5498	51.88 (51.84)	5.23 (5.28)	8.45 (8.66)
	1			1.4480			
$Et_3GeOC(C_6F_5)=CH_2$ (XVI)	2	68	80–82 (1)	1.4659	45.86 (45.59)	4.50 (4.64)	19.46 (19.68)
	1			1.4681			
⟶$OSiEt_3$ (XVII)	2	96	60–62 (4×10^{-2})	1.4688	72.23 (72.11)	11.30 (11.35)	10.68 (10.54)
⟶$OGeEt_3$ (XVIII)	2	92	81–83 (1.1×10^{-2})	1.4852	61.29 (61.79)	9.60 (9.72)	23.44 (23.34)

TABLE 1 (continued)

Compound	Method[h]	Yield (%)	B.p. (°C) (mmHg)	n_D^{20}	Analysis, found (calcd.) (%)		
					C	H	Si/Ge
Et₃SiO, Ph / C=C / Me, H (Z) (XIX)	2	78	62—64 (2.5 × 10⁻²)	1.6180	72.43 (72.52)	9.76 (9.74)	10.97 (11.30)
Et₃GeO, Ph / C=C / Me, H (Z) (XX)	2	79	81—83 (2.5 × 10⁻²)	1.5380	61.49 (61.50)	7.41 (8.25)	25.71 (24.78)
Et₃GeO, H / C=C / Me, Ph (E) (XXI)							
Et₃SiOCH=CMe₂[b] (XXII)	2	95[c]		1.4358	65.01 (64.45)	21.11 (11.90)	15.23 (15.06)
Et₃GeOCH=CMe₂ (XXIII)	2	95[c]		1.4551	52.52 (52.02)	9.98 (9.60)	30.31 (31.44)
Et₃SiO, H / C=C / Me₃C, Br (E) (XXIV)	2	84	48—49 (1)	1.4770	49.19 (49.14)	8.45 (8.59)	9.26 (9.58)
Et₃GeO, H / C=C / Me₃C, Br (E) (XXV)	2	93	51—52 (1)	1.4918	42.94 (42.46)	7.40 (7.46)	21.21 (21.49)
Et₃SiO / C=CH₂ (XXVI), BrCH₂	2	69	44—45 (1)	1.4731	43.43 (43.03)	7.78 (7.62)	11.07 (11.18)
Et₃GeO / C=CH₂ (XXVII), BrCH₂	2	72	48—50 (1)	1.4920	35.99 (36.55)	6.36 (6.48)	24.71 (24.54)

Compound	[h]	Yield	b.p. (mm)	n_D^{20}	C	H	found (calcd.)
Et₃SiO / H \ C=C / BrCH₂ \ Me (E) (XXX)	2	80	47—48 (1)	1.4810	45.16 (45.28)	8.15 (7.98)	10.64 (10.59)
Et₃SiO—C=CH₂ (XXVIII) / MeCHBr							
Et₃GeO / H \ C=C / BrCH₂ \ Me (E) (XXXI)	2	68	50—52 (1)	1.4970	38.71 (38.77)	6.79 (6.83)	22.97 (23.43)
Et₃GeO—C=CH₂ (XXIX) / MeCHBr							
Et₃GeCH(CN)CO₂Et [d] (XXXII)	2	78	93—94 (1)	1.4674			
Et₃GeCH(CO₂Et)₂ [e] (XXXIII)	2	84	102—104 (1)	1.4613			
Et₃SiO \ C=CHCN [f] (XXXIV) / EtO	2	57	108—109 (1)	1.4617			
Et₃SiO \ C=CHCO₂Et [g] (XXXV) / EtO	2	70	106—107 (1)	1.4609			

[a] Lit. [13]: b.p. 86—88°C/1.5; n_D^{20} 1.5062. [b] Lit. [40a]; b.p. 89°C/25 mm; n_D^{20} 1.4337. [c] GLC was used in determining yields and isolating pure samples for analysis and spectroscopy. [d] Lit. [37]; b.p. 94—95°C/1 mm; n_D^{20} 1.4650. [e] Lit. [38]: b.p. 154°C/14 mm; Lit. [37]: b.p. 110°C/1 mm; n_D^{20} 1.4600. [f] Lit. [37]: b.p. 108°C/1—2 mm; n_D^{20} 1.4590. [g] Lit. [37]. [h] 1, reaction with α-ketomercurials; 2, reaction with α-bromo carbonyl compounds.

TABLE 2

SOME IR AND ^{1}H NMR DATA FOR SILYL AND GERMYL ENOL ETHERS AND RELATED COMPOUNDS

No	IR (cm^{-1}) C=C (C=O)	^{1}H NMR, δ (ppm) J (Hz)					
		=CH cis ^{a}	=CH trans ^{a}	=C—CH$_n$ n = 1, 2, 3	CH$_2$	—CH$_3$	$(n)J$(HH)
III	1617	4.72 d	4.27 d				1.8(2)
IVa	1628	4.58 d	4.01 d				1.8(2)
IVb	(1662)			2.64 s			
VII	1667	4.73 t		1.96 m	1.55 m		2.8(3)
VIII	1660	4.42 t		1.89 m	1.53 m		2.8 (3)
IX	1625	5.00 s	4.94 s	2.22 s 1.85 s	4.01 k	1.22 t	7.5(3)
X	1602	4.73 s	4.89 s	2.20 s 1.79 s	3.98 k	1.29 t	7.5(3)
XIII	1615	4.76 d	4.34 d				1.8(2)
XIVa	1627	4.59 d	4.06 d				1.8(2)
XIVb	(1659)			2.59 s			
XV	1630	4.68 d	4.38 d, t				2.0(2)
XVI	1610	4.47 d	4.27 d, t				2.0(2)
XVII	1620	4.53 d		2.14 m	1.79 m 1.45 m	0.86 c 0.65 c	3.5(3)
XVIII	1610	4.27 d		2.09 m	1.77 m 1.42 m	0.84 c 0.69 c	3.4(3)
XIX	1657		5.29 k	1.91 d			0.9(4)
XX	1640		5.23 k	1.86 d			0.9(4)
XXI	1640	5.47 k		1.96 d			0.8(4)
XXII	1685	5.95 m		1.55 d 1.51 d			1.0(4) 1.2(4)
XXIII	1674	6.00 m		1.47 d 1.52 d			1.2(4) 1.0(4)
XXIV	1618	5.52 s				1.09 s	
XXV	1587 1602	5.15 s				1.06 s	
XXVI	1629	4.35 d	4.17 m	3.74 m			1.3(2) 0.6(4)
XXVII	1610 1638	4.13 d	3.89 d, t	3.65 d			1.3(2) 0.6(4)
XXX	1648	4.52 q		3.60 q		1.43 d, t	6.6(3) 0.7(5)
XXVIII		4.15 d	4.02 q	4.28 q		1.57 d	1.5(2) 6.6(3) 0.5(4)
XXXI	1650 1606	4.70 q		3.68 q		1.47 d, t	6.8(3) 0.7(5)
XXIX		4.12 d	3.82 q	4.42 q		1.68 d	1.5(2) 6.8(3) 0.5(4)

^{a} The cis and trans position of the H atom relative to OMEt$_3$ is related to the E- and Z-forms, respectively.
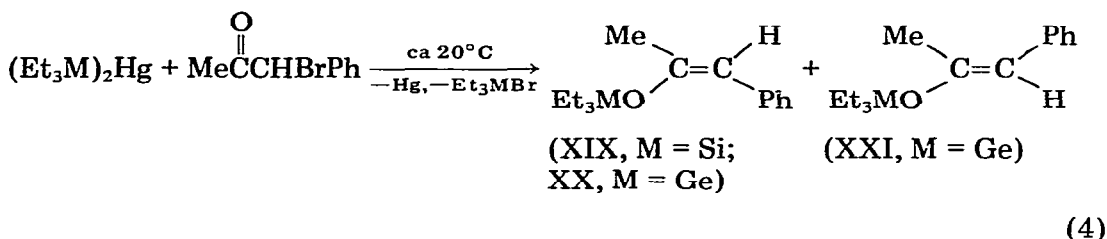
benzene and bromotrifluoroethylene [28]. Other steps of Scheme 2 have been discussed above.

In these reactions, the reactivity of α-bromoacetophenones is enhanced by a decrease in the electron-donating effect of the aromatic ring in the order: BrCH$_2$COC$_6$H$_5$ < BrCH$_2$COC$_6$H$_4$Br-p < BrCH$_2$COC$_6$F$_5$. Thus, with BrCH$_2$COC$_6$H$_5$ the reaction proceeds under more severe conditions (100°C) than those required for BrCH$_2$COC$_6$F$_5$ which reacts with mercurials I and II in hexane at —78°C.

We have prepared the product IVa by a photochemical reaction of α-bromo-acetophenone with II in hexane at 30°C. Under these conditions the reaction

is complete within ca. 15 min to yield a pure O-isomer. It has been shown that the above isomer, when kept in an evacuated ampoule (2 months at ca 20°C) isomerizes to product IVb. The overall yield (without isolation of IVa) is 20%.

Since the difficulty synthesized silyl enol ether of camphor was formed in good yield under some of the reaction conditions [29—34], 3-bromocamphor was treated with mercurials I and II in benzene to demonstrate the synthetic value of this reaction. The results are shown in Table 1. The yields of triethylsilyl enol ether (XVII) and its germanium analogue (XVIII) represent isolated yields of distilled material. A similar reaction with 1-phenyl-1-bromopropan-2-one proceeds under mild conditions in a highly stereoselective fashion, leading predominantly to the Z-isomer.

$$(Et_3M)_2Hg + MeCCHBrPh \xrightarrow[-Hg,-Et_3MBr]{ca\ 20°C}$$

Me C=C H ; Me C=C Ph
Et₃MO Ph + Et₃MO H

(XIX, M = Si; (XXI, M = Ge)
XX, M = Ge)

$$(4)$$

A special experiment has shown that the presence of the E-isomer (XXI) in the reaction mixture (isomer ratio is 90 : 10 from the ^1H NMR data) cannot be explained in terms of an isomerization XX → XXI. The reaction of 2-methyl-2-bromopropanal with I and II also affords silyl (XXII) and gernyl (XXIII) enol ethers, respectively.

Finally, in order to demonstrate the synthetic potential of these new reagents, we have used the method described above to effect a simple synthesis of bromo(triethylsiloxy)alkenes (i.e., triethylsilyl bromoenol ethers) and their germanium analogues. Two methods for the synthesis of such silyl enol ethers are known.
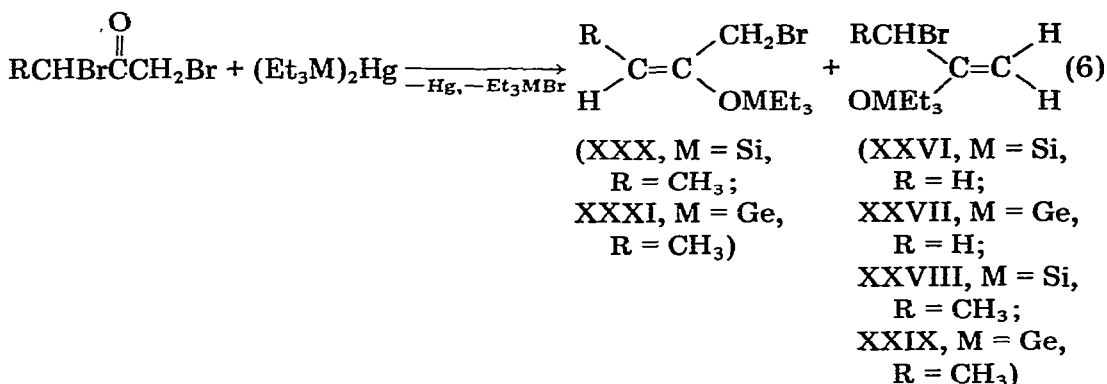
A recent report [35] describes that vic-bromo(trimethylsiloxy)alkenes can be prepared regioselectively from the appropriate silyl enol ethers via bromination at low temperature followed by dehydrobromination of the 1,2-dibromo-alkyl trimethylsilyl ether obtained. Another possible pathway involves treatment of 2-methyl-2-bromobutan-3-one with lithium diisopropylamide and subsequent reaction of the lithiated product with Me₃SiCl [36].

We have examined the reaction of mercurials I and II with α,α- and α,α'-dibromo carbonyl compounds. For example, of great interest was the success of such a reaction with Br₂CHCOt-Bu which did indeed give the expected (E)-3,3-dimethyl-2-triethylsiloxy-1-bromo-1-butene (XXIV) and its germanium analogue (XXV), respectively.
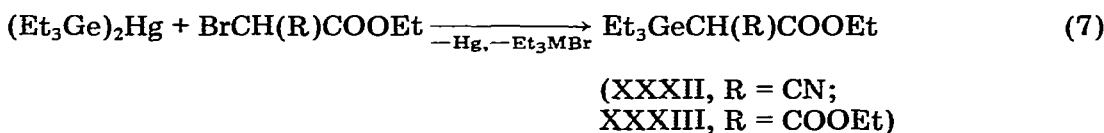
$$(Et_3M)_2Hg + Br_2CHCt-Bu \xrightarrow[-Hg,-Et_3MBr]{}$$

t-Bu C=C Br (E)
Et₃MO H

(XXIV, M = Si; XXV, M = Ge)

$$(5)$$
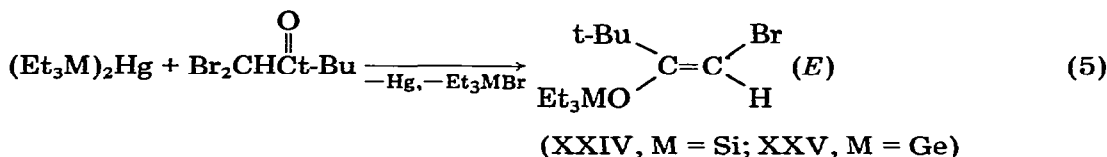
With α,α'-dibromo ketones, enol ethers with the bromine atom bound to the

sp^3 carbon atom are formed.

$$RCHBr\overset{O}{\overset{\|}{C}}CH_2Br + (Et_3M)_2Hg \xrightarrow[-Hg,-Et_3MBr]{} \underset{H}{\overset{R}{>}}C{=}C\underset{OMEt_3}{\overset{CH_2Br}{<}} + \underset{OMEt_3}{\overset{RCHBr}{>}}C{=}C\underset{H}{\overset{H}{<}} \quad (6)$$

(XXX, M = Si,   (XXVI, M = Si,
R = CH$_3$;   R = H;
XXXI, M = Ge,   XXVII, M = Ge,
R = CH$_3$)   R = H;
                            XXVIII, M = Si,
                              R = CH$_3$;
                            XXIX, M = Ge,
                            R = CH$_3$)

We have also studied the reactions of germylmercurial II with bromocyano-acetic and bromomalonic esters. These reactions were carried out in THF at room temperature. These conditions lead to the formation of the known *C*-germyl-ated products (XXXII and XXXIII) [cf. 37.38]. Only traces of the corresponding *O*-germylated isomers were detected in the reaction mixtures.

$$(Et_3Ge)_2Hg + BrCH(R)COOEt \xrightarrow[-Hg,-Et_3MBr]{} Et_3GeCH(R)COOEt \quad (7)$$

(XXXII, R = CN;
XXXIII, R = COOEt)

In contrast, the reactions of the same bromoesters with silylmercurial I in THF afford predominantly, if not exclusively, *O*-silylated products. The yields of 2-ethoxy-2-triethylsiloxy-2-propenenitrile (XXXIV) and the ethyl ester of the same acid (XXXV) are 57 and 70%, respectively. Products XXXIV and XXXV were identified by comparison of IR and NMR spectra with previously described [37] samples.

Experimental

All reactions were carried out in evacuated sealed ampoules following the technique described in ref. 39. The IR spectra were recorded on a UR-20 spectometer. NMR spectra were obtained on a Tesla BS 487C (80 MHz) instrument with hexamethyldisiloxane as internal standard. Typical experiments are given below.

3-Triethylgermoxy-1-cyclohexene (VIII)

A mixture of 3.8 g (7.3 mmol) II, 2.90 g (7.3 mmol) of Hg[$\overline{\text{CHCO(CH}_2)_3\text{CH}_2}$]$_2$ and 20 ml of THF was heated in an ampoule for 6 h at 65°C, the characteristic yellow colour of the germylmercurial having disappeared. Metallic mercury (2.93 g, ca. 100%) was precipitated. Distillation of the organic layer gave 2.70 g (72%) of compound VIII (see Table 1).

Photochemical reaction of the mercurial II with α-bromoacetophenone

A mixture of 3.46 g (17.4 mmol) of α-bromoacetophenone, 9.10 g (17.4

mmol) of II and 30 ml of hexane was irradiated in a molydenic glass ampoule at —30°C for 20 min. (DPT-375 lamp; 10 cm distance from the light source). The mixture was decanted from mercury (3.44 g, 99%) and the hexane and volatile products removed by recondensation in vacuo. Distillation of the residue gave 2.74 g (63%) of 1-phenyl-1-triethylgermoxyethylene (IVa) b.p. 103—105°C/1 mm Hg, n_D^{20} 1.5260. (Found: C, 60.01; H, 7.91; Ge, 25.53. $C_{14}H_{22}GeO$ calcd.: C, 60.29; H, 7.95; Ge, 26.02%). IR (cm^{-1}): ν(C=C) 1628. NMR (CCl$_4$) (δ, ppm): 4.59 (d, 1 H, =CH$_2$), 4.05 (d, 1 H, =CH$_2$). No C-isomer. IVb was detected in the reaction mixture. The volatiles were analyzed by GLC. Bromotriethylgermane (88%) was identified.

1-Pentafluorophenyl-1-triethylgermoxyethylene (XVI)

A solution of 2.81 g (10.4 mmol) of BrCH$_2$COC$_6$F$_2$ in 15 ml of hexane was degassed, frozen with liquid nitrogen and 5.61 g (10.8 mmol) of II was added. During the course of subsequent defrosting mercury was eliminated (2.04 g, 98%). The reaction was completed after 3—5 min. The organic layer was fractionated to obtain the desired product (2.71 g, 68%), b.p. 64—66°C/1 mm Hg, n_D^{20} 1.4658. (Found: C, 45.86; F, 25.71; Ge, 19.46. $C_{14}H_{17}F_5GeO$ calcd.: C, 45.59; H, 4.64; F, 25.74; Ge, 19.68%). IR (cm^{-1}): ν(C$_6$F$_5$) 1495, 1520, 1650, ν(C=C) 1610. NMR (CCl$_4$) (δ, ppm): 4.47 (q, 1 H, =CH$_2$), 4.27 (d, t, 1 H, =CH$_2$, ^2J(HH) 2.0 Hz).

(E)-3,3-Dimethyl-2-triethylgermoxy-1-bromo-1-butene (XXV)

Bis(triethylgermyl)mercury (4.65 g, 8.9 mmol) was added to a solution of 2.31 g (8.9 mmol) of BrCHCOt-Bu in 7 ml of benzene. The exothermal reaction was complete after 10—15 min when the organic layer was decanted from the metallic mercury (1.71 g, 96%). Distillation of the organic layer gave 2.81 g (93%) of XXV, b.p. 51—52°C/1 mm Hg, n_D^{20} 1.4918. (Found: C, 42.91; H, 7.40; Br, 23.59; Ge, 21.21. $C_{12}H_{25}BrGeO$ calcd.: C, 42.66; H. 7.46; Br, 23.65; Ge, 21.47%). (see Table 2). The volatiles were analyzed by GLC. Bromotriethylgermane (83%) was identified.

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