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FUNCTIONALLY-SUBSTITUTED ORGANOGERMANIUM COMPOUNDS

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In a previous paper we reported the results of our study on the reactions of esters of metalated carboxylic acids with halosilanes and the conditions of the rearrangement of *O*-silyl-*O*-alkylketeneacetals into esters of silylacetic acid[1]. The later investigation of the reaction of metalated (Hg, Sn) aldehydes, ketones and esters of carboxylic acids made it possible to develop a number of preparation techniques for synthesizing functionally-substituted organogermanium compounds using hydrides and halogermanes[2,2a]. These techniques enabled α-germylated ketones and esters to be obtained comparatively easily.

$$R_nGeX_{4-n} + Hg(CH_2COOR)_2 \left\{ \begin{array}{l} \xrightarrow{X=I} R_nGe(CH_2COOR)_{4-n} + HgI_2 \\ \xrightarrow{X=H} R_nGe(CH_2COOR)_{4-n} + Hg + CH_3COOR \end{array} \right.$$

$$R_2GeHX + Hg(CH_2COOR)_2 \left\{ \begin{array}{l} \xrightarrow{X=I} R_2Ge(H)CH_2COOR + IHgCH_2COOR \\ \xrightarrow{X=Cl} R_2Ge(Cl)CH_2COOR + Hg + CH_3COOR \end{array} \right.$$

$$R_3GeX + MCH_2COCH_3 \longrightarrow R_3GeCH_2COCH_3 + MX$$

$$(M = \tfrac{1}{2}\,Hg,\ IHg\text{-},\ R_3Sn\text{-};\ X = Cl,\ Br,\ I)$$

In the present paper we give the results of our work on the conditions for synthesizing functionally-substituted organogermanium compounds using (a) esters of (trialkylstannyl)acetic acid and halogermanes and (b) the reaction of alkoxygermanes with ketene.

Esters of (trialkylstannyl)acetic acid do not react so readily with halogermanes as with the corresponding halosilanes. In this case it is sometimes possible to react not only iodogermane, but also chlorogermanes which as a rule do not react with bis(carboalkoxymethyl)mercury. In the reaction of tetrahalogermanes with esters of (trialkylstannyl)acetic acid, one, two, three or four halogen atoms can be replaced by carbomethoxymethyl groups.

$$GeX_4 \xrightarrow[-\,R_3SnX]{+\,R_3SnCH_2COOCH_3} \left\{ \begin{array}{l} \xrightarrow{1:1} X_3GeCH_2COOCH_3 \\ \xrightarrow{1:2} X_2Ge(CH_2COOCH_3)_2 \\ \xrightarrow{1:3} XGe(CH_2COOCH_3)_3 \\ \xrightarrow{1:4} Ge(CH_2COOCH_3)_4 \end{array} \right.$$

$$X = Cl,\ Br,\ I$$

In each case, the yields amount to 75–90 %. The same results can be obtained also by successive replacement of the halogen atoms in halogermanes.

$$Cl_nGe(CH_2COOCH_3)_{4-n} \xrightarrow[-\,R_3SnCl]{+\,R_3SnCH_2COOCH_3} Cl_{n-1}Ge(CH_2COOCH_3)_{5-n}$$

Furthermore, alkoxygermanes react readily with esters of (trialkylstannyl)acetic acid.

$$(CH_3O)_3GeCl \xrightarrow[-\,R_3SnCl]{+\,R_3SnCH_2COOCH_3} (CH_3O)_3GeCH_2COOCH_3$$

In the case of trialkylhalogermanes the reaction proceeds readily with iodides (~ 80 %) and poorly with chlorides (27 %).

$$Et_3GeI \xrightarrow[-\,R_3SnI]{+\,R_3SnCH_2COOR'} Et_3GeCH_2COOR' \qquad (R' = CH_3,\ Bu)$$

A spectroscopic study of the reaction products was carried out in connection with the transfer of the molecule reaction center which occurs rather frequently in the reactions of metalated aldehydes, ketones and esters of carboxylic acids[3], where one can expect the formation of *O*-germyl-*O*-alkylketeneacetals as well as germylated

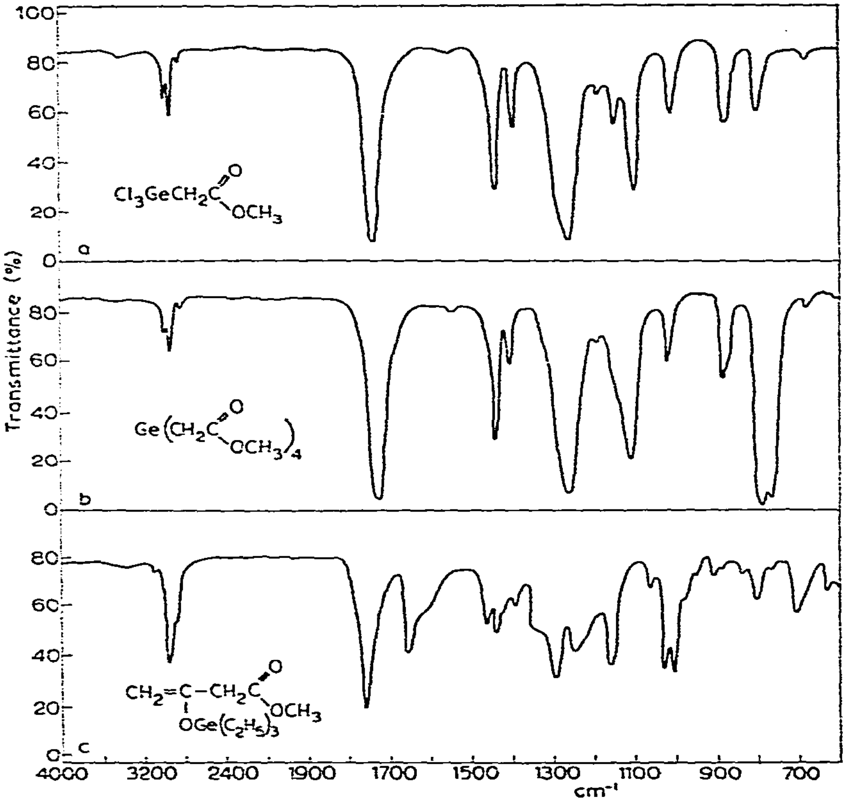
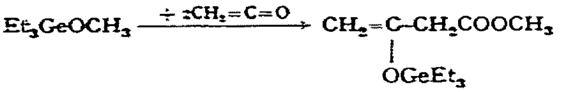


Fig. 1. (a), IR spectrum of methyl (trichlorogermyl)acetate; (b), IR spectrum of methyl (germyl)-tetrakisacetate; (c), IR spectrum of methyl 3-(triethylgermyloxy)-3-butenoate.

alkylacetates. Intensive absorption bands in the IR spectra*, at 1730–1750 cm^{-1}, corresponding to valency oscillations in the ester group of germylated alkylacetates, were detected in all cases (see Fig. 1). Stretching vibrations adequate to C=C absorption were absent in the spectra. ^{1}H NMR spectra were in agreement with the proposed structure[4].

When examining the interaction of the alkoxy derivatives of the elements of group IVB with ketene, we found that these derivatives react differently. Whereas alkoxystannanes react readily evolving heat to give high yields of the esters of stannylacetic acid[5], alkoxysilanes do not react with ketene under these conditions and trialkylalkoxygermanes react more sluggishly than the corresponding trialkylalkoxystannanes to give final products of different structure.

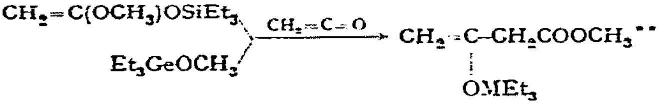
Methyl 3-(triethylgermyloxy)-3-butenoate in 70% yield was isolated from the reaction mixture obtained by saturating triethylmethoxygermane with ketene. The formation of this compound can be expressed by the following equation:



$$Et_3GeOCH_3 \xrightarrow{+2CH_2=C=O} CH_2=C(OGeEt_3)-CH_2COOCH_3$$

It can be assumed that, in this case, the reaction proceeds through the intermediate, *O*-triethylgermyl-*O*-methylketeneacetal, which reacts further to give methyl 3-(triethylgermyloxy)-3-butenoate. The assumption of the existence of the intermediate, *O*-triethylgermyl-*O*-methylketeneacetal (which was not isolated) is based mainly on the analogy with the studied reactions of *O*-silyl-*O*-alkylketeneacetals that have been isolated. This analogy can be seen from the following reactions.

I. On saturating both trialkylalkoxygermane and *O*-triethylsilyl-*O*-methylketeneacetal with ketene, compounds of the same structure are formed.



$$\left.\begin{array}{r} CH_2=C(OCH_3)OSiEt_3 \\ Et_3GeOCH_3 \end{array}\right\rangle \xrightarrow{CH_2=C=O} CH_2=C(OMEt_3)-CH_2COOCH_3{}^{**}$$

II. On heating *O*-triethylsilyl-*O*-methylketeneacetal with HgI$_2$, a irreversible isomerization to methyl (triethylsilyl)acetate occurs.

$$CH_2=C(OCH_3)OSiEt_3 \xrightarrow{HgI_2;\,t} Et_3SiCH_2COOCH_3$$

When ketene is passed into an alcoholic solution of trialkylalkoxygermane after the addition of a small amount of HgI$_2$, the ester of (trialkylgermyl)acetic acid is formed, in high yield, as the only product and alkyl 3-(trialkylgermyloxy)-3-butenoate is not formed at all.

$$Et_3GeOR + CH_2=C=O \xrightarrow{HgI_2 \cdot ROH} Et_3GeCH_2COOR \qquad (R = CH_3, Bu)$$

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* IR spectra were obtained with thin films using a spectrometer "Jasko", IR-S(KCl).

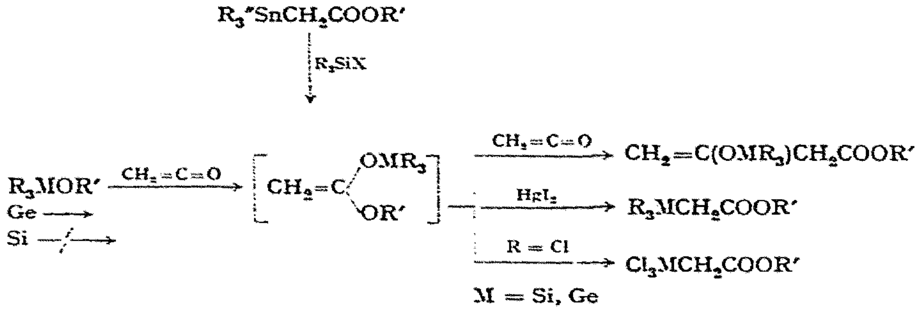
** The rearrangement, $CH_2=C(OMR_3)CH_2COOCH_3$ to $CH_3C(OMR_3)=CHCOOCH_3$, will be reported in a following paper.

III. As we have already reported[1], *O*-trichlorosilyl-*O*-methylketeneacetal is isomerized to methyl (trichlorosilyl)acetate at room temperature; the isomerization proceeds rapidly on moderate heating. If ketene is passed into trichloroalkoxygermanes, alkyl (trichlorogermyl)acetate is formed. In this case, the alkyl butenoate was again not isolated.

$$CH_2{=}C(OCH_3)OSiCl_3 \xrightarrow[0.5\ h]{70^\circ} Cl_3SiCH_2COOCH_3$$

$$Cl_3GeOR + CH_2{=}C{=}O \longrightarrow Cl_3GeCH_2COOR \qquad (R = CH_3, Et)$$

All these reactions can be tabulated in a scheme where the central position is taken by the keteneacetal derivative, isolated in the case of organosilicon compounds and assumed in the case of organogermanium compounds.



The facts presented above show that the formation of one isomeric form can result from the rearrangement of another form produced initially and the course of the reaction, therefore, depends on their relative stability. This fact must be taken into account, especially when considering schemes of product formation in the reactions of compounds that exhibit dual reactivity and frequently react with transfer of the reaction center.

EXPERIMENTAL*

Many of the compounds used in this work were prepared by methods already described in the literature, *e.g.*, methyl (triethylstannyl)acetate and methyl (tributylstannyl)acetate[5], triethyliodogermane and triethylchlorogermane[6], triethylmethoxygermane and trimethoxychlorogermane[7], trichloroethoxygermane[8].

1. Tributylbutoxystannane (*I*)

22 g (0.068 mole) of tributylmethoxystannane and 25 g (0.55 mole) of butyl alcohol were heated and the distillate of methyl alcohol collected. Fractionation yielded 20.7 g (84% yield) of (I), b.p. 112–113° at 1.5 mm, n_D^{20} 1.4705, d_4^{20} 1.0775; MR_D 94.21 (calcd. 93.78). (Found: C, 52.86; H, 9.98; Sn, 32.66. $C_{16}H_{36}SnO$ calcd.: C, 52.91; H, 9.99; Sn, 32.69%).

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* Together with the students, V. I. AVDEEVA and I. YU. BELAVIN.

TABLE 1

PROPERTIES OF THE COMPOUNDS PREPARED BY REACTION BETWEEN HALOGERMANES AND TRIALKYLSTANNYLACETATE

Compound	*No. of expt*	*% Yield*	*B.p. (mm)*	n_D^{20}	d_4^{20}	MR_D[a]		*Found (%)*			*Calcd. (%)*		
						Found	*Calcd.*	*C*	*H*	*Ge*	*C*	*H*	*Ge*
$Cl_3GeCH_2COOCH_3$	7	87	70–71° (6.5)	1.4820	1.6760	42.91	42.95	14.68	2.27		14.30	2.00	
$Cl_3GeCH_2COOCH_3$	4a	62	68–70 (7)	1.4835	1.6765	42.97	42.95	14.47	2.09		14.30	2.00	
Cl_3GeCH_2COOEt	4b	61	49–50 (1.5)	1.4750	1.5756	47.55	47.59	18.53	2.88		18.05	2.65	
$Cl_2Ge(CH_2COOCH_3)_2$	8	75	106–110 (2)	1.4870	1.5430	53.99							
$Cl_2Ge(CH_2COOCH_3)_2$	9	76	95–96 (0.5)	1.4870	1.5426	54.00	54.13	25.04	3.74	24.52	24.88	3.48	25.06
$ClGe(CH_2COOCH_3)_3$	10	77	131–133 (1)	1.4860	1.4412	65.20	65.34	32.94	4.59	22.09	33.03	4.62	22.18
$ClGe(CH_2COOCH_3)_3$	11	80	140–142 (2)	1.4855	1.4365	65.35	65.34						
$Ge(CH_2COOCH_3)_4$	12	77	125–126 (0.045)	1.4810	1.3589	76.42	76.50	39.22	5.90	20.12	39.50	5.52	19.90
$Br_3GeCH_2COOCH_3$	13	88	81–82 (2)	1.5613	2.3534	53.06	53.33	9.91	1.45		9.35	1.30	
$Br_2Ge(CH_2COOCH_3)_2$	14	70	114–116 (2)	1.5248	1.9220	60.42	60.06	19.04	2.66		19.45	2.57	
$(CH_3O)_3GeCH_2COOCH_3$	15	67	67–68 (1)	1.4400	1.3596	46.28	46.24	30.88	6.34	30.28	30.18	5.91	30.40
$Et_3GeCH_2COOCH_3$	16	85	80–82 (7)	1.4583	1.1070	57.43	57.30						
$Et_3GeCH_2COOCH_3$	5b	92	50–52 (1.5)	1.4563	1.1105	57.03	57.30						
Et_3GeCH_2COOBu	18	74	70–72 (1)	1.4580	1.0579	70.75	71.25						
Et_3GeCH_2COOBu	6	81	69–70 (1)	1.4578	1.0580	70.84	71.25	51.95	9.45	26.82	52.12	9.53	26.41
$CH_2{=}C(OGeEt_3)CH_2COOCH_3$	5a	69	81–83 (1)	1.4615	1.1272	66.98	67.12	48.63	8.18	25.83	48.06	8.07	26.41
$I_3GeCH_2COOCH_3$	19	65	116–117 (1)		2.90			7.21	0.94	13.69	6.84	0.96	13.76

[a] We used the following bond refractions: Ge–Cl, 7.94[10]; Ge–Br, 11.4[11]; other bond refractions were taken from ref. 12.

2. *Butyl (tributylstannyl)acetate, (II)*

On passing excess ketene through 21.2 g (0.058 mole) of (I), 18.9 g (80 % yield) of (II) are obtained, b.p. 122–123° at 1 mm, n_D^{20} 1.4772, d_4^{20} 1.1003; MR_D 104.09 (calcd. 103.58). (Found: C, 54.16; H, 9.71; Sn, 29.31. $C_{18}H_{38}O_2$ calcd.: C, 54.35; H, 9.45; Sn, 29.30 %).

3. *Triethylbutoxygermane, (III)*

Triethylchlorogermane (10.2 g, 0.052 mole) was added dropwise to 20.7 g (0.057 mole) of (I); the reaction mixture was heated for 0.5 h at 50–60°. Fractionation yielded 10.9 g (90 % yield) of (III), b.p. 81–82° at 9 mm, n_D^{20} 1.4420 (literature[9], b.p. 290° at 755 mm, n_D^{20} 1.4406).

4. *Reaction of trichloroalkoxygermanes with ketene*

(a) Methyl (trichlorogermyl)acetate, $Cl_3GeCH_2COOCH_3$, (IVa). Excess ketene was bubbled through 14 g (0.067 mole) of trichloromethoxygermane at 19–20°. Fractionation yielded 10 g (62 % yield) of (IVa), b.p. 68–70° at 7 mm.

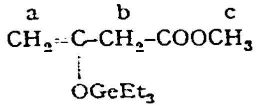
(*b*) *Ethyl (trichlorogermyl)acetate, Cl_3GeCH_2COOEt, (IVb).* On passing excess of ketene through 3.9 g (0.017 mole) of trichloroethoxygermane at 19–20°, 2.9 g (61 % yield) of IVb was obtained, b.p. 49–50° at 1.5 mm.

5. *Reaction of triethylmethoxygermane (V) with ketene*

(*a*) *Methyl 3-(triethylgermyloxy)-3-butenoate, $CH_2{=}C(OGeEt_3)CH_2COOCH_3$, (Va).* Ketene was passed through 3.4 g (0.017 mole) of (V) at −5–10°. Fractionation yielded 0.9 g of (V) and 2.5 g of (Va) (69 % yield based on reacted (V)), b.p. 81–83° at 1 mm.

The IR and ^1H NMR spectra of (Va) are in agreement with its structure. The IR spectrum of (Va) shows a C=C stretching vibration at 1650 cm⁻¹ and a C=O stretching vibration at 1750 cm⁻¹ (Fig. 1).

The ^1H NMR spectrum* of (Va) shows a pattern, which is interpreted as follows:



$$\overset{a}{CH_2}{=}\underset{\displaystyle OGeEt_3}{C}-\overset{b}{CH_2}-COO\overset{c}{CH_3}$$

a: = 3.81 and 3.85 ppm (two protons)

b: = 2.95 ppm (two protons)

c: = 3.6 ppm (three protons).

(*b*) *Methyl (triethylgermyl)acetate, $Et_3GeCH_2COOCH_3$, (Vb).* On passing ketene through a solution of 5.2 g (0.027 mole) of (V) and 0.4 g of HgI_2 in 6 ml of methyl alcohol, 5.8 g (92 % yield) of (Vb) are obtained, b.p. 50–52° at 1.5 mm (literature [2a], b.p. 89–92° at 9 mm, n_D^{20} 1.4570, d_4^{20} 1.1052).

6. *Reaction of triethylbutoxygermane, (VI), with ketene*

Butyl (triethylgermyl)acetate, Et_3GeCH_2COOBu, (VIa). Excess ketene was

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* The NMR spectrum was taken in carbon tetrachloride solution with tetramethylsilane as internal reference with a spectrograph Hittachi H-60.

TABLE 2

REACTION BETWEEN HALOGERMANES AND TRIALKYLSTANNYLACETATE (PRODUCTS AND CONDITIONS)

No. of expt.	*Product*	*Reagent*	*Mole*	*Reactant*	*Mole*	*Conditions*		*% Yield*
						Time of heating (h)	*Temp.*	
7	$Cl_3GeCH_2COOCH_3$	$GeCl_4$	0.37	$Bu_3SnCH_2COOCH_3$	0.28	4	60°	87
8	$Cl_2Ge(CH_2COOCH_3)_2$	$GeCl_4$	0.52	$Et_3SnCH_2COOCH_3$	0.10	5	100	75
9	$Cl_2Ge(CH_2COOCH_3)_2$	$Cl_3GeCH_2COOCH_3$	0.54	$Et_3SnCH_2COOCH_3$	0.54	3	100	76
10	$ClGe(CH_2COOCH_3)_3$	$GeCl_4$	0.084	$Et_3SnCH_2COOCH_3$	0.25	8	130	77
11	$ClGe(CH_2COOCH_3)_3$	$Cl_2Ge(CH_2COOCH_3)_2$	0.014	$Et_3SnCH_2COOCH_3$	0.014	8	120	80
12	$Ge(CH_2COOCH_3)_4$	$GeCl_4$	0.094	$Et_3SnCH_2COOCH_3$	0.56	7	130	77
13	$Br_3GeCH_2COOCH_3$	$GeBr_4$	0.10	$Bu_3SnCH_2COOCH_3$	0.085	3	60	88
14	$Br_2Ge(CH_2COOCH_3)_2$	$GeBr_4$	0.10	$Et_3SnCH_2COOCH_3$	0.18	2	60	70
15	$(CH_3O)_3GeCH_2COOCH_3$	$(CH_3O)_3GeCl$	0.027	$Bu_3SnCH_2COOCH_3$	0.033	4	130	67
16	$Et_3GeCH_2COOCH_3$	Et_3GeI	0.026	$Bu_3SnCH_2COOCH_3$	0.028	2	100	85
17	$Et_3GeCH_2COOCH_3$	Et_3GeCl	0.03	$Bu_3SnCH_2COOCH_3$	0.03	4	100	27
18	Et_3GeCH_2COOBu	Et_3GeI	0.022	Bu_3SnCH_2COOBu	0.024	3	120	74
19	$I_3GeCH_2COOCH_3$	GeI_4	0.11	$Et_3SnCH_2COOCH_3$	0.11	6	80	65

bubbled through a solution of 3.9 g (0.017 mole) of (VI) and 0.3 g of HgI_2 in butyl alcohol. Fractionation yielded 3.7 g (81% yield) of (VIa), b.p. 69–70° at 1 mm.

7–19. Reaction of halogermanes with alkyl (trialkylstannyl)acetate

This followed a conventional pattern. The alkyl (trialkylstannyl)acetate was added dropwise, with vigorous stirring, to the halogermane. The reaction mixture was stirred and heated during several hours. The product was generally isolated by distillation. The ratio of reactants, and reaction conditions are summarized in Table 2.

The properties of the compounds prepared in this investigation are summarized in Table 1.

ACKNOWLEDGEMENT

The authors express their appreciation to E. I. FEDIN and L. I. PETROVSKAJA who provided the NMR spectra and assisted in interpreting them.

SUMMARY

A number of germylated alkyl acetates have been synthesized by the reaction of halogermanes with alkyl (trialkylstannyl)acetates and the reaction of alkoxygermane with ketene. It has been assumed that, in the last case, the reaction proceeds through an intermediate keteneacetal derivative.

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