Chlorotrimethylgermane

$$\boxed{Me_3GeCl}$$

[1529-47-1] C_3H_9ClGe (MW 153.16)

InChI = 1/C3H9ClGe/c1-5(2,3)4/h1-3H3

InChIKey = ZZBNZZCHSNOXOH-UHFFFAOYAP

(precursor of germanium masked dienolate for regioselective C–C bond formation;[1] germanium enolates and α-germyl ester for aldol,[10] Peterson-type reaction,[8] and Claisen rearrangement[11])
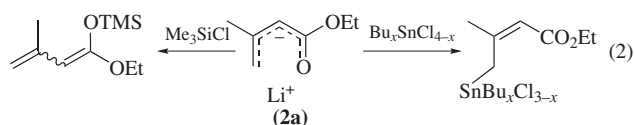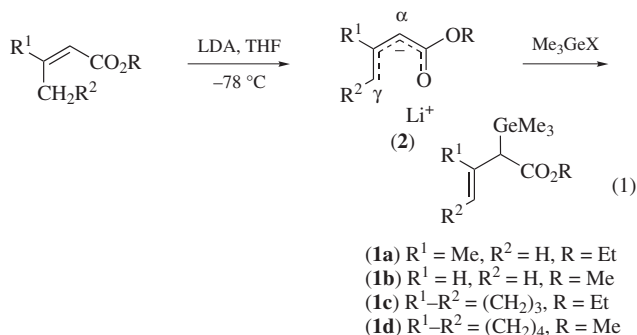
Alternate Name: trimethylgermanium chloride.

Physical Data: mp $-13\,°C$; bp $102\,°C$; d $1.240\ g\,cm^{-3}$.

Solubility: sol ether, THF, hexane, benzene, CH_2Cl_2, $CHCl_3$.

Form Supplied in: colorless liquid; widely available.

Handling, Storage, and Precautions: is air-stable, but moisture sensitive. Germanium compounds are reputed to be of lower toxicity than stannanes. Use in a fume hood.

Allylgermanes. The reaction of certain lithium dienolates with trimethylgermanium halides (Me_3GeCl and Me_3GeBr) produces the α-trimethylgermylated β,γ-unsaturated esters (**1**) (eq 1).[1] On the other hand, the reaction of lithium dienolate (**2a**) with tin chlorides Bu_xSnCl_{4-x} ($x = 0$–3) produces the γ-stannylated α,β-unsaturated esters, and the same reaction with *Chlorotrimethylsilane* gives the *O*-silylated dienol ethers (eq 2). The α-germylation of (**2**) is a reflection of kinetic control, as is observed in the alkylation of (**2**) with alkyl halides. The γ-stannylation is due to the thermodynamic stability of the product, and the *O*-silylation is ascribed to the strong affinity of Si for oxygen. In fact, the α-germylated (**1a**) undergoes rearrangement to the γ-isomer upon heating. Further, treatment of (**2a**) with chlorotriphenylgermane gives the γ-germylated product, owing to the steric bulkiness of the triphenylgermyl group.

(**1a**) R^1 = Me, R^2 = H, R = Et
(**1b**) R^1 = H, R^2 = H, R = Me
(**1c**) R^1–R^2 = $(CH_2)_3$, R = Et
(**1d**) R^1–R^2 = $(CH_2)_4$, R = Me

In general, lithium dienolates (for example **2**) react with carbon electrophiles at the α-position and thus the carbon chain elongation at the γ-position is not easy. However, C–C bond formation at the γ-position takes place via the α-germylated compounds (**1**), which are α-alkoxycarbonylallylgermane derivatives. The Lewis acid mediated reactions of (**1**) with acetals, aldehydes, and reactive halides afford the γ-alkylated α,β-unsaturated esters having predominant (*E*) geometry (eq 3). The reaction of allylic halides with (**1a**) in the presence of TMSCl at 10 kbar is highly regioselective and gives the head-to-tail coupling product in high yields (e.g. eq 4). The use of high pressures and TMSCl is essential to this regioselective allylic–allylic coupling. The amination reaction of lithium dienolates often produces a mixture of α- and γ-amino acid derivatives. However, the Lewis acid mediated reaction of α-germyl (Ge-masked dienolates) derivatives (**1**) with DEAD (*Diethyl Azodicarboxylate*) regioselectively provides the γ-adduct (see eq 5).[1,2] On the other hand, the *Zinc Chloride* mediated reaction of the γ-stannylated dienolates (shown in eq 2) with DEAD gives the α-adduct.
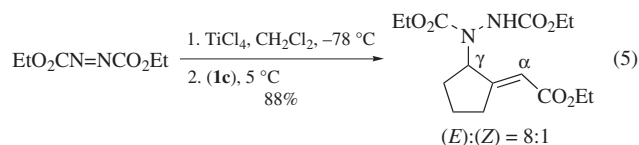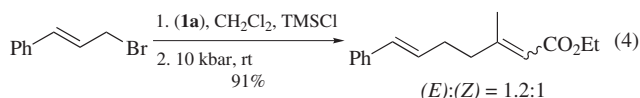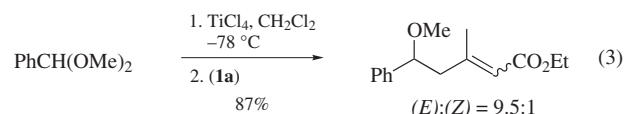
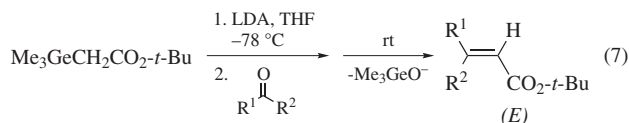The reaction of Ge-masked dienolates (**1**) with Michael acceptors in the presence of Lewis acids produces the 1,4-γ-adduct regioselectively, whereas the reaction in the presence of *Tetrabutylammonium Fluoride* gives the 1,4-α-adduct exclusively (eq 6).[3] The coupling between cyclopentenone and the crotonate lithium dienolate gives a 1,4-α-adduct,[4] and the reaction of some enones with the vinylogous Reformatsky reagent derived from ethyl 4-bromocrotonate to some enones affords a 1,4-α-adduct under the controlled reaction conditions.[5] The 1,2-γ-selectivity is obtained in the reaction of lithium dienolates with certain enones[6] and enols.[7]
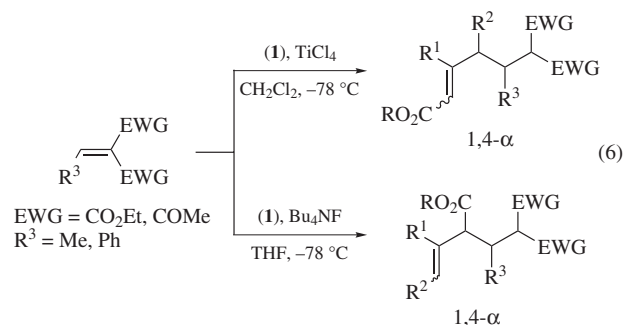
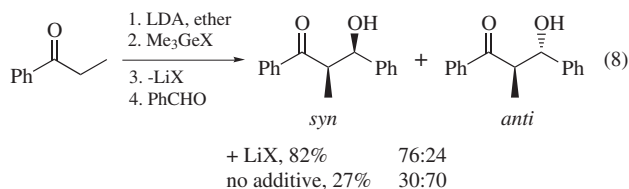**Germanium Enolates and α-Germyl Esters.** Peterson-type reaction of *t*-butyl (trimethylgermyl)acetate, derived from lithium *t*-butylacetate and Me_3GeCl, with aldehydes and ketones gives stereoselectively (*E*)-2-alkenoic acid esters (eq 7).[8] Normally, high (*E*)-selectivity is obtained: $(E)/(Z) = 93:7$ for $R^1 = Me(CH_2)_6$,

$R^2 = H$; $(E)/(Z) = >99:1$ for $R^1 = Ph$, $R^2 = Me$. The (E) selectivity via trimethylgermylacetate is higher than that via trimethylsilylacetates.[9]

$$Me_3GeCH_2CO_2\text{-}t\text{-}Bu \xrightarrow[\substack{2. \\ R^1 \overset{O}{\underset{}{\parallel}} R^2}]{1.\ LDA,\ THF\ -78\ °C} \xrightarrow[-Me_3GeO^-]{rt} \begin{matrix} R^1 \\ R^2 \end{matrix}{=}\begin{matrix} H \\ CO_2\text{-}t\text{-}Bu \end{matrix} \quad (7)$$
(E)

The germanium enolate of propiophenone, prepared in situ by the reaction with **Lithium Diisopropylamide** in ether followed by treatment with Me_3GeCl, reacts with benzaldehyde to give mainly the *syn*-aldol, while the same enolate produces the *anti*-aldol predominantly if the coexisting lithium halides are removed before condensation (eq 8).[10] The chemical yield is low in the absence of LiX, but is increased in the presence of **Boron Trifluoride Etherate** The salt effect on the diastereoselectivity is not observed with the germanium enolate prepared with chlorotriphenylgermane.

$$Ph\overset{O}{\underset{}{\parallel}}CH_3 \xrightarrow[\substack{3.\ \text{-LiX} \\ 4.\ PhCHO}]{\substack{1.\ LDA,\ ether \\ 2.\ Me_3GeX}} Ph\overset{O}{\underset{}{\parallel}}\overset{OH}{\underset{}{}}Ph \ + \ Ph\overset{O}{\underset{}{\parallel}}\overset{OH}{\underset{}{}}Ph \quad (8)$$

	syn	*anti*
+ LiX, 82%	76:24	
no additive, 27%	30:70	

The asymmetric Claisen rearrangement of allyl vinyl ethers is effected with a chiral organoaluminum reagent, (R)-(**3**) or (S)-(**3**).[11] This method provides a facile asymmetric synthesis of various acylgermanes (and acylsilanes) with high enantiomeric purity (eq 9). The reactions of the trimethylgermyl derivative proceeds with higher enantioselectivity (91% ee) than that of the trimethylsilyl analog (80% ee).

$$ \xrightarrow[\substack{CH_2Cl_2 \\ -78\ \text{to}\ -40\ °C \\ 73\%}]{(R)\text{-}(\mathbf{3})} \quad (9)$$
91% ee (S)
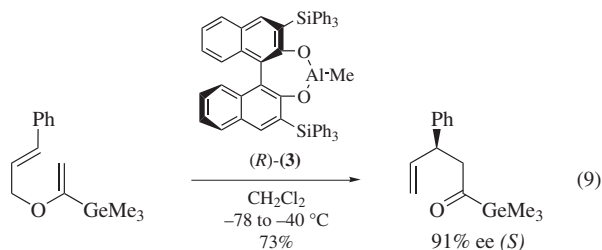
Other Trimethylgermyl Derivatives. Reactions of α-stannylvinyllithiums $RR'C{=}C(Li)SnMe_3$ with Me_3MCl (M = Si, Ge, Pb) give the corresponding mixed bis(trimethylmetal)alkenes, $RR'C{=}C(SnMe_3)MMe_3$.[12] Irradiation of acyltriphenylgermanes in THF gives five- and six-membered cyclic ketones bearing an α-(triphenylgermyl)methyl group (eq 10).[12] Cyanotrimethylgermane, prepared from Me_3GeCl and **Silver(I) Cyanide**, reacts with terminal alkynes in the presence of **Palladium(II) Chloride** catalyst in toluene to produce (Z)-3-trimethylgermyl-2-alkenenitriles in good yields.[13] Similar addition reactions take place with **Cyanotrimethylsilane**, but the reaction is slower than that of Me_3GeCN.

$$ \xrightarrow[\substack{rt,\ THF \\ 27\text{-}97\%}]{h\nu\ (400\ W\ Hg\ lamp)} \quad (10)$$
n = 1, 2
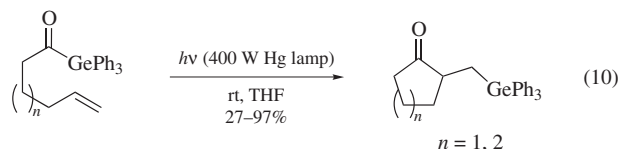
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