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Trimethylgermylation of Ketones

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Treatment of lithium enolates of ketones with chlorotrimethylgermane gave preferentially α-trimethylgermyl ketones in hexane.

Introduction

α-Trimethylsilyl ketones are versatile synthetic reagents for organic syntheses.[1] However, they are relatively inaccessible because trimethylsilylation of the corresponding ketones gives only the silyl enol ethers.[2] Roundabout ways have been employed for their syntheses.[3] Larson reported that methyldiphenylsilylation of esters favors the formation of the C-silylated product,[4] but this procedure was unsuccessful in attempts to produce the α-silylated products from ketones.[5]

Trialkylstannylation of ketones via the reaction of their enol acetates with trialkylmethoxystannane gave mixtures of the stannyl enol ethers and the α-stannyl ketones.[6]

In this paper, we report the direct synthesis of α-trimethylgermyl ketones from the corresponding ketones. Organogermanium compounds have reactivities similar to those of organosilicon compounds and are useful for organic syntheses.[7]

Results and Discussion

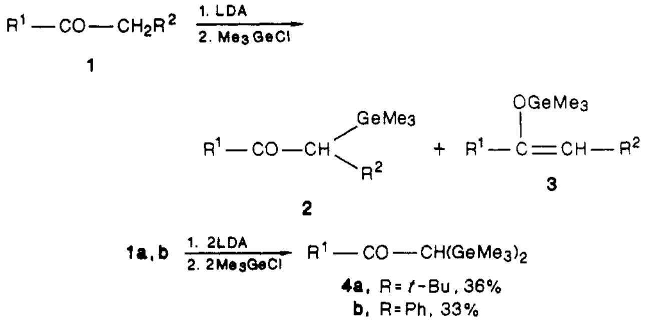
The reaction of lithium enolates of pinacolone (**1a**) and acetophenone (**1b**) with chlorotrimethylgermane in ether gave moderate yields of trimethylgermyl ketones (**2a,b**) (Table I, entries 1 and 3). However, similar treatment of diethyl ketone (**1c**), propiophenone (**1d**), and cyclopentanone (**1e**) gave mixtures of α-trimethylgermyl ketones (**2**) and germyl enol ethers (**3**), which were rapidly hydrolyzed to the starting compounds by aqueous workup (entries 4, 6, and 9).

Table I. Trimethylgermylation of Carbonyl Compounds

en-try		R^1	R^2	reaction condition: solv	reaction condition: temp, °C/time, h	% yield[a] of **2**	ratio[b] of **2**:**3**
1	**1a**	*t*-Bu	H	Et_2O	–78/0.5	69	86:14
2	**1a**	*t*-Bu	H	hexane	0/2	77[c]	98:2
3	**1b**	Ph	H	Et_2O	0/2, then room temp/3	56	93:7
4	**1c**	Et	Me	Et_2O	0/4	*d*	50:50
5	**1c**	Et	Me	hexane	0/10	56[c]	>99:<1
6	**1d**	Ph	Me	Et_2O	0/3, then room temp/10	*e*	12:88
7	**1d**	Ph	Me	hexane	0/10	12[c]	79:21
8	**1e**	$-(CH_2)_3-$		THF	–78/0.25	3[f]	3:97
9	**1c**	$-(CH_2)_3-$		Et_2O	0/2, then room temp/2	27[f]	67:33
10	**1e**	$-(CH_2)_3-$		hexane	0/2, then room temp/2	63[f]	93:7
11	**1f**	$-(CH_2)_4-$		hexane	0/10	19[c]	40:60

[a] Isolated yield. [b] Determined by GLC. [c] Reverse addition. [d] Not isolated. [e] 1-Phenyl-1-(trimethylgermoxy)-2-pentene (**3d**) was isolated in 44% yield. [f] GLC yield.

Scheme I



Some reaction conditions were examined for the reaction of **1e**. The ratio of C-germylation products **2e** and O-germylation products **3e** depends on the polarity of the solvent employed. The O-isomers **3** were formed selectively in THF (entry 8) whereas the C-isomers **2e** were formed preferentially in hexane (entry 10). Similar solvent effects were observed on the reaction of other ketones (entries 2, 5, and 7). However, considerable amounts of α,α-bis(trimethylgermyl)-substituted ketones (**4**) were formed by the addition of chlorotrimethylgermane to the lithium ketone enolate. Reverse addition must be used in order to avoid contamination by **4**. When the reaction was performed in the presence of 2 equiv of lithium diisopropylamide (LDA) and chlorotrimethylgermane, **4** was obtained as the main product.

Lutsenko reported that there is an equilibrium between (trimethylgermyl)acetone and trimethyl(isopropenyloxy)germane with the relative amount of the latter increasing upon heating.[8] Indeed, the germyl ketones **2** tend to be degermylated to give **1** which are obviously hydrolyzed products of **3** upon heating. Therefore, distillations

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Table II. α-Trimethylgermyl and α,α-Bis(trimethylgermyl) Ketones

compd	bp, °C (p, mmHg)[a]	IR, cm^{-1} C=O	^1H NMR ($CDCl_3$), δ Me$_3$Ge	^1H NMR ($CDCl_3$), δ COCH-Ge	elemental anal. or high MS (m/z) found (calcd) C	elemental anal. or high MS (m/z) found (calcd) H
2a	85 (70)	1675	0.28	2.40 (s)	50.03 (49.85)	9.11 (9.30)
2b	95 (9)	1660	0.23	2.84 (s)	238.04400 (238.04111)	
2c	100 (10)	1685	0.23	2.56 (q, J = 6.8 Hz)	47.09 (47.38)	8.70 (8.94)
2d	60–65 (3)	1660	0.09	3.49 (q, J = 6.4 Hz)	252.05584 (252.05675)	
2e	75 (5)	1710	0.25	1.6–2.5[b]	48.21 (47.85)	8.08 (8.03)
2f	100 (6)	1680	0.27	1.2–2.5[b]	216.05784 (216.05675)	
4a	100 (25)	1655	0.26	2.58 (s)	43.02 (43.21)	8.41 (8.46)
4b	105–110 (4)	1635	0.27	3.12 (s)	47.82 (47.57)	6.85 (6.85)

[a] Oven temperature of a Büchi Kugelrohr distillation apparatus. [b] Insufficient separation with other protons.

were carried out below 100 °C. Purification by silica gel chromatography resulted in considerable degermylation, especially in the case of the aryl ketones. However, the α,α-bis(trimethylgermyl) ketones **4** are quite stable, and cleavage of the Ge–C bonds were not observed during usual distillation and column chromatography.

Yamamoto has observed the reaction of chlorotri-*n*-butylstannane or chlorotriphenylstannane with the lithium enolates of **1b** and **1d** by ^1H NMR spectroscopy.[9] Acetophenone (**1b**) was converted into α-(tributylstannyl) or α-(triphenylstannyl)acetophenone in THF at 0 °C, while **1d** gave the corresponding tributylstannyl or triphenylstannyl enol ether. This result is comparable with that of trimethylgermylation of **1b** and **1d** in ether (entries 3 and 6 in Table I). We expect similar solvent effects on the triorganostannylation of ketones, with the α-stannyl ketones being formed in hexane.

The fluoride ion induced reaction of α-(trimethylsilyl)acetophenone with carbon electrophiles was reported by Fiorenza et al.[1d] The reaction of **2b** with benzaldehyde, as well as the sila analogue, gave a moderate yield of chalcone in the presence of a catalytic amount of tetra-*n*-butylammonium fluoride in THF.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran were dried by distillation from sodium benzophenone ketyl prior to use. Hexane was distilled from sodium wire. ^1H NMR spectra were recorded on a JEOL JNM-PMX 60 or JNM-MH-100 spectrometer using Me_4Si as internal standard. IR spectra were recorded on a JASCO IRA-2 spectrometer. Mass spectral data were obtained by using a JEOL JMS-DX 300 GC-MS system (70 eV, EI; 3% silicone SE-30, 2-m column). Gas chromatographic analyses were carried out on a Gasukuro Kogyo Model-370 chromatograph with TCD detector using a 20% silicone SE-30, 1-m column. All melting points and boiling points are uncorrected.

Trimethylgermylation of Ketones. (A) Reaction in Diethyl Ether (Entries 1, 3, 4, and 6). *n*-BuLi (10 w/v % in hexane, 0.76 mL, 1.2 mmol) was added to a solution of diisopropylamine (121 mg, 1.2 mmol) in diethyl ether (4 mL) at 0 °C with continuous stirring for 0.5 h. To this LDA solution was added dropwise a solution of the ketones **1a–e** (1.0 mmol) in diethyl ether (3 mL) at −78 or 0 °C. After 1 h, a solution of chlorotrimethylgermane (184 mg, 1.2 mmol) in diethyl ether (3 mL) was added dropwise, and stirring was continued under the conditions described in Table I. The resulting solution was quenched with saturated aqueous NH_4Cl and extracted with diethyl ether (except for entry 6). The organic layer was washed with water, dried over anhydrous $MgSO_4$, and concentrated. Kugelrohr distillation of the residue gave the respective α-trimethylgermyl ketone **2**. Their characteristic data are summarized in Table II.

The GC–mass spectral analysis of the unhydrolyzed reaction mixture revealed the presence of two isomers that showed the same M^+ peaks and similar fragmentation patterns. One was identified as **2**, and the other was assigned to the trimethylgermyl enol ether **3** because the latter disappeared after aqueous workup as described above with an increasing peak area of the contaminated **1** on the GLC analysis. The retention time was **2** > **3** on a SE-30 silicone column. The ratio of **2** to **3** was calculated on the basis of the integrated values of GLC peaks of the reaction mixture.

In the case of entry 6, the reaction mixture was concentrated under reduced pressure, and the precipitated crystals were filtred and washed with hexane. The filtrate and washings were combined and distilled to give 1-phenyl-1-(trimethylgermoxy)-2-pentene (**3d**) (111 mg, 44%): bp 115–120 °C (9 mmHg); NMR ($CDCl_3$) δ 0.39 (9 H, s, $GeMe_3$), 1.74 (3 H, d, J = 6.8 Hz, Me), 5.34 (1 H, q, J = 6.8 Hz, =CH), 7.16–7.73 (5 H, m, Ph); mass spectrum, m/z 252.05486 (M^+) (calcd for $C_{12}H_{18}GeO$ 252.05675).

(B) Reaction in Hexane (Entries 2, 5, 7, 10, and 11). A solution of **1a,c,d,f** (3.6 mmol) in hexane (5 mL) was added to a solution of LDA in hexane, prepared from *n*-BuLi (2.3 mL, 3.6 mmol) and diisopropylamine (364 mg, 3.6 mmol) in hexane (10 mL) at 0 °C, and stirring was continued for 1 h at the same temperature. This cold mixture was added dropwise to a solution of chlorotrimethylgermane (459 mg, 3.0 mmol) in hexane (10 mL) at 0 °C. After being stirred for 10 h, the solution was poured into a precooled phosphate buffer solution (pH 7). The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined extracts were washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. Kugelrohr distillation of the residual oil gave **2**.

Reaction of Lithium Enolate of Cyclopentanone (1e) with Chlorotrimethylgermane (Various Conditions) (Entries 8–10). A mixture of **1e** (84 mg, 1.0 mmol) and cyclohexylbenzene (internal standard, 160 mg, 1.0 mmol) was treated in a manner similar to that described for above (A) and (B). The yield of **2e** was measured on the reaction mixture by GLC using a calibrated internal standard. The ratio of **2e** and **3e** was determined on the basis of the integrated values of the GLC.

2,2-Diemthyl-4,4-bis(trimethylgermyl)-3-butanone (4a). To a solution of LDA, prepared from *n*–BuLi (4.6 mL, 7.2 mmol) and diisopropylamine (728 mg, 7.2 mmol) in diethyl ether (5 mL), was added dropwise a solution of pinacolone (**1a**, 300 mg, 3.0 mmol) in diethyl ether (3 mL) at 0 °C. After 1 h of stirring, a solution of chlorotrimethylgermane (1.10 g, 7.2 mmol) in diethyl ether (3 mL) was added and stirring was continued for 5 h at 0 °C. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with diethyl ether. The extract was washed with water, dried over anhydrous $MgSO_4$, and then concentrated under reduced pressure. Kugelrohr distillation of the residue gave **2a** (262 mg, 40%) and **4a** (360 mg, 36%).

2,2-Bis(trimethylgermyl)acetophenone (4b). Acetophenone (120 mg, 1.0 mmol), diisopropylamine (222 mg, 2.2 mmol), *n*-BuLi (1.4 mL), and chlorotrimethylgermane (368 mg, 2.4 mmol) was treated in a manner similar to that described for **4a**. The ethereal extract was chromatographed on a silica gel column (hexane/diethyl ether = 10:1) to give **4b** (117 mg, 33%) and **1h** (28 mg, 23%).

Reaction of α-(Trimethylgermyl)acetophenone (2b) with Benzaldehyde. To a solution of **2b** (178 mg, 0.75 mmol) and benzaldehyde (105 mg, 1.0 mmol) in THF (4 mL) was added tetra-*n*-butylammonium fluoride (0.5 mL of 0.2 M solution in THF, 0.1 mmol) at −78 °C. After 0.5 h of stirring, the reaction

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mixture was concentrated on a rotary evaporator and chromatographed on a silica gel column (hexane/ether = 10:1 to 5:1) to give 80 mg (51%) of chalcone.

Registry No. **1a**, 75-97-8; **1b**, 98-86-2; **1c**, 96-22-0; **1d**, 93-55-0; **1e**, 120-92-3; **1f**, 108-94-1; **2a**, 110614-54-5; **2b**, 41492-37-9; **2c**, 110614-55-6; **2d**, 110614-56-7; **2e**, 110614-57-8; **2f**, 110614-58-9; **3a**, 110614-59-0; **3b**, 41492-33-5; **3c**, 110614-60-3; **3d**, 110614-61-4; **3e**, 110614-62-5; **3f**, 110614-63-6; **4a**, 110614-64-7; **4b**, 38860-13-8; Me_3GeCl, 1529-47-1; benzaldehyde, 100-52-7; chalcone, 94-41-7.

Stereochemical and Electrochemical Characterization of the Iron–Iron Multiple-Bonded $[Fe_2(\eta^5\text{-}C_5H_{5-x}Me_x)_2(\mu\text{-}NO)_2]^n$ Dimers (x = 0, 1, 5; n = 0, 1–): A Structural-Bonding Analysis of the Iron and Cobalt Nitrosyl-Bridged $[M_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}NO)_2]^n$ Series (M = Fe, n = 0, 1–; M = Co, n = 1+, 0)

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In connection with our previous investigations of the 32/33-electron $[Co_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}CO)_2]^n$ series (n = 0, 1–), we have carried out structural-bonding studies of the 32-electron $Fe_2(\eta^5\text{-}C_5H_{5-x}Me_x)_2(\mu\text{-}NO)_2$ dimers (x = 0, 1, 5) and the 33-electron $[Co_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}NO)_2]^+$ monocation. The results reported herein include the following: (1) Cyclic voltammetric measurements showed that the three neutral iron dimers undergo similar one-electron reversible reductions to their respective monoanions. The $E_{1/2}$ values exhibit a linear change in negative voltage per methyl ring substituent consistent with increased difficulty in reduction upon methyl ring substitution. (2) An X-ray crystallographic determination of the 32-electron $Fe_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}NO)_2$ disclosed a planar $Fe_2(NO)_2$ core of crystallographic C_{2h}—$2/m$ site symmetry with an Fe–Fe distance of 2.326 (4) Å which is identical with that in the previously characterized $Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}NO)_2$. (3) An X-ray crystallographic determination of the 33-electron $[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}NO)_2]^-$ monoanion (isolated as the $[PPN]^+$ salt) showed that the salient geometrical change resulting from the oxidation of the monoanion to its 32-electron neutral parent is a decrease in the Fe–Fe distance from 2.378 (1) (av) to 2.326 (4) Å. This 0.052-Å shortening in the metal–metal distance (upon oxidation) is completely compatible with the unpaired electron in the monoanion occupying a HOMO mainly composed of out-of-plane d_π dimetal-antibonding character. This geometrical change provides an experimental operational test that the isoelectronic $[Fe_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}NO)_2]^n$ and $[Co_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}CO)_2]^n$ series (n = 0, 1–) have similar corresponding LUMO's (n = 0) and HOMO's (n = 1–). (4) In light of the previously reported (and theoretically inexplicable) bond-length decrease of 0.05 Å in the mean Co–NO distance upon oxidation of the 34-electron $Co_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}NO)_2$ neutral parent to its 33-electron monocation, a crystallographic determination of the corresponding $[Co_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}NO)_2]^+$ monocation (isolated as the $[PF_6]^-$ salt) was performed. An examination of the centrosymmetric $Co_2(NO)_2$ cores in these C_5H_4Me- and C_5H_5-containing dimers revealed abnormally elongated out-of-plane thermal ellipsoids for the nitrogen and oxygen atoms in both monocations. We propose that the similarly short mean Co–NO bond lengths in these monocations are due in large part to an artifact of crystal disorders involving a superposition of at least two nonplanar orientations for each nitrosyl ligand; hence, the *actual* Co–NO bond lengths in these cobalt monocations may *not* be smaller than those in their neutral parents. $Fe_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}NO)_2$: M_r 329.95; monoclinic; $C2/m$; a = 7.966 (4) Å, b = 8.644 (2) Å, c = 9.833 (4) Å, β = 113.36 (3)°, V = 621.6 (4) $Å^3$ at T = 233 K; d_{calcd} = 1.76 g/cm^3 for Z = 2; anisotropic least-squares refinement converged at $R_1(F)$ = 7.3% and $R_2(F)$ = 8.9% for 737 independent reflections ($I > 2.0\sigma(I)$). $[(PPh_3)_2N]^+[Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}NO)_2]^-$: M_r 840.19; triclinic; $P\bar{1}$; a = 11.266 (4) Å, b = 17.613 (4) Å, c = 10.362 (4) Å, α = 102.06 (3)°, β = 93.17 (3)°, γ = 92.06 (2)°, V = 2005 (1) $Å^3$ at T = 295 K; d_{calcd} = 1.39 g/cm^3 for Z = 2; anisotropic least-squares refinement for one independent cation and two independent half-anions of C_i—$\bar{1}$ site symmetries converged at $R_1(F)$ = 4.3% and $R_2(F)$ = 5.7% for 4174 independent reflections ($I > 2\sigma(I)$). $[Co_2(\eta^5\text{-}C_5H_4Me)_2(\mu\text{-}NO)_2]^+[PF_6]^-$: M_r 481.09; monoclinic; $C2/c$; a = 17.07 (1) Å, b = 7.530 (8) Å, c = 14.51 (1) Å, β = 113.51 (6)°; V = 1708 (3) $Å^3$ at T = 203 K; d_{calcd} = 1.87 g/cm^3 for Z = 4; anisotropic least-squares refinement converged at R_1 (F) = 8.5% and $R_2(F)$ = 10.7% for 1194 independent data ($I > 1.5\sigma(I)$).

Introduction

Our investigation of the physicochemical behavior of the 32-electron $Fe_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}NO)_2$ dimers, which formally possess an Fe–Fe double bond, was a consequence of earlier studies[2-6] which showed that the isoelectronic $Co_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}CO)_2$ dimers (R = H,[2-5] Me[5,6]) are reversibly reduced to their respective monoanions. The instability of the neutral unsubstituted cyclopentadienyl cobalt dimer

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[1] (a) Based in part on the Ph.D. thesis of K. A. Kubat-Martin at the University of Wisconsin—Madison, June, 1986. Present address: Los Alamos Scientific Laboratory, University of California, Los Alamos, NM 87545. (b) On sabbatical leave (June 1985–Dec 1985) at UW—Madison from the Department of Chemistry, Beloit College, Beloit, WI 53511.

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