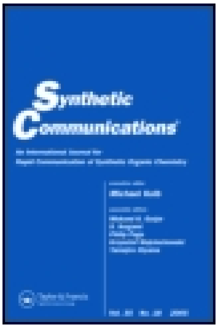

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Tetraorganogallate Complexes in Organic Chemistry: Michael Addition to α,β-unsaturated Compounds

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TETRAORGANOGALLATE COMPLEXES IN ORGANIC CHEMISTRY: MICHAEL ADDITION TO α, β-UNSATURATED COMPOUNDS

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ABSTRACT: Tetraorganogallate complexes, prepared *in situ* by addition of an organolithium reagent to a triorganogallium, reacted smoothly with α,β-unsaturated compounds to give Michael addition products in high yields, and mixed gallates display very high chemoselectivity in the transfer of one of their ligands.

Michael addition is one of the most important reactions in organic synthesis[1]. In order to uncover and develop the synthetic utility of the long forgotten group 13 organometallics: gallium, indium and thallium[2-3], we have reported the gallium and its compounds-mediated selectivity reactions[4]. Also, we have described a novel, efficient and versatile method for the preparation of ketones from acyl chlorides via tetraorganogallate complexes[5], and a simple,

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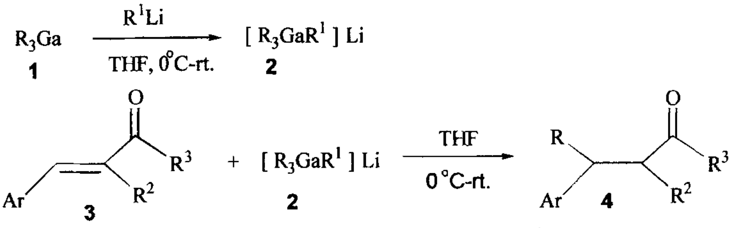
efficient, straightforward method for the preparation of propargylic alcohols from 1-alkynes and aldehydes promoted by gallium triiodide and an amine[6]. In this communication, we would like to report another chemical behavior of tetraorganogallate complexes: Michael addition to α,β-unsaturated compounds(**Scheme 1**).

Tetraorganogallate complex, prepared by the addition of an organolithium reagent to a triorganogallium, reacted with α, β-unsaturated carbonyl compound



R = Ph, Bu, R^1 = Me, Et, Bu, R^2 = H, Ph, CO_2Et, CN, R^3 = Me, Ph, OEt

Scheme 1

to produce 1,4- and / or 1,2-adducts (**Table 1**). **Table 1** and **Scheme 1** show that the regioselectivity largely depends on the structure of substrate. α,β-Unsaturated aldehyde (**Entry 1**) gave exclusively 1,2-adduct almost quantitatively. Methyl α,β-unsaturated ketone (**Entry 6,7**) mainly yielded 1,4-adduct and a little 1,2-adducts. Chalcone, α,β-unsaturated esters and nitriles gave only 1,4-adducts. All of them (from **Entry 3 to 11**) were selectively phenylated to electrophiles, no alkylated products were detected. It is in sharp comparison that thallate complexes reacted with α,β-unsaturated compounds to produce 1,2 adducts[7]. The corresponding indium ate complexes gave mainly Michael products[8]. In addition, under the same conditions the reaction between gallates with α,β-unsaturated mononitrile,

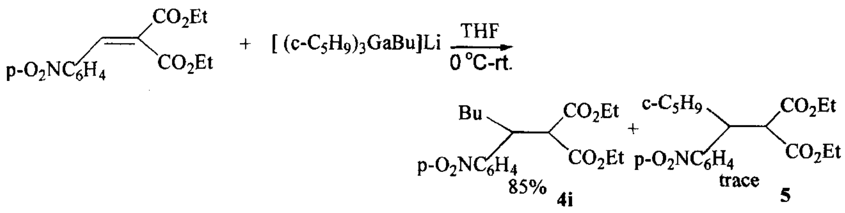
Table 1. Michael Additions of Tetraorganogallate Complexes with α,β-Unsaturated Carbonyl Compounds

Entry	Substrate	Reagent	Product	Yield(%)[a]
1	(E)-PhCH=CHCHO	n-$\mathrm{Bu_4GaLi}$	(E)-PhCH=CHCH(OH)Bu **4a**	98
2	(E)-PhCH=CHCOPh	n-$\mathrm{Bu_4GaLi}$	$\mathrm{PhCH(Bu^n)CH_2COPh}$ **4b**	78
3	(E)-PhCH=CHCOPh	$\mathrm{[Ph_3GaMe]Li}$	$\mathrm{Ph_2CHCH_2COPh}$ **4c**	85
4	(E)-PhCH=CHCOPh	$\mathrm{[Ph_3GaBu\text{-}n]Li}$	$\mathrm{Ph_2CHCH_2COPh}$ **4c**	85
5	(E)-PhCH=CHCOPh	$\mathrm{[n\text{-}Bu_3GaPh]Li}$	$\mathrm{Ph_2CHCH_2COPh}$ **4c**	79
6	(E)-$\mathrm{PhCH{=}CHCOCH_3}$	$\mathrm{[Ph_3GaMe]Li}$	$\mathrm{Ph_2CHCH_2COCH_3}$ **4d**	67(8)[b]
7	(E)-$\mathrm{PhCH{=}CHCOCH_3}$	$\mathrm{[Ph_3GaBu\text{-}n]Li}$	$\mathrm{Ph_2CHCH_2COCH_3}$ **4d**	74(6)[b]
8	$\mathrm{PhCH{=}C(CO_2Et)_2}$	$\mathrm{[Ph_3GaBu\text{-}n]Li}$	$\mathrm{Ph_2CHCH(CO_2Et)_2}$ **4e**	95
9	p-$\mathrm{O_2NC_6H_4CH{=}C(CO_2Et)_2}$	$\mathrm{[Ph_3GaBu\text{-}n]Li}$	p-$\mathrm{O_2NC_6H_4CH(Ph)CH(CO_2Et)_2}$ **4f**	93
10	(E)-p-$\mathrm{ClC_6H_4CH{=}C(CO_2Et)CN}$	$\mathrm{[Ph_3GaBu\text{-}n]Li}$	p-$\mathrm{ClC_6H_4CH(Ph)CH(CO_2Et)CN}$ **4g**	91[c]
11	(E)-p-$\mathrm{ClC_6H_4CH{=}C(CO_2Et)CN}$	$\mathrm{[Ph_3GaMe]Li}$	p-$\mathrm{ClC_6H_4CH(Ph)CH(CO_2Et)CN}$ **4g**	89[c]
12	$\mathrm{PhCH{=}C(CO_2Et)_2}$	$\mathrm{Bu_4GaLi}$	$\mathrm{PhCH(Bu)CH(CO_2Et)_2}$ **4h**	95
13	p-$\mathrm{O_2NC_6H_4CH{=}C(CO_2Et)_2}$	$\mathrm{Bu_4GaLi}$	p-$\mathrm{O_2NC_6H_4CH(Bu)CH(CO_2Et)_2}$ **4i**	90

a) Isolated yield based on α, β-unsaturated compounds b) Data in parentheses refer to the 1,2-adduct yields of phenyl transfer. c) The syn:anti = 1 : 1, were estimated by 300 MHz ^{1}H NMR spectral data according to the coupling constant.

monoester can not take place. Heating reaction mixture (50° C), TLC shows that reactions are complicated.

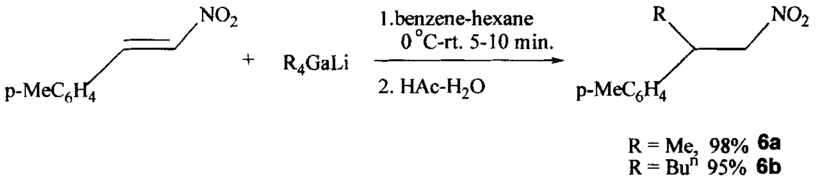
It is particularly noteworthy that, using mixed lithium butyl tricyclopentylgallate containing primary group and secondary alkyl groups, the primary group is transferred nearly exclusively to the Michael acceptor (**Scheme 2**). Similar result was observed in across-coupled reaction of this gallate with acyl chloride[5].



Scheme 2

Also, α,β-unsaturated nitro olefins are exceptional Michael acceptors and they are versatile intermediates in organic synthesis[9]. The reactions of many organometallic reagents with nitro olefins have been reported[10]. However, reaction conditions of these organometallic reagents with nitro olefins are often not mild to afford Michael products in moderate to satisfactory yields. Under mild condition, we carried out the reaction of gallate complexes with nitro olefin to obtain Michael products in excellent yields in a few minutes (**Scheme 3**).

In conclusion, Michael addition of gallates to α,β-unsaturated compounds would broaden the scope of utility of organogallium reagents in organic synthesis. In particular, reactions of gallates with nitro olefins represent one of efficient



Scheme 3

synthetic methods of very useful saturated nitro compounds. Further studies of the reactions of gallates with α,β-unsaturated compounds are now in progress in our group.

Experimental:

^{1}H NMR spectral were recorded on a Bruke 300 MHz in $CDCl_3$ or a Varian EM 390 MHz spectrometer in CCl_4 with $SiMe_4$ as the internal standard. Chemical shifts are given in ppm (δ) units. Coupling constant (J) are reported in Hertz. IR spectra were recorded on a Shimadzu IR-440 spectrometer; ν frequencies are given in cm^{-1}. Mass spectra were obtained by electron ionization(EI) on GC-HP5989 spectrometer.

Materials:

All α,β-unsaturated compounds except chalcone and cinnamaldehyde were prepared from the corresponding aldehydes and active α-H compounds according to literature. All triorganogallium were obtained by means of the reaction of gallium trichloride and Grignard reagents in Et_2O. All tetraorganogallate complexes were prepared *in situ* by addition of an organolithium reagent to a triorganogallium compound.

General Procedure:

Butyllithium (1.2 mmol, 76.8 mg, 1.6M, 0.75 mL in hexane, Aldrich) was slowly added into triphenylgallium (361 mg, 1.2 mmol) in 4 mL THF at 0°C and stirred for 30 min. under argon. The gallate was dropped by a syringe into chalcone (208 mg, 1 mmol) in 2 mL THF at 0°C for 30 min., then allowed to warm to room temperature. After aqueous work-up and chromatography on a silica gel plate, the pure product (175 mg) was obtained in 85% yield.

4a: b. p. 125-128°C / 2 mmHg (lit.[11] 145-148°C / 4 mmHg). ^{1}H NMR(CCl_4, TMS, 90MHz) : δ(ppm) 0.90(t, 3H, J = 7Hz), 1.3-1.5(m, 6H), 2.48(s, 1H), 4.08(m, 1H), 6.0(dd, 1H, J_1 = 6Hz, J_2 = 16Hz), 6.40(d, 1H, J =16Hz), 7.12(s, 5H). EIMS m/z (relative intensity): 190(M^+, 6.27), 172(M-H_2O , 42.71), 157(M-H_2O-CH_3, 21.05).

4b: m. p. 55-57°C (lit.[12] 58°C). ^1H NMR($CDCl_3$, TMS, 90MHz): δ(ppm) 0.80(t, 3H, J = 7Hz), 1.25(m, 4H), 1.60(m, 3H), 3.2(m, 1H), 3.4(d, 2H, J = 8Hz), 7.30(m, 8H), 7.80(m, 2H). IR(CCl_4): 1690(s), 1600(w) cm^{-1}. EIMS m/z (relative intensity): 266(M^+, 43.41), 251[$(M-CH_3)^+$, 21.38], 161[$(M-PhCO)^+$, 17.92], 105[($PhCO^+$), 67.92].

4c: m. p. 94-96°C (lit.[13] 94°C). ^1H NMR(CCl_4, TMS, 90MHz): δ(ppm) 3.5(d, 2H, J = 8Hz), 4.6(t, 1H, J = 8Hz), 7.0-7.4(m, 13H), 7.6-7.9(m, 2H). IR(CCl_4): 1695(s), 1600(s) cm^{-1}. EIMS m/z (relative intensity): 286(M^+, 32.76), 209[$(M-Ph)^+$, 44.11], 181[$(M-PhCO)^+$, 19.54], 105[$(PhCO)^+$, 63.52].

4d: m. p. 92-93°C (lit.[14] 90-92°C). ^1H NMR($CDCl_3$, TMS, 90MHz): δ(ppm) 2.03(s, 3H), 3.13(d, 2H, J = 7.6Hz), 4.52(t, 1H, J = 7.5Hz), 7.18(s, 10H). IR(CCl_4): 1690(s), 1600(s) cm^{-1}. EIMS m/z (relative intensity): 225 [$(M+1)^+$, 23.19], 224(M^+, 37.99), 209[$(M-CH_3)^+$, 61.22], 147[$(M-Ph)^+$, 29.01].

4e: Colorless oil, ^1H NMR($CDCl_3$, TMS, 300MHz): δ(ppm) 1.02(t, 3H), 3.99(q, 4H), 4.33(d, 1H, J = 12.1Hz), 4.77(d, 1H, J = 12.1Hz), 7.20-7.30(m, 10H). IR(CCl_4): 3030(w), 2930(w), 1740(vs), 1600(v), 1490(w), 1450(w), 1360(w), 1310(m), 1260(m), 1170(m), 1030(m), 870(m), 770(vs), 700(s), 660(w) cm^{-1}. EIMS m/z (relative intensity): 326(M^+, 11.04), 281[$(M-OEt)^+$, 33.19], 249[(M-

Ph)$^+$, 5.90], 167{[M-CH(CO_2Et)$_2$]$^+$, 24.22}. Calcd for ($C_{20}H_{22}O_4$): C, 73.59, H, 6.78; Found: C, 73.90, H, 6.79.

4f: Light yellow oil, ^{1}H NMR($CDCl_3$, TMS, 300MHz): δ(ppm) 1.04(m, 6H), 4.03(m, 4H), 4.35(d, 1H, J = 12.1Hz), 4.89(d, 1H, J = 12.1Hz), 7.28(m, 5H), 7.47(m, 2H), 8.14(m, 2H), IR(CCl_4): 3050(w), 2950(m), 1740(vs), 1600(m), 1520(s), 1450(m), 1340(s), 1300(s), 1260(s), 1180(s), 1100(m), 1030(m), 860(m), 770(vs), 700(s), 620(m), 600(w) cm^{-1}. EIMS m/z (relative intensity): 371(M$^+$, 17.00), 326[(M-OEt)$^+$, 4.68], 325[(M-HOEt)$^+$, 14.08], 298[(M-CO_2Et)$^+$, 36.92], 297[(M-1-CO_2Et)$^+$, 61.81], 280(17.45), 252(100.00), 225(34.97), 212(55.12), 178(32.06), 165(58.57). Calcd for ($C_{20}H_{21}NO_6$): C, 64.68, H, 5.70, N, 3.77; Found: C, 64.93, H, 5.75, N, 3.73;

4g: Colorless oil, ^{1}H NMR($CDCl_3$, TMS, 300 MHz): δ(ppm) 1.12(t, 3H, J = 7.0Hz), 4.11(q, 2H, J = 7.0Hz), 4.18(d, 1H, J = 5.4Hz), 4.22(d, 1H, J = 5.3Hz), 4.70(d, 1H, J = 4.0Hz), 4.73(d, 1H, J = 3.9Hz), 7.30(m, 9H), (syn/anti = 50/50); IR(KBr): 2982(w), 2246(w), 1918(w), 1743(vs), 1600(w), 1493(v), 1465(v), 1453(v), 1405(v), 1370(v), 1301(v), 1300(v), 12799(v). EIMS m/z(relative intensity): 313(M$^+$,1.76), 268[(M-OEt)$^+$, 0.20), 251(7.45), 201(100.00), 178(4.21), 165(34.05). Cacld. for ($C_{18}H_{16}ClNO_2$): C, 68.90, H, 5.14, N, 4.46; Found: C, 68.62 ,H, 5.26, N, 4.22;

4h: Colorless oil, ^{1}H NMR($CDCl_3$, TMS, 300 MHz): δ(ppm) 0.80(t, 3H, J = 7.2Hz), 0.95(m, 3H), 1.0-1.3(m, 7H), 1.65(m, 2H), 3.36(m, 1H), 3.64(d, 1H, J = 10.9Hz), 3.89(q, 2H, J = 7.1Hz), 4.26(q, 2H, J = 7.10Hz), 7.25(m, 5H); IR(neat):

2950(v) ,2830(m), 1740(vs), 1490(w), 1450(m), 1370(m), 1300(s), 1240(s), 1160(s), 1030(s), 860(m), 760(m), 700(s), 660(w) cm^{-1}. EIMS m/z (relative intensity): 306(M$^+$, 14.67), 291[(M-CH$_3$)$^+$, 24.12], 261[(M-OEt)$^+$, 35.64], 233[(M-CO$_2$Et)$^+$, 17.19). Calcd for ($C_{18}H_{26}O_4$): C, 70.56, H, 8.55; Found: C, 70.77, H, 8.65.

4i: Colorless oil, ^{1}H NMR(CDCl$_3$, TMS, 300 MHz) δ 0.80(t ,3H, J = 7.3Hz), 1.0(t, 3H, J = 7.1Hz), 1.05-1.35(m ,7H), 1.62-1.75(m, 2H), 3.50(m, 1H), 3.67(d, 1H, J = 10.8Hz), 3.93(m, 2H), 4.26(q, 2H, J = 7.1Hz), 7.38(m, 2H), 8.17(m, 2H). IR: 2920(m), 2850(w), 1740(vs), 1600(w), 1520(s), 1460(w), 1340(s), 1300(m), 1240(m), 1170(m), 1030(m), 850(m), 750(w), 660(w) cm^{-1}. EIMS m/z(relative intensity) 351(M$^+$, 19.07), 294[(M-Bu)$^+$, 4.75), 277(55.18), 260(44.56), 248(24.05), 235(41.38), 220(12.79) ,192(15.55), 176(23.94), 160(100.00). Calcd for $C_{18}H_{25}NO_6$: C, 61.52; H, 7.17; N, 3.98. Found: C, 61.60; H, 7.12; N, 4.12.

6a: Colorless oil, ^{1}H NMR(CDCl$_3$, TMS, 90MHz): δ(ppm) 1.37(d, 3H, J = 8Hz), 2.33 (s, 3H), 3.60 (m, 1H), 4.50 (d, 2H, J = 8Hz), 7.16 (s, 4H). IR (neat): 2930 (vs), 1545 (vs), 1530 (v), 1380 (v), 1100 (m), 820 (vs) cm^{-1}. EIMS m/z(relative intensity): 179(M$^+$, 15.31), 164[(M-CH$_3$), 21.86], 133(M-NO$_2$, 16.03). Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.33; N, 7.81. Found: C, 66.78; H, 7.12; N, 7.56.

6b: Colorless oil, ^{1}H NMR(CDCl$_3$, TMS, 90MHz): δ(ppm) 0.90 (t, 3H, J = 7.5Hz), 1.30 - 1.70 (m, 4H), 2.37 (s, 3H), 3.40 (m, 1H), 4.55 (d, 2H, J = 7.5Hz), 7.20 (m, 4H); IR (neat): 2950 (m), 1545 (vs), 1526 (m), 1380 (v), 820 (v), 720 (w) cm^{-1}. EIMS m/z(relative intensity): 221(M$^+$, 6.91), 206[(M-CH$_3$), 31.97], 175(M-NO$_2$, 53.46). Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.67; N, 6.33. Found: C, 70.24; H, 8.39; N, 6.09.

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