Reformatsky Type Reaction with New Aluminium Reagents Containing Al-Sn or Al-Pb Linkage[1)]

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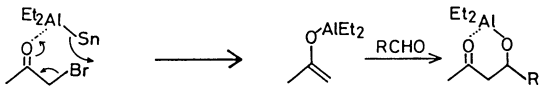
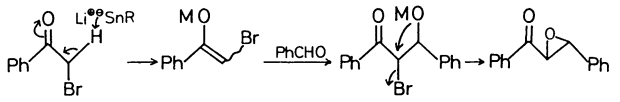
Treatment of α-bromo carbonyl compounds with the reagent prepared from *n*-Bu_3SnLi and Et_2AlCl or from $SnCl_2$ and Et_2AlCl affords enolates which react with ketone or aldehyde to give β-hydroxy carbonyl compounds in good to excellent yields. The reactions proceed similarly with the reagents which are generated from R_3PbLi (R=Ph, *n*-Bu) and Et_2AlCl. Catalysis by the added $Pd(PPh_3)_4$ complex promotes the reduction effectively and improves the yields of the desired adducts. The regio- and stereoselectivities are disclosed.

Cross aldol condensation is one of the most versatile method of making a carbon–carbon bond. The old procedures, however, have some drawbacks of accompanying self aldol condensation and retro-aldol reaction, which provide undesired by-products.[2)] During the past decade, numerous efforts have been made to overcome these shortages.[3)] Among many metal enolates such as Li,[2)] Mg,[2)] Zn,[2)] Ti,[4a)] B,[4b)] Al,[4c,4d,4e)] Si,[4f)] and Sn,[4g)] having been explored, aluminium enolate is suitable for trapping the initially formed aldol adducts as stable chelates.[4c)] Previously reported[4c)] aldol reaction is based on the generation of the regiospecific aluminium enolate by the coupled attack of Et_2AlCl and Zn on the α-halo carbonyl compounds. Here we wish to describe another effective method for the regioselective formation of aluminium enolates which are sufficiently reactive to attack carbonyl components under mild conditions.

A novel reagent which is believed to have an aluminium-tin single bond[5)] is produced by treatment of *n*-Bu_3SnLi[6)] with an equimolar amount of Et_2AlCl. The aluminium atom should behave as a Lewis acid center, which will coordinate the carbonyl oxygen and will give rise to *n*-Bu_3Sn anion acting as a potent reductant (Scheme 1). In fact, treatment of an α-bromo carbonyl compound with this reagent gave an enolate which reacted with a ketone or aldehyde to afford a β-hydroxy carbonyl compound in good yield after aqueous work-up. The success is ascribed to the strong affinity of tin for bromine[7)] as well as that of aluminium for oxygen. Actually, treatment of a mixture of α-bromoacetophenone and benzaldehyde with *n*-Bu_3SnLi alone gave a small amount of β-hydroxy ketone (<5%) in addition to 1,3-diphenyl-2,3-epoxy-1-propanone (33% yield), a Darzens type product.[8)] The latter compound was produced exclusively in 63% yield in the reaction of *n*-Bu_3SnLi–Me_3Al combination instead of *n*-Bu_3SnLi–Et_2AlCl. Strong basicity of the Sn^- anion accompanying Li^+ ion explains the observed results (Scheme 2).

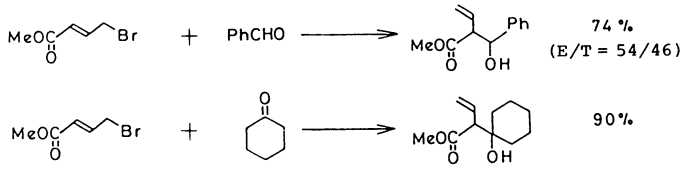


Scheme 1.

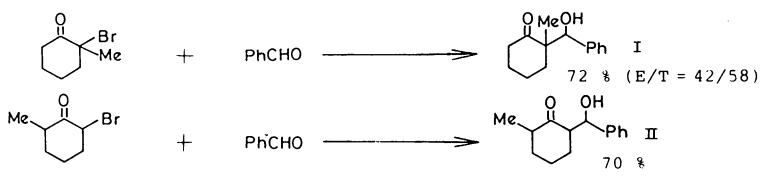


Scheme 2.

As shown in Table 1, the *n*-Bu_3SnLi–Et_2AlCl reagent can be applied equally well to the Reformatsky reaction[9–11)] of α-bromo esters. Reactions of methyl γ-bromocrotonate shown in Scheme 3 gave the α-adducts exclusively in contrast to the normal Reformatsky reactions producing mixtures of α-adducts and γ-adducts in roughly 7:3 ratios.[12)] This high regioselectivity is a characteristic of the aluminium dienolate.[4c,4e)]

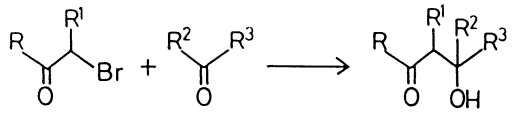


Scheme 3.



Scheme 4.

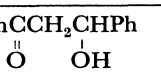
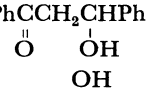
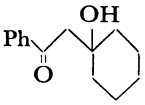
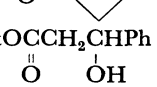
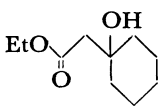
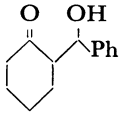
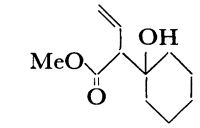
Table 1. Reformatsky type reaction with n-Bu_3SnLi-Et_2AlCl system



Run	R	R^1	R^2	R^3	Additive	Yield/%	E/T
1	Ph	H	Ph	H	—	92[a]	—
2	Ph	H	$-(CH_2)_5-$		—	76[a]	—
3	Ph	H	n-C_8H_{17}	H	—	79	—
4	Ph	H	Ph	H	—	54[a,c]	—
5	Ph	H	Ph	H	$Pd(PPh_3)_4$[b]	70[a,c]	—
6	Ph	H	Me	H	—	53[c]	—
7	Ph	H	Me	H	$Pd(PPh_3)_4$[b]	77[c]	—
8	EtO	H	Ph	H	—	58[a]	—
9	EtO	H	$-(CH_2)_5-$		—	87[a]	—
10	EtO	H	Ph	H	—	54[c]	—
11	EtO	H	Ph	H	$Pd(PPh_3)_4$[b]	75[c]	—
12	$-(CH_2)_5-$		Ph	H	—	69[a]	25/75[d]
13	$-(CH_2)_5-$		Ph	H	$Pd(PPh_3)_4$[b]	75[a]	26/74[d]
14	n-C_6H_{13}	H	Ph	H	—	81	—
15	n-C_6H_{13}	H	$-(CH_2)_5-$		—	54	—
16	n-C_6H_{13}	H	$-(CH_2)_5-$		$Pd(PPh_3)_4$[b]	85	—
17	Et	Me	Ph	H	—	61[e]	50/50[f]

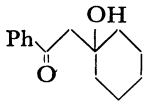
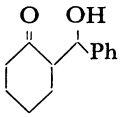
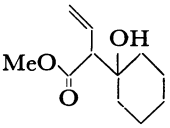
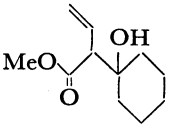
a) These compounds gave satisfactory specra data. See Ref. 4c. b) A catalytic amount of $Pd(PPh_3)_4$ (5 mol%) was added. c) No 1,4-adduct was detected among the reaction mixture. d) The ratio of the stereoisomers (erythro and threo) was determined by an absorption due to the benzylic proton. See Ref. 4 g. e) This compound was identical with the authentic sample. See Ref. 4f. f) Determined by nmr analysis. See Ref. 4f.

Table 2. Reformatsky type reactions with $SnCl_2$-Et_2AlCl system

Run	Bromo ketone or bromo ester	Ketone or aldehyde	Additive	Products	Yield/%
1	$PhCOCH_2Br$	PhCHO	—		70
2	$PhCOCH_2Br$	PhCHO	$Pd(PPh_3)_4$[a]		91
3	Ethyl bromoacetate	Cyclohexanone	$Pd(PPh_3)_4$[a]		89
4	Ethyl bromoacetate	PhCHO	$Pd(PPh_3)_4$[a]		88
5	Ethyl bromoacetate	Cyclohexanone	$Pd(PPh_3)_4$[a]		61
6	2-Bromocyclohexanone	PhCHO	$Pd(PPh_3)_4$[a]		95 (31/69)[b]
7	*Methyl γ-bromo-*crotonate	PhCHO	—[c]		80 (41/59)[d]

a) A catalytic amount of $Pd(PPh_3)_4$ (5 mol%) was added. b) The ratio of the stereo isomers (erythro and threo) was determined by an absorption due to the benzylic proton. See Ref. 4g. c) Palladium catalyst was not effective. d) Erythro/threo ratio was determined by an absorption due to the methoxyl proton. See Ref. 4c.

TABLE 3. REFORMATSKY TYPE REACTIONS WITH R_3PbLi-Et_2AlCl SYSTEM

Run	Bromo ketone or bromo ester	Ketone or aldehyde	Reagent	Products	Yield/%
1	$PhCOCH_2Br$	PhCHO	A	$PhCCH_2CHPh$ (O, OH)	86
2	$PhCOCH_2Br$	PhCHO	B	$PhCCH_2CHPh$ (O, OH)	78
3	$PhCOCH_2Br$	Cyclohexanone	A		61
4	$PhCOCH_2Br$	Cinnamaldehyde	B[a]	$PhCCH_2$-CH-CH=CHPh (O, OH)	84
5	2-Bromocyclohexanone	PhCHO	A		77 (28/72)[b]
6	Methyl γ-bromo-crotonate	Cyclohexanone	A[a]		74
7	Methyl γ-bromo-crotonate	Cyclohexanone	A		56

Reagent A: n-Bu_3PbLi-Et_2AlCl; Reagent B: Ph_3PbLi-Et_2AlCl. a) A catalytic amount of $Pd(PPh_3)_4$ (5 mol%) was added. b) The ratio of the stereo isomers (erythro and threo) was determined by an absorption due to the benzylic proton. See Ref. 4g.

The regioselectivity of the reaction was demonstrated by the following two examples (Scheme 4). Treatment of a mixture of 2-bromo-2-methylcyclohexanone[13] and benzaldehyde with n-Bu_3Sn-$AlEt_2$ gave the expected β-hydroxy ketone I.[4a] Meanwhile, the reaction of 2-bromo-6-methylcyclohexanone[14] provided the regioisomer II[4a] exclusively. Each product I or II was obtained as a single product without any contamination of the opposite regioisomer. Since the starting bromides are prepared with high regioselectivity, the present method provided us with a simple route to the β-hydroxy ketones I and II.

It should be noted that these reactions proceeded more effectively in the presence of a catalytic amount of $Pd(PPh_3)_4$ (Run 5, 7, 11, 13, and 16). For instance, the yield of the adduct of α-bromoacetophenone and cinnamaldehyde was increased from 54% to 75% in the presence of a catalytic amount of $Pd(PPh_3)_4$.[15] We may safely assume that Pd(0) facilitates the reduction of bromo ketone[16] to the aluminium enolate.

The addition of a hexane solution of Et_2AlCl to a suspension of anhydrous $SnCl_2$ in dichloromethane gave a dark red homogeneous solution.[17] The reagent thus prepared also was found to be effective for the Reformatsky type reaction (Table 2). The stereochemistry of the adducts and the regiochemistry of these reactions are similar to those with n-Bu_3SnLi-Et_2AlCl reagent (Run 6, 7).

The use of $PhMe_2SiLi$[18] and Ph_3GeLi[19] instead of n-Bu_3SnLi resulted in a formation of only a small amount of desired β-hydroxy ketone in addition to unidentified products. The combination of R_3PbLi-Et_2AlCl[20] (R=n-Bu, Ph), however, proved to be as effective as n-Bu_3SnLi-Et_2AlCl system (Table 3). The stereochemical outcomes were almost same as those with n-Bu_3SnLi-Et_2AlCl system.

Experimental

The IR spectra were determined on a Shimadzu IR-27-G spectrometer, the mass spectra on a Hitachi M-80 machine, and the NMR spectra on a Varian EM-390 spectrometer. The chemical shifts are given in δ, with TMS as an internal standard. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl. Purification of products were performed by column chromatography on silica gel (Wakogel C-100) or preparative thin-layer chromatography (TLC). Analytical GLPC was performed with a Yanagimoto GCG-550-F and a Shimadzu GC-4CPT.

Preparation of β-Hydroxy Carbonyl Compounds with the Reagent Prepared from n-Bu_3SnLi-Et_2AlCl. A hexane solution of butyllithium (1.6 M†, 3.8 ml, 6.0 mmol) was added to a suspension of anhydrous tin(II) chloride (0.38 g, 2.0 mmol) in THF (4 ml) at 0 °C. After being stirred for 20 min, the reaction mixture was treated with a hexane solution of diethylaluminum chloride (1.0 M, 2.0 ml, 2.0 mmol) at 0 °C. After the resulting mixture was stirred for another 20 min, a mixture of α-bromo carbonyl compound (1.0 mmol) and ketone or aldehyde (1.0 mmol) in THF (3 ml) was added [$Pd(PPh_3)_4$ (58 mg, 0.05 mmol) was added successively, if necessary] and the whole was stirred for 30 min. The reaction mixture was poured into 1M hydrochloric acid (20 ml) and

† 1 M=1 mol dm^{-3}.

extracted with ether. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by silica-gel column chromatography (hexane–ethyl acetate, 2:1).

3-Hydroxy-1-phenyl-1-undecanone: Mp 41.5 °C (pentane); IR (nujol) 3500, 1672, 1205 cm^{-1} NMR (CCl_4): δ=0.90 (t, J=6 Hz, 3H), 1.05—1.70 (m, 14H), 2.80—3.20 (m, 3H), 3.85—4.25 (m, 1H), 7.20—7.60 (m, 3H), 7.75—8.00 (m, 2H); MS m/z (%): 244 (30; M^+-18), 220 (34), 120 (35) 105 (100); Found: C, 77.75; H, 10.22%. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99%.

(E)-3-Hydroxy-1-phenyl-4-hexen-1-one: Bp 80 °C (bath temp, 1 Torr[††]); IR (neat): 3350, 2875, 1700, 1660, 1428 cm^{-1}; NMR (CCl_4) δ=1.68 (d, J=5.7 Hz, 3H), 2.80 (bs, 1H), 3.02 (d, J=6.0 Hz, 2H), 4.40—4.70 (m, 1H), 5.36—5.90 (m, 2H), 7.2—7.65 (m, 3H), 7.75—8.05 (m, 2H); MS m/z (%) 172 (2, M^+-18), 120 (30), 105 (100), 77 (52); Found: C, 75.60; H, 7.50%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%.

Ethyl (E)-3-Hydroxy-5-phenyl-4-pentenoate: Bp 75 °C (bath temp, 1 Torr); IR (neat): 3400, 1705, 1150, 1020, 960 cm^{-1}; NMR (CCl_4): δ=1.25 (t, J=7.5 Hz, 3H), 2.50 (d, J=6 Hz, 2H), 2.90 (bs, 1H), 4.10 (q, J=7.5 Hz, 2H), 4.35—4.75 (m, 1H), 6.33 (d,d, J=6.7 Hz, 15.3 Hz, 1H), 6.90—7.40 (m, 6H); MS m/z (%): 220 (19, M^+), 202 (25), 174 (15), 129 (71), 104 (100), 91 (19); Found: C, 71.04, H, 7.50%. Calcd for $C_{13}H_{16}O_3$: C, 70.89, H, 7.32%. Saponification and dehydration gave 5-phenylpentadienoic acid, which was identical with an authentic sample.[21]

1-Hydroxy-1-phenyl-3-nonanone: Bp 104 °C (bath temp, 0.7 Torr); IR (neat): 3400, 2899, 1679, 1443 cm^{-1}; NMR (CCl_4): δ=0.90 (t, J=6 Hz, 3H), 1.05—1.70 (m, 8H), 2.35 (t, J=6.6 Hz, 2H), 2.60 (d, J=6 Hz, 1H), 2.63 (d, J=7.5 Hz, 1H), 3.15—3.45 (m, 1H), 4.8—5.1 (m, 1H), 6.95—7.30 (m, 5H); MS m/z (%): 234 (0.5, M^+), 216 (3.8), 146 (69), 131 (100), 77 (13), 58 (26); Found: C, 77.05, H, 9.60%. Calcd for $C_{15}H_{22}O_2$: C, 76.88, H, 9.46%.

1-(1-Hydroxycyclohexyl)-2-octanone: Bp 58 °C (bath temp, 1 Torr); IR (neat): 3455, 1690, 1400, 970 cm^{-1}; NMR (CCl_4): δ=0.90 (t, J=6 Hz, 3H), 1.0—2.0 (m, 18H), 2.30 (t, J=6.6, 2H), 2.40 (s, 2H), 3.30 (bs, 1H); MS m/z (%): 226 (15, M^+), 208 (35), 156 (8), 113 (100), 99 (51); Found: C, 74.38, H, 11.87%. Calcd for $C_{14}H_{26}O_2$: C, 74.29, H, 11.58%.

Methyl 2-(1-Hydroxycyclohexyl)-3-butenoate: Bp 51 °C (bath temp, 0.7 Torr); IR (neat): 3450, 1700, 1620, 1155, 985, 905 cm^{-1}; NMR (CCl_4): δ=0.80—1.90 (m, 10H), 2.82 (bs, 1H), 2.91 (t, J=9 Hz, 1H), 3.67 (s, 3H), 5.07 (d,d, J=16.5, 1.5 Hz, 1H), 5.13 (d,d, J=7.5, 1.5 Hz, 1H), 5.90 (d,d,d, J=16.5, 7.5, 1.5 Hz, 1H); MS m/z (%): 198 (0.76, M^+), 183 (2.5), 155 (10), 100 (100), 99 (92), 81 (36), 69 (17), 68 (29); Found: C, 77.05, H, 9.60%. Calcd for $C_{11}H_{18}O_3$: C, 76.88, H, 9.46%.

Preparation of β-Hydroxy Carbonyl Compounds with the Reagent Prepared from $SnCl_2$–Et_2AlCl. A hexane solution of diethylaluminum chloride (1.0 M, 2.0 ml, 2.0 mmol) was added to a suspension of anhydrous tin (II) chloride (0.38 g, 2.0 mmol) in CH_2Cl_2 (5 ml) at 0 °C. The solution turned to red immediately. After being stirred for 20 min, a mixture of α-bromo carbonyl compound (1.0 mmol) and ketone or aldehyde (1.0 mmol) in CH_2Cl_2 (3 ml) was added [$Pd(PPh_3)_4$ (58 mg, 0.05 mmol) was added at the same time, if necessary] and the whole was stirred for 1 h. The reaction mixture was poured into 1M hydrochloric acid (30 ml) and extracted with ether. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by silica-gel column chromatgraphy (hexane–ethyl acetate, 2:1).

Preparation of β-Hydroxy Carbonyl Compounds with the Reagent Prepared from R_3PbLi–Et_2AlCl. A hexane solution of butyllitium (1.6 M, 3.8 ml, 6.0 mmol) or an ether solution of phenyllilitum (2.7 M, 2.2 ml, 6.0 mmol) was added to a suspension of a lead (II) chloride (0.56 g, 2.0 mmol) in THF (4 ml) at 0 °C. After being stirred for 20 min, the whole was cooled to −20 °C, and a hexane solution of diethylaluminum chloride (1.0 M, 2.0 ml, 2.0 mmol) was added at the same temperature. After the resulting mixture was stirred for another 20 min, a mixture of α-bromo carbonyl compound (1.0 mmol) and ketone or aldehyde (1.0 mmol) in THF (3 ml) was added [$Pd(PPh_3)_4$ (58 mg, 0.05 mmol) was added at this time, if necessary] and the whole was warmed up to 0 °C and stirred for 30 min. The reaction mixture was poured into 1 M hydrochloric acid and extracted with ether. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated. The residual liquid was submitted to silica-gel column chromatgraphy with hexane–ethyl acetate=2:1 as an eluent.

Darzens Type Reactions with n-Bu_3SnLi–Me_3Al System. A hexane solution of trimethylaluminium (1.0 M, 2.0 ml, 2.0 mmol) was added to a solution of *n*-Bu_3SnLi prepared from *n*-BuLi (6.0 mmol) and $SnCl_2$ (0.38 g, 2.0 mmol) as described above, in THF (3.0 ml) at 0 °C. After stirring for 2 h, a mixture of α-bromoacetophenone (0.20 g, 1.0 mmol) and benzaldehyde (0.11 g, 1.0 mmol) in THF (2.0 ml) was added at 0 °C and the resulting mixture was stirred for another 20 min. The reaction mixture was poured into 1 M hydrochloric acid (30 min) and extracted with ether. The combined organic layers washed with brine, dried and concentrated. Purification by preparative TLC on silica-gel (hexane-ethyl acetate, 5:1) gave 1,3-diphenyl-2,3-epoxy-1-propanone in 63% yield.

1,3-Diphenyl-2,3-epoxy-1-propanone: Mp 88.5 °C (CH_2Cl_2/penthane); IR (CCl_4): 3000, 1680, 1590, 1500, 1210, 1000, 890 cm^{-1}; NMR (CCl_4): δ=3.90—4.05 (m, 2H) 6.90—7.60 (m, 3H), 7.27 (s, 5H), 7.80-8.10 (m, 2H); MS m/z (%): 224 (12.4, M^+), 165 (9), 105 (100), 91 (23), 77 (64), 65 (16), 51 (31); Found C, 79.87, H, 5.30. Calcd for $C_{15}H_{12}O_2$: C, 80.34, H, 5.39%.

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References

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