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Wittig-type Reaction of Dimetallated Carbodianion Species as Produced by Zinc Reduction of *gem*-Polyhalogen Compounds in the Presence of Lewis Acids

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Treatment of R^1COR^2 with a suspension prepared from diiodomethane, trimethylaluminum and excess zinc in tetrahydrofuran at room temperature affords olefins $R^1R^2C{=}CH_2$ in fair (R^1,R^2=alkyl) to good (R^1=alkyl, R^2=H) yields. The ketone methylenation is better carried with another system consisting of CH_2Br_2–Zn–$TiCl_4$. Ketones and aldehydes are transformed into α-chloro α,β-unsaturated esters or α,β-unsaturated esters in good yields on treatment with methyl trichloroacetate or *t*-butyl dichloroacetate (ethyl dibromoacetate) in the presence of diethylaluminum chloride and zinc.

Metallic zinc is widely used in organic synthesis[1] and often activated by plating the surface with such metals as copper, mercury or silver.[2] The organoaluminum compounds have been found to facilitate the reduction of α-halo carbonyl compounds with zinc greatly and the dramatic effect of co-existing diethylaluminum chloride on the Reformatsky type aldol reaction has been observed.[3] We report here further exploitation for (1) terminal olefin synthesis[4] and (2) α,β-unsaturated ester synthesis by means of species as produced upon zinc reduction of *gem*-polyhalogen compounds in the presence of certain Lewis acid reagents.

Terminal Olefin Synthesis. The Wittig type carbonyl methylenation by means of CH_2I_2–Zn has been described already especially in the presence of a large excess of zinc,[5,6] although the recorded yields are far from satisfactory from the preparative point of view. We wish to report that a mixture of CH_2I_2, Zn, and trimethylaluminum (1: 3: 0.2 mol ratio) reacts with carbonyl compounds to produce olefins much more effectively as summarized in Table 1.

TABLE 1. REACTION OF R^1COR^2 WITH CH_2I_2–Zn–Me_3Al AFFORDING $R^1R^2C{=}CH_2$[a)]

Entry	R^1COR^2		Temp	Time	$R^1R^2C{=}CH_2$
	R^1	R^2	°C	h	Y/%[b)]
1	Ph	H	25	1	86[c)]
2	Ph	Me	25	2	67[c)]
3	PhCH=CH–	H	0	1	75
4	$CH_3(CH_2)_{10}$–	H	0	4	81
5	$CH_3(CH_2)_7$–	$CH_3(CH_2)_2$–	25	2	62
6	–$(CH_2)_{11}$–		25	6	65
7	(citral)		25	4	80

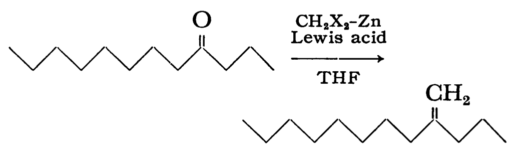
a) Three mol of CH_2I_2, nine mol of Zn and 0.6 mol of Me_3Al were employed per mol of carbonyl compounds. b) Isolated yield unless otherwise specified. c) GLPC yield by internal standard method.

Rather surprisingly, careful examination of the products failed to prove any traces of cyclopropane derivatives, which should be ascribed to the Simmons-Smith reaction of the olefinic linkage of the carbonyl components (entry 3, 7) or of the resulting $R^1R^2C{=}CH_2$. Although the reaction of the Simmons-Smith reagent with Me_3SnCl gives ICH_2SnMe_3,[7] the present reagent has been found to afford $CH_2(SnMe_3)_2$[8] exclusively under the same conditions and no ICH_2SnMe_3.

We therefore are tempted to attribute the formation of Wittig type olefins to the carbodianion species, although the identity of counter ions attached are still not clear. This *gem*-dimetallic nature of the present reactive intermediate has been further confirmed by the fact that preformed iodohydrin $PhCH(OH)CH_2I$[9] was recovered practically unchanged after treatment with excess of the reagent prepared as above. Olefination of aldehyde and ketone carbonyls by *gem*-dimetallic reagent of the type Mtl–CH_2–Mtl′ has been described to afford variable yields.[10] Exclusive carbonyl methylenation of enals (entry 3, 7) is unprecedented.

The yields of the methylenated products from ketones could not be improved over 70% in spite of various attempts made by means of the CH_2I_2, Zn, and R_3Al system. Other Lewis acids have been examined in the

TABLE 2. EFFECTS OF VARIOUS LEWIS ACID ON THE TRANSFORMATION OF 4-DODECANONE TO 2-PROPYL-1-DECENE[a)]



Lewis acid	Yield/% of 2-Propyl-1-decene	
	CH_2I_2	CH_2Br_2
Me_3Al	62	14
Et_3Al	55	27
Et_2AlCl	56	23
$AlCl_3$	42	<5
$TiCl_4$	83	89
VCl_4	73	20
$ZrCl_4$	34	<5
WCl_6	<5	<5

a) Three mol of CH_2I_2 or CH_2Br_2, 9 mol of Zn and 1 mol of Lewis acid were employed per mol of 4-dodecanone. Reaction mixture was stirred for 12 h at 25 °C and 2-propyl-1-decene was isolated by column chromatography.

transformation of 4-dodecanone to 2-propyl-1-decene with CH_2X_2 and zinc (Table 2). Among them, $TiCl_4$ has proved to be the best enabling to use CH_2Br_2 instead of CH_2I_2.

The results of methylenation with CH_2Br_2, Zn, $TiCl_4$ system are shown in Table 3. Neither cyclopropane compounds nor isomerized olefins were isolated. Entry 3[11] and 4[12] showed the superiority of the method over the Wittig reaction. The reductive coupling of the carbonyl component[13] was observed only with an aldehyde (entry 6), although the desired olefin was still predominant.

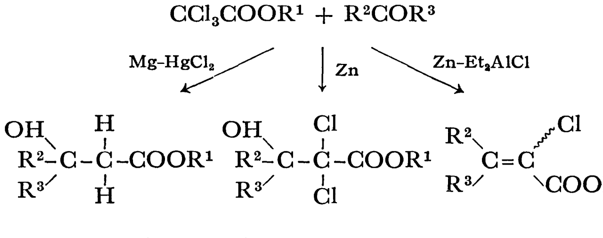
Both systems of CH_2I_2–Zn–Me_3Al and CH_2Br_2–Zn–$TiCl_4$ are complementary. The mild conditions and high yields characterize the two systems as a useful alternative for the Wittig carbonyl methylenation.[14]

Table 3. Reaction of R^1COR^2 with CH_2Br_2–Zn–$TiCl_4$ affording $R^1R^2C{=}CH_2$[a]

Entry	R^1COR^2		Temp	Time	$R^1R^2C{=}CH_2$
	R^1	R^2	°C	h	Y/%[b]
1	$CH_3(CH_2)_7$–	$CH_3(CH_2)_2$–	25	12	89
2	–$(CH_2)_{11}$–		25	12	80
3	–$(CH_2)_6$–		25	6	83[c]
4	(camphor)		25	40	92[c]
5	(geranylacetone)		25	12	83
6	$CH_3(CH_2)_{10}$–	H	0	4	55[d]

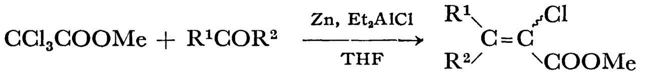
a) One and a half mol of CH_2Br_2, 4.5 mol of Zn and 1.1 mol of $TiCl_4$ were employed per mol of carbonyl compounds. b) Isolated yield. c) GLPC yield by internal standard method. d) $CH_3(CH_2)_{10}CH(OH)$-$CH(OH)(CH_2)_{10}CH_3$ was also obtained (24%).

α-Chloro α,β-Unsaturated Ester and α,β-Unsaturated Ester Syntheses. The reaction between ethyl trichloroacetate and carbonyl compounds in the presence of zinc[15] or Mg–$HgCl_2$[16] has been reported to result in the formation of α,α-dichloro β-hydroxy esters or the further reduced β-hydroxy esters. Meantime, we have disclosed that co-existence of diethylaluminum chloride in these classical Reformatsky reaction changes the reaction path dramatically to afford α-chloro α,β-unsaturated esters[17] instead. The results are summarized in Table 4.



Remarkably, a Reformatsky product $Me_2C{=}CHCH_2$-$CH_2C(CH_3)(OH)CCl_2COOMe$ prepared by the conventional way has been recovered unchanged on treatment with the Zn–Et_2AlCl system. Furthermore, α,β-unsaturated esters were produced in the similar reaction of dichloro- or dibromoacetate with carbonyl in fair yields, which are shown in Table 5. The present method provides an alternative for the Emmons-Wadsworth-Horner reaction[18] and would very probably involve a Mtl–C(X)=C(OMtl′)OR (X=Cl or H) type species. It should be noted that the presence of diethylaluminum chloride is crucial to the formation of α,β-unsaturated esters, since its absence results in ordinary Reformatsky products, halohydrins.[24]

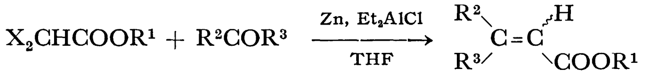
Table 4. Synthesis of α-chloro α,β-unsaturated esters



Entry	R^1COR^2		Conditions		Product	
	R^1	R^2	°C	h	Y/%[a]	E/Z
1	Ph	H	0	4	51	<5/>95
2	–$(CH_2)_5$–		0	6	81	—
3	$Me_2C{=}CH(CH_2)_2$–	CH_3	0	6	90	28/72
4	Ph	CH_3	0	4	86	9/91

a) Isolated yields.

Table 5. Synthesis of α,β-unsaturated esters



Ester		R^2COR^3		Conditions		Product	
X	R^1	R^2	R^3	°C	h	Y/%[a]	E/Z
Cl	^{t}Bu	Ph	CH_3	25	6	67	62/38
Cl	^{t}Bu	–$(CH_2)_{11}$–		25	8	61	—
Cl	^{t}Bu	$Me_2C{=}CH(CH_2)_2$–	CH_3	25	6	52	59/41
Br	Et	Ph	H	25	3	42	>95/<5
Br	Et	$CH_3(CH_2)_{10}$–	H	25	3	43	>95/<5

a) Isolated yields.

Experimental

The IR spectra were determined on a Shimadzu IR-27-G spectrometer; the mass spectra, on a Hitachi RMU-6L machine; and the NMR spectra, on a JEOL C-60-H or a Varian EM-390H spectrometer. The chemical shifts are given in δ, with TMS as the internal standard. The analyses were carried out by the staff at the Elemental Analyses Center of Kyoto University. Commercial zinc dust was washed several times with 5% hydrochloric acid, washed in turn with water, methanol, and ether, and dried.[19] Tetrahydrofuran (THF) was dried on benzophenone ketyl and distilled. All the experiments were carried out under an argon atmosphere. Purification of products were performed by preparative thin layer chromatography (TLC) or column chromatography on silica gel (Merck Kieselgel 60). Analytical GLPC was performed with a Yanagimoto GCG-550-F. Product percentages were calculated from peak area ratios without correction for detector response. Preparative GLPC was performed with a JEOL-JGC-20K apparatus.

Preparation of Terminal Olefins by Means of CH_2I_2–Zn–Me_3Al System. To a suspension of zinc dust (1.18 g, 18 mmol) and diiodomethane (1.61 g, 6.0 mmol) in dry THF (10 ml) was added a hexane solution of trimethylaluminum (1.0 M, 1.2 ml, 1.2 mmol) at 25 °C. The resulting mixture was stirred until the exothermic reaction had subsided (10 min). A solution of carbonyl compound (2.0 mmol) in THF was added dropwise at 25 °C (0 °C). After stirring at this temperature for an appropriate time described in Table 1, the reaction mixture was diluted with ether (10 ml), poured into 1 M hydrochloric acid (20 ml), and extracted with ether. The separated organic layer was washed with brine (2×20 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (20 g) using hexane as an eluent.

Preparation of Terminal Olefins by Means of CH_2Br_2–Zn–$TiCl_4$ System. To a suspension of zinc dust (0.59 g, 9.0 mmol) and dibromomethane (0.52 g, 3.0 mmol) in THF (10 ml) was added a dichloromethane solution of titanium tetrachloride (1.0 M, 2.2 ml, 2.2 mmol) at 25 °C. Instantaneous reaction occurred under evolution of heat and rapid color change to dark brown. After 15 min, a THF solution of carbonyl compound (2.0 mmol) was added dropwise and the resulting mixture was stirred at 25 °C (0 °C) for an appropriate time described in Table 3. The reaction mixture was diluted with ether (10 ml), poured into 1 M hydrochloric acid (20 ml), and extracted with ether. The separated organic layer was washed with brine (2×20 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (20 g) using hexane as an eluent.

2-Propyl-1-decene: Bp 82 °C (bath temp, 2 Torr); IR (neat): 3080, 1643, 1470, 890 cm^{-1}; NMR (CCl_4): δ 0.90 (t, J=6 Hz, 6H), 1.15—1.55 (bm, 14H), 1.94 (t, J=6 Hz, 4H), 4.60 (s, 2H); MS *m/e* (%): 182 (M$^+$, 4), 139 (5), 97 (12), 56 (100); Found: C, 85.73; H, 14.62%. Calcd for $C_{13}H_{26}$: C, 85.63; H, 14.37%.

Methylenecyclododecane: Bp 85 °C (bath temp, 2 Torr); IR (neat): 3080, 1645, 1485, 1445, 890 cm^{-1}; NMR (CCl_4): δ 1.15—1.60 (bm, 18H), 1.93—2.20 (bt, 4H), 4.80 (s, 2H); MS *m/e* (%): 180 (M$^+$, 18), 109 (32), 97 (66), 82 (82), 55 (100). The compound was identical with the authentic sample.[20]

4,8-Dimethyl-1,3,7-nonatriene: Bp 53 °C (bath temp, 2 Torr); IR (neat): 3080, 1648, 1600, 1450, 990, 892 cm^{-1}; NMR (CCl_4): δ 1.60 (s, 3H), 1.67 (s, 3H), 1.74 (s, 3H), 1.95—2.17 (bm, 4H), 4.80—5.15 (bm, 3H), 5.76 (d, J=10 Hz, 1H), 6.46 (ddd, J=10, 10, 17 Hz, 1H); MS *m/e* (%): 150 (M$^+$, 7), 135 (6), 107 (11), 81 (18), 69 (100); Found: C, 87.87; H, 12.21%. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07%.

Methylenecycloheptane: Bp 135 °C (1 atm); IR (neat): 3100, 1640, 1450, 880 cm^{-1}; NMR (CCl_4): δ 1.53 (bm, 8H), 2.23 (bt, 4H), 4.60 (s, 2H); MS *m/e* (%): 110 (M$^+$, 19), 95 (55), 82 (74), 67 (100). The compound was identical with the authentic sample.[21]

2-Methylenebornane: Mp 67—70 °C (sublimes appreciably at room temperature); IR (neat): 3070, 1655, 1450, 870 cm^{-1}; NMR (CCl_4): δ 0.77 (s, 3H), 0.88 (s, 6H), 1.08—2.60 (m, 7H), 4.40—4.65 (bdd, 2H); MS *m/e* (%): 150 (M$^+$, 25), 135 (45), 121 (24), 107 (100), 79 (79). The compound was identical with the authentic sample.[12]

2,6,10-Trimethyl-1,5,9-undecatriene: Bp 78 °C (bath temp, 2 Torr); IR (neat): 3080, 1650, 1450, 885, 825 cm^{-1}; NMR (CCl_4): δ 1.57, 1.65, 1.67, 1.70 (s, 12H), 1.85—2.20 (bm, 8H), 4.62 (s, 2H), 4.90—5,14 (bm, 2H); MS *m/e* (%): 192 (M$^+$, 3), 177 (3), 136 (9), 121 (9), 81 (52), 69 (100); Found: C, 87.20; H, 12.82%. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58%.

1-Phenyl-1,3-butadiene and 1-Tridecene: These compounds were identical with the authentic samples.[22,23]

Reaction of Dodecanal with the Reagent Prepared from CH_2Br_2–Zn–$TiCl_4$ System. Dodecanal (0.37 g, 2.0 mmol) was treated with the reagent prepared from dibromomethane (0.52 g, 3.0 mmol), zinc (0.59 g, 9.0 mmol), and titanium tetrachloride (2.2 ml of a 1.0 M dichloromethane solution, 2.2 ml) in THF (10 ml) at 25 °C. The crude product was submitted to preparative TLC (hexane–ether, 1: 1) on silica gel. The faster-moving band (R_f=0.79) provided the desired olefin, 1-tridecene (0.20 g, 55%). The slower-moving band (R_f=0.25) consisted of 12,13-tetracosanediol (89 mg) as a solid; mp 88 °C; IR (KBr): 3300, 2900, 1470, 1068, 708 cm^{-1}; NMR ($CDCl_3$): δ 0.89 (t, J=6 Hz, 6H), 1.10—1.52 (m, 40H), 3.30—3.60 (m, 2H); Found: C, 77.77; H, 13.82%. Calcd for $C_{24}H_{50}O_2$: C, 77.77; H, 13.60%. The compound was identical with the authentic sample.[13]

Reaction of Trimethyltin Chloride with the Reagent Derived from CH_2I_2–Zn–Me_3Al in THF. The reagent was prepared from diiodomethane (0.54 g, 2.0 mmol), zinc (0.39 g, 6.0 mmol), and trimethylaluminum (0.5 ml of a 1.0 M hexane solution, 0.5 mmol) in THF (10ml) as mentioned before. After stirring at 25 °C for 30 min, the mixture was allowed to stand for 20 min and the supernatant was transformed to an another flask. To this was added a THF solution of trimethyltin chloride (0.80 g, 4.0 mmol) at *ca.* 40 °C and the resulting mixture was stirred at the same temperature for 4 h. After a usual workup, the crude product was purified by column chromatography on silica gel (10 g) using hexane as an eluent (R_f=0.55 (hexane)). Successive distillation gave methylenebis (trimethylstannane) (0.18 g, 27%) as a colorless oily liquid; bp 63 °C (bath temp, 5 Torr); IR (neat): 1465, 1262, 1190, 1100, 1025, 955, 760, 600 cm^{-1}; NMR (CCl_4) δ 0.05 (Sn–CH_3, 18H, J_{Sn-H}=51 Hz), −0.29 (Sn–CH_2–Sn, 2H, J_{Sn-H}=55 Hz); MS *m/e* (%): 329 (56), 327 (67), 325 (M$^+$–CH_3, 64), 165 (100). Values of *m/e* are given for the isotope ^{118}Sn. The relative intensities of the peaks of the isotopic varieties of the ions correspond to the calculated values; Found: C, 24.63; H, 6.17%. Calcd for $C_7H_{20}Sn_2$: C, 24.61; H, 5.90; Sn, 69.49%. The compound was identical with the authentic sample.[8]

Preparation of α-Chloro α,β-Unsaturated Esters by Means of CCl_3COOMe–Zn–Et_2AlCl System. To a stirred suspension of zinc dust (0.39 g, 6.0 mmol) and diethylaluminum chloride (0.67 ml of a 1.5 M hexane solution, 1.0 mmol) in THF (10 ml) was added a THF solution of methyl trichloroacetate (0.43 g, 2.4 mmol) and carbonyl compound (2.0 mmol) at 0 °C over a period of 3 h. After stirring for an additional 1 h, the resulting mixture was diluted with ether (20 ml), poured into 1 M hydrochloric acid (20 ml), and extracted with ether. The separated organic layer was washed with brine (2 × 20 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane–ether, 20: 1) on silica gel (20 g).

Methyl (Z)-2-Chloro-3-phenylpropenoate: Bp 87 °C (bath temp, 2 Torr); IR (neat): 2955, 1730, 1620, 1495, 1450, 1438, 1265, 1040, 765, 690 cm^{-1}; NMR (CCl_4): δ 3.83 (s, 3H), 7.20—7.90 (m, 6H); MS *m/e* (%): 198 ($M^+ + 2$, 21), 196 (M^+, 62), 165 (22), 161 (73), 160 (24), 137 (35), 129 (52), 102 (100); Found C, 61.38; H, 4.69%. Calcd for $C_{10}H_9O_2Cl$: C, 61.08; H, 4.61%. (*E*)-Isomer was not detected by GLPC.

Methyl Chlorocyclohexylideneacetate: Bp 80 °C (bath temp, 3 Torr); IR (neat): 2950, 1725 ,1610, 1438, 1270, 1245, 1210, 1030, 760 cm^{-1}; NMR (CCl_4): δ 1.50—1.80 (m, 6H), 2.38—2.55 (bt, J=6 Hz, 2H), 2.55—2.75 (bt, J=6 Hz, 2H), 3.75 (s, 3H); MS *m/e* (%): 190 ($M^+ + 2$, 32), 188 (M^+, 91), 157 (54), 156 (50), 134 (65), 121 (96), 93 (100), 91 (64); Found: C, 57.29; H, 7.32%. Calcd for $C_9H_{13}O_2Cl$: C, 57.30; H, 6.95%.

Methyl (E)- and (Z)-2-Chloro-3,7-dimethyl-2,6-octadienoate: GLPC (20% PEG 6000, 2 m, 150 °C) indicated two peaks, T_r=14.1 min ((*E*)-isomer, 28%), T_r=12.4 min ((*Z*)-isomer 72%). The analytically pure samples of both isomers were prepared by preparative GLPC (20% PEG 6000). (*E*)-Isomer: bp 70 °C (bath temp, 2 Torr); IR (neat): 2940, 1772, 1645, 1438, 1260, 1020, 760 cm^{-1}; NMR (CCl_4): δ 1.62 (s, 3H), 1.68 (s, 3H), 1.95—2.67 (m, 4H), 2.15 (s, 3H), 3.76 (s, 3H), 5.07 (bt, 1H); MS *m/e* (%): 218 ($M^+ + 2$, 1), 216 (M^+, 3), 181 (9), 148 (14), 139 (9), 116 (10), 69 (100), 53 (10); Found: C, 61.24; H, 8.15%. Calcd for $C_{11}H_{17}O_2Cl$: C, 60.97; H, 7.91%. (*Z*)-Isomer: bp 72 °C (bath temp, 2 Torr); IR (neat): 2940, 1722, 1615, 1438, 1250, 1025, 775 cm^{-1}; NMR (CCl_4): δ 1.63 (s, 3H), 1.69 (s, 3H), 2.02 (s, 3H), 2.05—2.70 (m, 4H), 3.27 (s, 3H), 5.08 (bt, 1H); MS *m/e* (%): 216 (M^+, 1), 181 (12), 148 (13), 139 (7), 116 (10), 69 (100), 41 (51); Found: C, 60.93; H, 8.09%. Calcd for $C_{11}H_{17}O_2Cl$: C, 60.97; H, 7.91%.

Methyl (E)- and (Z)-2-Chloro-3-phenyl-2-butenoate: GLPC (10% PEG 20 M, 2 m, 140 °C) indicated two peaks, T_r=27.0 min ((*E*)-isomer, 9%), T_r=19.6 min ((*Z*)-isomer, 91%). The analytically pure samples of both isomers were prepared by preparative GLPC (30% PEG 20 M). (*E*)-Isomer: bp 85 °C (bath temp, 2 Torr); IR (neat): 2960, 1730, 1492, 1440, 1250, 1048, 760, 695 cm^{-1}; NMR (CCl_4): δ 2.39 (s, 3H), 3.80 (s, 3H), 7.00—7.40 (m, 5H); MS *m/e* (%): 212 ($M^+ + 2$, 15), 210 (M^+, 44), 180 (24), 179 (30), 178 (56), 116 (19), 115 (100); Found: C, 63.01; H, 5.41%. Calcd for $C_{11}H_{11}O_2Cl$: C, 62.72; H, 5.26%. (*Z*)-Isomer: bp 87 °C (bath temp, 2 Torr); IR (neat): 2960, 1735, 1620, 1495, 1440, 1240, 1090, 695 cm^{-1}; NMR (CCl_4): δ 2.26 (s, 3H), 3.46 (s, 3H), 7.00—7.38 (m, 5H); MS *m/e* (%): 212 ($M^+ + 2$, 13), 210 (M^+, 40), 180 (23), 179 (24), 178 (66), 116 (21), 115 (100); Found: C, 62.87; H, 5.36%. Calcd for $C_{11}H_{11}O_2Cl$: C, 62.72; H, 5.26%.

Preparation of α,β-Unsaturated Esters from Ketones by Means of Cl_2CHCOO^tBu-Zn-Et_2AlCl System. To a stirred suspension of zinc dust (0.59 g, 9.0 mmol) and diethylaluminum chloride (2.0 ml of a 1.5 M hexane solution, 3.0 mmol) in THF (10 ml) was added a THF solution of *t*-butyl dichloroacetate (0.56 g, 3.0 mmol) and ketone (2.0 mmol) at 25 °C over a period of 3 h. After stirring for additional 3 h, the resulting mixture was diluted with ether (10 ml), poured into 1 M hydrochloric acid (20 ml), and extracted with ether. The separated organic layer was washed with brine (2 × 20 ml), dried over anhydrous sodium sulfate and evaporated to remove solvent. The crude product was purified by column chromatography (hexane–ether, 20: 1) on silica gel (20 g) and distilled *in vacuo*.

t-Butyl (E)- and (Z)-3-Phenyl-2-butenoate: TLC (hexane–ether, 10: 1) showed two UV active bands, R_f=0.28 ((*E*)-isomer, 62%), R_f=0.42 ((*Z*)-isomer, 38%). (*E*)-Isomer: bp 61 °C (bath temp, 2 Torr); IR (neat): 2980, 1725, 1720, 1640, 1368, 1300, 1145, 960, 860 cm^{-1}; NMR (CCl_4): δ 1.20 (s, 9H), 2.12 (s, 3H), 5.72 (s, 1H), 7.05—7.40 (bm, 5H); MS *m/e* (%): 218 (M^+, 3), 162 (100), 161 (72), 145 (50), 144 (72), 117 (22), 116 (26), 115 (34), 57 (30): Found: C, 77.06; H, 8.44%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%. (*Z*)-Isomer: bp 60 °C (bath temp, 2 Torr); IR (neat): 2970, 1710, 1632, 1368, 1274, 1145, 870, 768 cm^{-1}; NMR (CCl_4): δ 1.48 (s, 9H), 2.50 (s, 3H), 5.96 (s, 1H), 7.20—7.50 (bm, 5H); MS *m/e* (%): 218 (M^+, 4), 162 (100), 161 (70), 145 (63), 144 (71), 117 (25), 116 (29), 115 (41), 57 (42); Found: C, 77.07; H, 8.54%. Calcd for $C_{14}H_{18}O_2$: C, 77.07, H, 8.31%.

t-Butyl Cyclododecylideneacetate: Bp 120 °C (bath temp, 1.5 Torr); IR (neat): 2980, 1712, 1640, 1470, 1364, 1240, 1130, 874, 708 cm^{-1}; NMR (CCl_4): δ 1.20—1.40 (bm, 18H), 1.43 (s, 9H), 2.13 (t, J=6 Hz, 2H), 2.62 (t, J=6 Hz, 2H), 5.53 (s, 1H); MS *m/e* (%): 224 ($M^+ - (H_2C{=}CMe_2)$, 64), 207 (38), 164 (56), 100 (48), 57 (88), 55 (60), 41 (100); Found: C, 77.36; H, 11.77%. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50%.

t-Butyl (E)- and (Z)-3,7-Dimethyl-2,6-octadienoate: GLPC (10% PEG 20 M, 2 m, 120 °C) indicated two peaks, T_r=7.4 min ((*E*)-isomer, 59%), T_r=9.7 min ((*Z*)-isomer, 41%). The analytically pure samples of both isomers were prepared by preparative GLPC (30% PEG 20 M). (*E*)-Isomer: bp 65 °C (bath temp, 2 Torr); IR (neat): 2980, 1710, 1648, 1450, 1364, 1240, 1144, 852 cm^{-1}; NMR (CCl_4): δ 1.44 (s, 9H), 1.60 (s, 3H), 1.65 (s, 3H), 2.00—2.10 (bm, 7H), 5.10 (bt, 1H), 5.48 (s, 1H); MS *m/e* (%): 224 (M^+, trace), 168 ($M^+ - (H_2C{=}CMe_2)$, 17), 151 (16), 123 (22), 100 (33), 69 (100), 57 (30); Found: C, 74.84; H, 10.97%. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78%. (*Z*)-Isomer: bp 67 °C (bath temp, 2 Torr); IR (neat): 2990, 1715, 1670, 1368, 1230, 1135, 865 cm^{-1}; NMR (CCl_4): δ 1.44 (s, 9H), 1.57 (s, 3H), 1.66 (s, 3H), 2.00—2.20 (bm, 7H), 5.02 (bt, 1H), 5.48 (s, 1H); MS *m/e* (%): 168 ($M^+ - (H_2C{=}CMe_2)$, 20), 151 (16), 125 (9), 123 (24), 100 (44), 69 (100), 57 (40); Found: C, 74.96; H, 10.95%. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78%.

Preparation of α,β-Unsaturated Esters from Aldehydes by Means of $Br_2CHCOOEt$-Zn-Et_2AlCl System. To a stirred suspension of zinc dust (0.91 g, 14.0 mmol) and diethylaluminum chloride (2.0 ml of a 1.5 M hexane solution, 3.0 mmol) in THF (10 ml) was added a THF solution of ethyl dibromoacetate (0.98 g, 4.0 mmol) and aldehyde (2.0 mmol) at 25 °C over a period of 2 h. After stirring for an additional 1 h, the resulting mixture was diluted with ether (20 ml), poured into 1 M hydrochloric acid (20 ml), and extracted with ether. The separated organic layer was washed with brine (2 × 20 ml), dried over anhydrous sodium sulfate, and evaporated to remove solvent. The crude product was purified by column chromatography (hexane–ether, 20: 1) on silica gel (20 g).

Ethyl (E)-2-Tetradecenoate: Bp 115 °C (bath temp, 2 Torr); IR (neat): 2925, 1725, 1660, 1604, 1470, 1264, 1234, 1040, 975 cm^{-1}; NMR (CCl_4): δ 0.87 (t, J=6 Hz, 3H), 1.27 (bm, 23H), 2.03—2.33 (bt, 2H), 4.08 (q, J=6 Hz, 2H), 5.66 (d, J=16 Hz, 1H), 6.82 (dt, J=6, 16 Hz, 1H); MS *m/e* (%): 254 (M^+, 7), 209 (33), 166 (25), 127 (29), 101 (63), 55 (93), 43 (100);

Found: C, 75.67; H, 11.92%. Calcd for $C_{16}H_{30}O_2$: C, 75.54; H, 11.89%. The product was contaminated by $<$5% of the (*Z*)-isomer (by NMR).

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