stereogenic center and with high levels of regio- and acyclic stereocontrol. Additionally, a synthetically useful β-dicarbonyl functionality is introduced.

Experimental Section

Compound (±)-**5**: (±)-**1** (402 mg, 1.0 mmol) and ethyl acetoacetate (156 mg, 1.2 mmol) were added sequentially to a solution of $[RhH(CO)(PPh_3)_3]$ (9.2 mg, 1×10^{-2} mmol) in toluene (3 mL) at 20 °C (with exclusion of air and moisture). The solution was stirred for 5 min and then piperidine (17 mg, 0.2 mmol) and acetic acid (12 mg, 0.2 mmol) were added sequentially. The resulting solution was transferred by cannula (rinsed with 2 mL of toluene) into an evacuated and argon-filled stainless-steel autoclave. The autoclave was heated to 90 °C and pressurized with 20 bar H_2/CO (1:1). After stirring for 24 h at this temperature the autoclave was cooled rapidly to 20 °C and depressurized. The reaction solution was filtered through a small pad of silica with *tert*-butylmethylether (50 mL). After evaporation of the solvent, the crude product was analyzed by NMR spectroscopy to determine the diastereomeric ratio (*syn*/*anti* 96:4). Subsequent purification by column chromatography on silica with petroleum ether (40/60)/*tert*-butylmethylether (4:1) provided the β-ketoester (±)-**5** (390 mg, 71%) as a highly viscous oil. ^{1}H NMR (500.130 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.77-0.87$ (m, 9H), 1.05–1.10 (m, 1H), 1.24 (m_c, 3H), 1.69–1.92 (m, 5H), 2.15 [2.18] (s, 3H), 3.24 [3.30] (pt, $J = 7.3$ Hz, 1H), 4.11–4.21 (m, 2H), 4.81 (m_c, 1H), 6.91 (m_c, 1H), 7.25–7.31 (m, 10H), 7.38 (m_c, 2H), 8.08 (m_c, 1H); ^{13}C NMR (125.758 MHz, $CDCl_3$, 25 °C): $\delta = 13.7$ [13.8], 14.0, 18.2 [18.4], 19.1 [19.2], 25.6 [25.7], 28.7 [29.0], 29.5, 31.2 [31.4], 34.3, 56.6 [59.9], 61.2 [61.3], 81.5 [81.8], 128.1 (d, $^3J_{C,P} = 2.8$ Hz), 128.4 (d, $^3J_{C,P} = 6.9$ Hz, 2C), 128.4–128.5 (2C), 130.4, 131.8 (d, $^3J_{C,P} = 6.4$ Hz), 133.7–134.3 (8C), 138.1–138.3 (2C), 140.9 (d, $^1J_{C,P} = 28.2$ Hz) [141.0 (d, $^1J_{C,P} = 27.6$ Hz)], 166.30 [166.32], 169.6 [169.7], 203.2 [203.3]; ^{31}P NMR (202.457 MHz, $CDCl_3$, 25 °C, 85% H_3PO_4): $\delta = -4.49$ (s) [−4.51 (s)]; elemental analysis: calcd. (%) for $C_{33}H_{39}O_5P$: C 72.51, H 7.19; found C 72.62, H 7.34.

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[11] All compounds were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis. The β-diketones show keto–enol tautomerism. The ratios of the enolic form range from 32% (Table 2, entry 3) to 56% (Table 2, entries 6 and 9).

[12] The relative configurations of the domino reaction products were determined at the stage of the aldehyde, since the stereochemistry-determining step is the hydroformylation step.[8,14,15] This was confirmed by stepwise transformation of the known aldehyde (±)-**3**, derived from olefin (±)-**1**,[8] into the domino hydroformylation/Knoevenagel reaction/hydrogenation product (±)-**5**: a) 1.2 equiv $MeCOCH_2CO_2Et$, 0.2 equiv piperidine/AcOH, toluene, 70 °C, 4 h, →α,β-unsaturated β-ketoester (40%); b) 1 mol% $[Rh(H)(CO)(PPh_3)_3]$, H_2 (20 bar), toluene, 90 °C, 24 h, →(±)-**5** (10%)+several side products). Obviously, the domino reaction process gives a significantly higher yield than the same reaction executed in a stepwise manner.

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Dialkenylation of Carbonyl Groups by Alkenyllithium Compounds: Formation of Cyclopentadiene Derivatives by the Reaction of 1,4-Dilithio-1,3-dienes with Ketones and Aldehydes**

Zhenfeng Xi,* Qiuling Song, Jinglong Chen, Hairong Guan, and Pixu Li

The development of methodologies for carbon–carbon bond formation by deoxygenation of the C=O moieties in carbonyl compounds has attracted much attention as a powerful synthetic strategy.[1] In general, two types of C–C bond-forming reactions that involve the deoxygenation of C–O double bonds in carbonyl compounds are known (Scheme 1, Type I and Type II). Type I reactions give rise to a C–C double bond. The Wittig-type reactions,[2] Tebbe's reagent or Grubbs' titanacycle,[3] and the McMurry reaction[4] have been utilized extensively to convert carbonyl compounds into alkenes. Type II reactions form two $C(sp^3)$–$C(sp^3)$ bonds. Reetz's direct geminal dialkylation, which uses organotitanium reagents[5] and $AlMe_3$,[6] and direct geminal diallylation, which uses vanadium(II) species[7] have been reported. We

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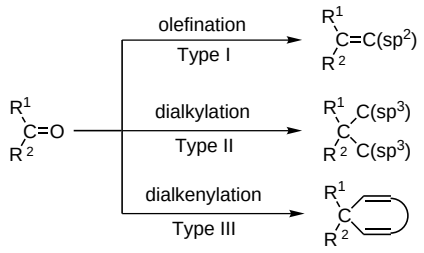
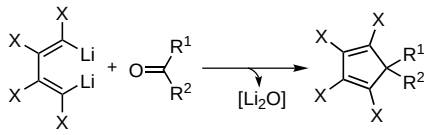


Scheme 1. Types of reactions for the formation of C–C bonds from C=O bonds.

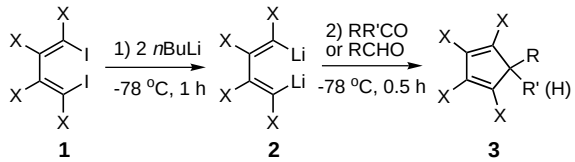
recently described an $AlCl_3$-mediated reaction of zirconacyclopentadienes with aldehydes to afford cyclopentadiene derivatives.[8] Although the complete deoxygenation of the carbonyl group and the quaternization of its carbon atom can lead to useful methods for the formation of quaternary carbons or complex structures, such kinds of procedures are surprisingly rare, probably because reactions of ketones or aldehydes with reactive organometallic compounds, especially organolithium or Grignard reagents, normally result in alcohols.[9]

We report herein a new reaction of ketones and aldehydes with organolithium compounds which involves the deoxygenation of the C=O moieties. Type III reactions (Scheme 1) form $C(sp^3)$–$C(sp^2)$ bonds in the direct cyclodialkenylation of ketones and aldehydes with dilithium compounds to form cyclopentadiene derivatives ([Eq. (1)]; the substituents X are not necessarily identical).



(1)

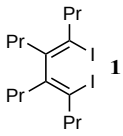
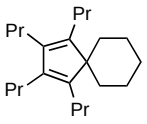
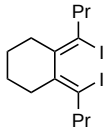
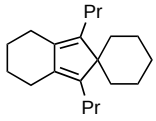
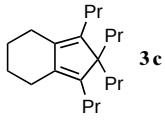
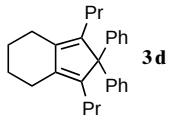
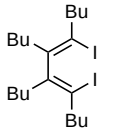
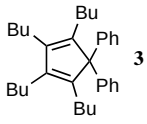
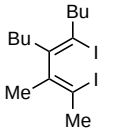
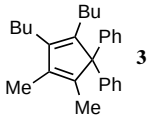
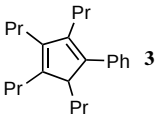
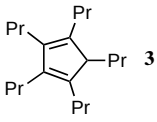
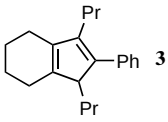
The reaction of organomonolithium compounds, including alkyl- and alkenyllithium compounds, with carbonyl groups is normally straightforward, and gives alcohols after hydrolysis, or α-deprotonation products.[9] However, when dialkenyllithium compounds (1,4-dilithio-1,3-diene derivatives **2** generated in situ from their corresponding diiodo compounds **1** and *n*BuLi[10–12]) were treated with one equivalent of a ketone or an aldehyde at $-78\,^{\circ}C$, cyclopentadiene derivatives **3** were formed within 1 h in high yields [Eq. (2)].



1 **2** **3** (2)

With this method, spiro compounds **3a** and **3b** were obtained from cyclohexanone in high yields (Table 1). The reactions of the lithium derivative of **1b** with 4-heptanone and benzophenone afforded tetrahydroindene derivatives **3c** and **3d**. Hexasubstituted cyclopentadienes **3e** and **3f** were isolated in good yields. Compounds **3c**–**f** were the only isomers obtained from the reactions described in Table 1. However, in the case of benzophenone (Table 1, entries 4–6), hexamethyl phosphoramide (HMPA) was needed to achieve a complete reaction.

Table 1. Reactions of 1,4-dilithio-1,3-dienes with ketones and aldehydes.[a]

Entry	Diiodo compound	Ketone or aldehyde	Product	Yield [%][b]
1	 **1a**		 **3a**	75
2	 **1b**		 **3b**	74 (3:1)[c]
3	**1b**		 **3c**	92
4	**1b**		 **3d**	75
5	 **1c**		 **3e**	72
6	 **1d**		 **3f**	67
7	**1a**	PhCHO	 **3g**	56
8	**1a**	PrCHO	 **3h**	53 (3:1)[c]
9	**1b**	PhCHO	 **3i**	70 (4:1)[c]

[a] Conditions: a molar ratio of 2:1 of *n*BuLi and a diiodo compound in diethyl ether at $-78\,^{\circ}C$ for 1 h, then 1.1 equivalent of a ketone or an aldehyde at $-78\,^{\circ}C$ for 0.5 h. [b] Yields refer to isolated amounts after column chromatography. [c] Ratios of double-bond positional isomers; the minor isomer has an exocyclic double bond.

Similarly, aromatic and aliphatic aldehydes reacted with 1,4-dilithio-1,3-dienes to form pentasubstituted cyclopentadienes in good yields (Table 1, entries 7–9). Characterization data for **3g**–**i** are consistent with those previously reported.[8] In most cases, the corresponding alcohols were not detected at all.

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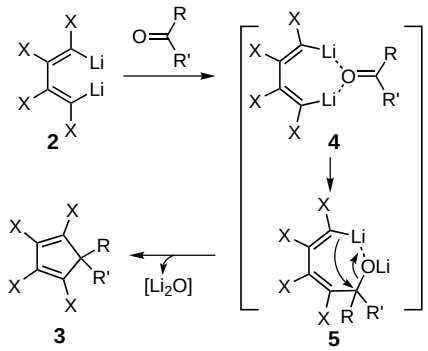
The interaction (or chelation) of the alkenyllithium moieties with the carbonyl group (e.g. **4**), although very weak, is proposed to be essential in this inter/intramolecular reaction (Scheme 2).[13–17] One of the two alkenyllithium moieties



Scheme 2. Proposed reaction mechanism for the reaction between dialkenyllithium compounds (e.g. **2**) and ketones or aldehydes.

reacts first with the carbonyl group to form **5**, which then undergoes an intramolecular attack by the remaining alkenyllithium moiety to give cyclopentadiene derivatives, with the concomitant release of lithium oxide. This result is in sharp contrast to the case of organomonolithium reactions with carbonyl groups, which usually afford alcohols after hydrolysis.[9] The inter/intramolecular reaction, the chelation effect of the alkenyllithium moieties, and the formation of stable cyclopentadiene derivatives and of lithium oxide are assumed to be the driving forces in this novel reaction.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively. All spectra were measured in $CDCl_3$ at 25 °C, with TMS as internal reference.

Typical procedure: *n*BuLi (2.2 mmol, 1.6 M in hexane) was added to a solution of **1a** (1 mmol) in diethyl ether (5 mL) at −78 °C. The reaction mixture was then stirred at −78 °C for 1 h to generate **2a**, which was monitored by GC analysis or by TLC. After the addition of cyclohexanone (1.1 mmol) at −78 °C, the mixture was stirred at −78 °C for 0.5 h. The reaction mixture was quenched with HCl (3 N) and extracted with hexane. The extract was washed with $NaHCO_3$ and brine, and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a brown oil, which was purified by column chromatography (silica gel, hexane) to afford **3a** as a colorless liquid (226 mg, 75 %). ^{1}H NMR: $\delta = 0.81-1.01$ (m, 12H), 1.07–1.66 (m, 18H), 2.03–2.16 (m, 6H), 2.85 (t, $J = 6.6$ Hz, 1H), 5.20 (t, $J = 6.4$ Hz, 1H); ^{13}C NMR: $\delta = 14.48$, 14.77, 15.01, 15.20, 20.26, 22.09, 23.04, 23.45, 23.75, 24.31, 26.06, 27.04, 28.11, 29.12, 33.14, 35.64, 45.14, 50.88, 118.70, 135.91, 147.56, 149.44; HRMS calcd for $C_{22}H_{38}$: 302.2974; found: 302.2977.

3b: Colorless liquid, 3:1 mixture of positional double-bond isomers (201 mg, 74 %); ^{13}C NMR (mixture): $\delta = 15.31$, 15.32, 15.46, 21.29, 23.68, 23.97, 24.09, 24.29, 24.55, 25.26, 26.34, 26.90, 28.35, 30.34, 33.35, 37.41, 43.45, 47.49, 52.66, 66.81, 102.14, 115.63, 132.18, 133.18, 141.31, 147.81, 148.64, 148.76; HRMS calcd for $C_{20}H_{32}$: 272.2504; found: 272.2496.

3c: Colorless liquid (264 mg, 92 %); ^{1}H NMR: $\delta = 0.71-0.95$ (m, 16H), 1.12–1.68 (m, 12H), 1.96 (t, $J = 6.4$ Hz, 4H), 2.40–2.48 (br s, 4H); ^{13}C NMR: $\delta = 14.50$, 15.16, 16.50, 21.74, 24.14, 28.24, 29.41, 38.12, 61.57, 136.63, 140.56.

3d: Sticky liquid (267 mg, 75 %); ^{1}H NMR: $\delta = 0.50-0.85$ (m, 10H), 1.18–1.57 (m, 4H), 1.99 (t, $J = 7.0$ Hz, 4H), 2.30–2.36 (br s, 4H), 7.06–7.17 (m, 10H); ^{13}C NMR: $\delta = 13.60$, 20.84, 22.77, 23.55, 28.41, 71.45, 124.96, 126.88, 127.44, 136.17, 141.01, 144.69; HRMS calcd for $C_{27}H_{32}$: 356.2504; found: 356.2488.

3e: Colorless liquid (318 mg, 72 %); ^{1}H NMR: $\delta = 0.63-1.48$ (m, 28H), 2.08 (t, $J = 6.4$ Hz, 4H), 2.25 (t, $J = 7.8$ Hz, 4H), 7.10–7.26 (m, 10H); ^{13}C NMR: $\delta = 13.67$, 14.08, 23.36, 26.18, 26.88, 29.45, 31.87, 32.46, 71.94, 125.97, 127.96, 128.48, 140.97, 141.98, 147.77; HRMS calcd for $C_{33}H_{46}$: 442.3600; found: 442.3616.

3f: Colorless liquid (238 mg, 67 %); ^{1}H NMR: $\delta = 0.64-1.28$ (m, 14H), 1.63 (s, 3H), 1.85 (s, 3H), 2.11 (t, $J = 8.4$ Hz, 2H), 2.26 (t, $J = 7.6$ Hz, 2H), 7.08–7.25 (m, 10H); ^{13}C NMR: $\delta = 11.15$, 11.37, 13.64, 14.10, 23.22, 26.24, 26.94, 29.44, 32.17, 32.25, 71.66, 125.96, 128.04, 128.40, 135.72, 141.28, 142.25, 142.37, 147.88; HRMS calcd for $C_{27}H_{34}$: 358.2661; found: 358.2669.

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