[12] R. Fränkel, U. Kernbach, M. Bakola-Christianopoulou, U. Plaia, M. Suter, W. Ponikwar, H. Nöth, C. Moinet, W. P. Fehlhammer, *J. Organomet. Chem.* **2001**, *617–618*, 530–545.
[13] a) R. Fränkel, M. Mühl, U. Kernbach, C. Birg, C. Moinet, H. Nöth, W. P. Fehlhammer, *XVIIIth International Conference on Organometallic Chemistry* (Munich), **1998**; b) R. Fränkel, U. Kernbach, N. M. Bakola-Christianopoulou, C. Moinet, H. Nöth, W. P. Fehlhammer, *2nd International Conference of the Chemical Societies of the South-Eastern European Countries on Chemical Sciences for Sustainable Development* (Chalkidiki, Greece), **2000**.
[14] R. Fränkel, J. Kniczek, W. Ponikwar, H. Nöth, K. Polborn, W. P. Fehlhammer, *Inorg. Chim. Acta* **2000**, *312*, 23–39.
[15] a) Crystal structure analysis of **5**: Siemens-CCD Area Detector, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 193(2)$ K, Structure solution program: SHELXS-97 (G. M. Sheldrick, Universität Göttingen, **1997**), Structure refinement program: SHELXL-97 (G. M. Sheldrick, Universität Göttingen, **1997**; b) crystal data for **5**: $C_{15}H_{22}BLiN_6$ ($M_r = 304.14$), colorless prisms, $0.30 \times 0.20 \times 0.20$ mm, monoclinic, space group $P2_1/n$, $a = 9.7923(7)$, $b = 11.7392(9)$, $c = 15.4036(12)$ Å, $\alpha = \gamma = 90.00$, $\beta = 100.406(2)^\circ$, $V = 1741.6(2)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.160$ g cm$^{-3}$, $\mu = 0.072$ mm$^{-1}$, $F(000) = 648$, range $4.38 < 2\theta < 57.64^\circ$ in $-11 \le h \le 11$, $-14 \le k \le 15$, $-19 \le l \le 19$, 9396 measured reflections, 3039 independent reflections ($R_{int} = 0.0874$), observed reflections 2230 ($F > 4\sigma(F)$). Structure solution was with direct methods, data:parameter ratio 14.3:1; $R1 = 0.0610$ , $wR2 = 0.1584$ (for $F > 4\sigma(F)$); $R1 = 0.0873$, $wR2 = 0.1778$ (all values), GOF($F^2$) = 1.035, max./min. residual electron density 0.367/ − 0.330 e Å$^{-3}$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151146 (**4**) and -151147 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[16] Of the isomeric tris(pyrazolyl)borates (Tp)[11] that have been studied extensively to date, only one lithium compound phenyltris(3-*tert*-butylpyrazolyl)boratolithium has been characterized by X-ray crystallography. Because of the sterically demanding substituents a dimer is not formed, instead the cation exists as a LiTp species coordinated by three N groups.[17a] The isoelectronic compound tris(pyrazolyl)-methanelithiumtetrahydroborate [{HC(3,5-$Me_2$pz)$_3$}Li($\eta^3$-$BH_4$)] is also a monomer.[17b]
[17] a) J. L. Kisko, T. Hascall, C. Kimblin, G. Parkin, *J. Chem. Soc. Dalton Trans.* **1999**, 1929–1935; b) D. L. Reger, J. E. Collins, *Inorg. Chem.* **1997**, *36*, 6266–6269.
[18] D. Thoennes, E. Weiss, *Chem. Ber.* **1978**, *111*, 3157–3161.
[19] Reviews of the structural chemistry of organolithium complexes: a) J. P. Oliver, *Adv. Organomet. Chem.* **1977**, *15*, 235–271; b) W. N. Setzer, P. von R. Schleyer, *Adv. Organomet. Chem.* **1985**, *24*, 353–451; c) C. E. Housecroft, *Comprehensive Organometallic Chemistry*, *Vol. 1* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), 2. ed., Pergamon, Oxford, **1995**, pp. 18–34.
[20] a) B. Schiemenz, P. P. Power, *Angew. Chem.* **1996**, *108*, 2288–2290; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2150–2152; b) K. Ruhlandt-Senge, J. J. Ellison, R. J. Wehmschulte, F. Pauer, P. P. Power, *J. Am. Chem. Soc.* **1993**, *115*, 11353–11357.
[21] In the dimeric imidazolatolithium complex described by Boche a preference for short Li–N and noticeably longer Li–C bonds (> 2.5 Å) was noted.[5a]
[22] A. J. Arduengo III, M. Tamm **1994**, unpublished results, compare ref. [22] in ref.[5b].
[23] Suitable crystals of **4** could be obtained from a saturated toluene solution at $-30\,^\circ$C.[24]. The endocyclic N-C(carbene)-N angles (between 109.8(4) and 110.9(4)°) lie in the range typical for imidazolinium salts and are clearly larger than the corresponding values for **5** ($103.7 \pm 1^\circ$). A second significant difference concerns the N-C(carbene) bonds in the carbene complex **5** (1.361(3) to 1.370(3) Å) which are clearly longer than the corresponding bonds in the imidazolinium precursor **4** (1.318(5)–1.328(5) Å); apart from these the bonding parameters differ only slightly.[1, 25, 26]
[24] C. Birg, Dissertation, Ludwig-Maximilians Universität Munich, **2000**.
[25] a) V. Langer, K. Huml, *Acta Crystallogr. Sect. B* **1982**, *38*, 298–300; b) A. K. Abdul-Sada, A. M. Greenway, P. B. Hitchcock, T. J. Mohammed, K. R. Seddon, J. A. Zora, *J. Chem. Soc. Chem. Commun.* **1986**, 1753–1754; c) G. Bruno, F. Nicolo, *Acta Crystallogr. Sect. C* **1994**, *50*, 428–430.
[26] D. A. Dixon, A. J. Arduengo III, *J. Phys. Chem.* **1991**, *95*, 4180–4182.
[27] A. J. Arduengo III, J. C. Calabrese, F. Davidson, H. V. Raskia Dias, J. R. Goerlich, R. Krafczyk, W. J. Marshall, M. Tamm, R. Schmutzler, *Helv. Chim. Acta* **1999**, *82*, 2348–2364.

## Domino Hydroformylation/Knoevenagel/Hydrogenation Reactions**

Bernhard Breit* and Stephan K. Zahn

*Dedicated to Professor Barry M. Trost on the occasion of his 60th birthday*

Efficient synthetic transformations are those forming new carbon–carbon bonds with complete control of chemo-, regio-, and stereoselectivity.[1] Reactions in accord with the criteria of atom economy are particularly useful.[2] In this context, the industrially important hydroformylation of olefins would be an ideal transformation if selectivity, in particular stereoselectivity, could be controlled.[3] We recently devised one solution to this problem by making more efficient use of substrate control with the aid of a substrate-bound catalyst-directing group.[4]

Although the hydroformylation of a carbon–carbon double bond introduces the preparatively useful aldehyde functionality, in terms of synthetic efficiency the reaction suffers from the fact that it provides only a one carbon chain elongation. One way to overcome this deficiency could be to incorporate this reaction as a key step in a domino-type process.[5, 6] In this context we recently developed a domino hydroformylation/Wittig olefination protocol.[7] In an extension of this study we herein report on the first domino hydroformylation/Knoevenagel reaction/hydrogenation process of acyclic olefinic substrates, which occurs with concomitant control of regio- and stereoselectivity and, additionally, provides useful building blocks for polyketide synthesis.

When the methallyl *ortho*-diphenylphosphanylbenzoate (±)-**1** was subjected to hydroformylation conditions in the presence of 1.5 equivalents of dimethylmalonate and 0.3 equivalents of piperidinium acetate (Scheme 1), the substituted malonate (±)-**2** could be isolated in satisfactory yield and with good diastereoselectivity (*syn*/*anti* 96:4, Table 1, entry 6). Malonate (±)-**2** is obviously the final product of a sequential domino hydroformylation/Knoevenagel reaction/

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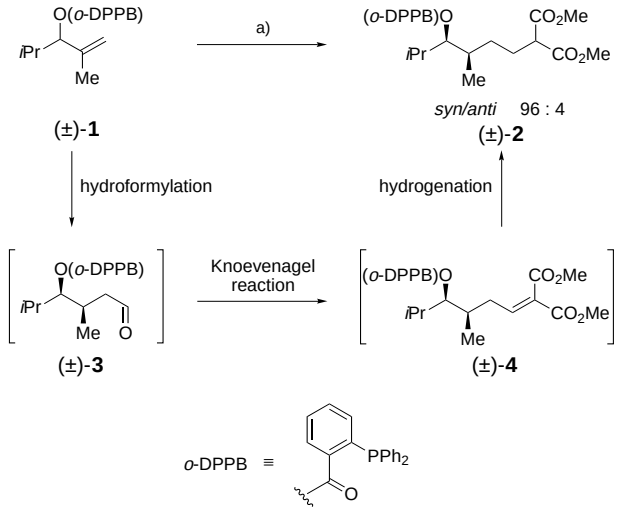
Table 1. Optimization of reaction conditions for the domino hydroformylation/Knoevenagel reaction/hydrogenation cascade of methallyl alcohol derivative (±)-**1** with dimethylmalonate.

| Entry | Equiv malonate | Rh Cat. | Base/equiv | *T* [°C] | Yield[a] [%] | d.r.[b] (*syn*/*anti*) |
|---|---|---|---|---|---|---|
| 1 | 1.0 | $[RhH(CO)(PPh_3)_3]$ | piperidine/0.5 | 70 | 20 | 96:4 |
| 2 | 1.0 | $[RhH(CO)(PPh_3)_3]$ | piperidine/0.5 | 90 | 36 | 96:4 |
| 3 | 1.0 | $[\{Rh(cod)Cl\}_2]$[c] | piperidine/0.5 | 90 | 42 | 96:4 |
| 4 | 1.0 | $[Rh(CO)_2(acac)]/4\,P(OPh)_3$ | piperidine/0.5 | 90 | 41 | 96:4 |
| 5 | 1.0 | $[RhH(CO)(PPh_3)_3]$ | pyridine/0.5 | 90 | 0 | – |
| 6 | 1.5 | $[RhH(CO)(PPh_3)_3]$ | piperidiniumacetate/0.3 | 90 | 51 | 96:4 |

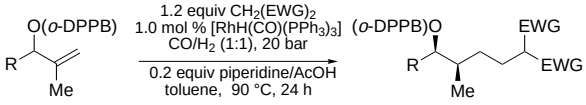
[a] Determined after workup and purification by column chromatography. [b] Determined through NMR spectroscopic analysis of the crude product. [c] cod = cycloocta-1,5-diene.




Scheme 1. Domino hydroformylation/Knoevenagel reaction/hydrogenation process [(±)-**1** → (±)-**2**] and proposed mechanism. a) $CH_2(CO_2Me)_2$, 1.0 mol % Rh cat., 20 bar $CO/H_2$ (1:1), amine base, toluene, Δ, 24 h.

hydrogenation cascade. As we have shown previously, diastereoselectivity in the course of the hydroformylation reaction is controlled by the substrate-bound catalyst-directing *o*-DPPB.[8] The yield and stereoselectivity of this new transition metal catalyzed domino process are basically independent from the rhodium-catalyst precursor that is used (Table 1, entries 2–4), but they depend strongly on the nature of the amine base employed (Table 1, entries 2, 5, 6). While pyridine was completely unsuccessful, the best result was obtained with catalytic amounts of piperidinium acetate.[9] Hence, this new domino process allows in a single operational step the formation of two carbon–carbon single bonds under almost neutral reaction conditions and simultaneously introduces the synthetically useful malonate functionality. Additionally, a new stereogenic center is formed with excellent levels of acyclic stereocontrol.

In addition to malonates, β-ketoesters such as ethyl acetoacetate (Scheme 2; Table 2, entries 2, 5, 7, 8) could be

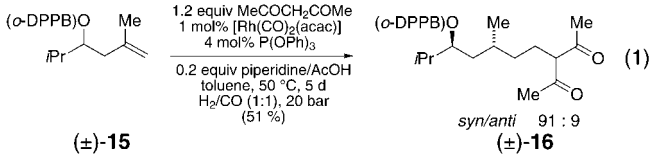



Scheme 2. Domino hydroformylation/Knoevenagel reaction/hydrogenation process. EWG = electron withdrawing group.

employed to give the corresponding domino products **5**, **9**, **12**, and **14** in generally better yields. Furthermore β-diketones undergo a similar cascade reaction to give the formally alkylated and saturated derivatives **6**, **10**, and **16** (Table 2, entries 3, 6, 9).

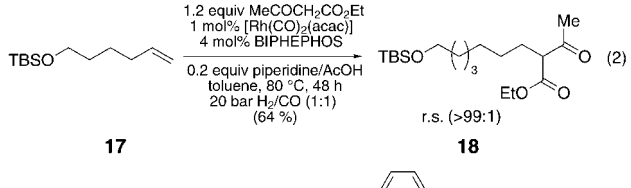
The reaction could be used for the construction of the *anti*–*syn* and the all-*anti* stereotriad sequences (Table 2, entries 7, 8), which are known to be central building blocks of polyketide natural products.[13] In all the reactions 1,2-asymmetric induction was controlled during the hydroformylation step either by making use of the substrate-bound catalyst-directing *o*-DPPB group (entries 1–7),[7, 8] or by substrate control through conformational constraints (entry 8).[14]

The domino reaction could also be applied to a homomethallyl *o*-DPPB ester (±)-**15** [Eq. (1); acac = acetylacetone]. The substrate-bound catalyst-directing *o*-DPPB group al-




lowed the control of diastereoselectivity by making efficient use of 1,3-asymmetric induction.[15] Thus, the functionalized β-diketone (±)-**16** was obtained in good yield and with good diastereoselectivity.

Additionally, a regioselective hydroformylation of a monosubstituted alkene with the BIPHEPHOS/rhodium catalyst[16] could be employed as the key step in this domino process to give the linear β-ketoester **18** in good yield and with excellent regioselectivity [Eq. (2)].



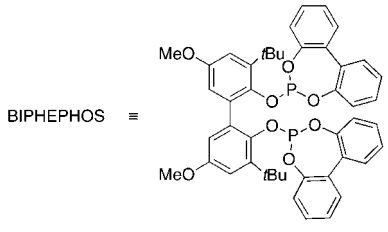




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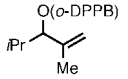
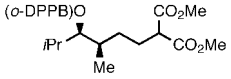
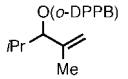
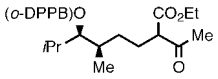
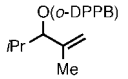
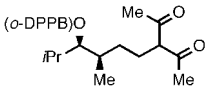
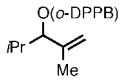
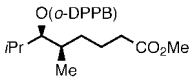
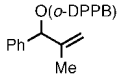
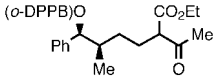
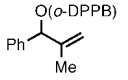
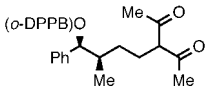
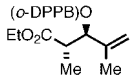
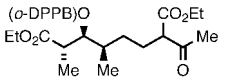
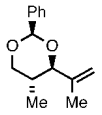
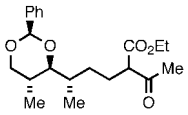
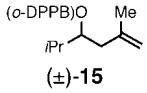
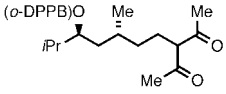
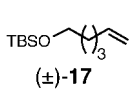
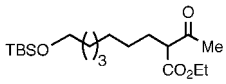
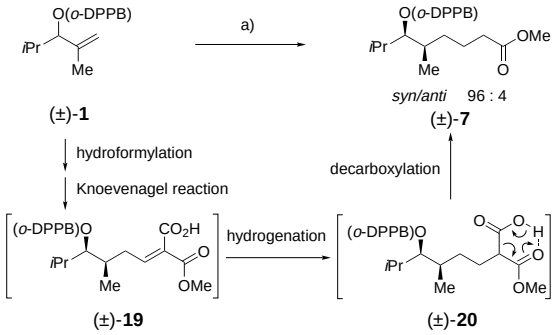
Table 2. Results of the regio- and stereoselective domino hydroformylation/Knoevenagel reaction/hydrogenation process.[a]

| Entry | Alkene[10] | $CH_2(EWG)_2$ | Product[11, 12] | Yield[b] [%] | d.r.[c] (*syn*/*anti*) |
|---|---|---|---|---|---|
| 1 |  (±)-**1** | $CH_2(CO_2Me)_2$ |  (±)-**2** | 51 | 96:4 |
| 2 |  (±)-**1** | $MeCOCH_2CO_2Et$ |  (±)-**5** | 71 | 96:4 |
| 3 |  (±)-**1** | $MeCOCH_2COMe$ |  (±)-**6** | 52 | 96:4 |
| 4 |  (±)-**1** | $HO_2CCH_2CO_2Me$ |  (±)-**7** | 41 | 96:4 |
| 5 |  (±)-**8** | $MeCOCH_2CO_2Et$ |  (±)-**9** | 64 | 92:8 |
| 6 |  (±)-**8** | $MeCOCH_2COMe$ |  (±)-**10** | 60 | 92:8 |
| 7 |  (±)-**11** | $MeCOCH_2CO_2Et$ |  (±)-**12** | 55 | 96:4 |
| 8[d] |  (±)-**13** | $MeCOCH_2CO_2Et$ |  (±)-**14** | 62 | > 98:2 |
| 9[e] |  (±)-**15** | $MeCOCH_2COMe$ |  (±)-**16** | 51 | 91:9 |
| 10[e] |  (±)-**17** | $MeCOCH_2CO_2Et$ |  (±)-**18** | 64 | > 99: < 1[f] |

[a] For a representative procedure, see the Experimental Section. TBS = *tert*-butyldimethylsilyl. [b] Determined after workup and purification by column chromatography. [c] Determined through NMR or GC analysis of the crude product. [d] Conditions: 1 mol% $[Rh(CO)_2(acac)]$/4 mol% $P(OPh)_3$, 0.2 equiv piperidine. [e] For detailed reaction conditions, see Equations (1) and (2). [f] Ratio of regioisomers (linear/branched).

When malonic acid monomethyl ester was used as the CH-acidic Knoevenagel component the monoester derivative (±)-**7** was obtained as the sole product (Table 2, entry 4). Hence, the mechanism of this sequential transformation must involve four separate steps (Scheme 3). First, *o*-DPPB-directed stereoselective hydroformylation provides the aldehyde (±)-**3**,[8] which should condense immediately with the malonic acid methylester to form the corresponding doubly acceptor-activated alkene derivative (±)-**19**. Rhodium-catalyzed hydrogenation of this alkene and subsequent decarboxylation conclude the sequence of events affording the isolable ester (±)-**7**.

Hence, the new sequential transformation described herein allows the formation of two carbon–carbon single bonds in a single operational step, with concomitant generation of a new




Scheme 3. Proposed mechanism of the domino hydroformylation/Knoevenagel reaction/hydrogenation/decarboxylation cascade ((±)-**1** → (±)-**7**). a) 1.1 equiv $HO_2CCH_2CO_2Me$, 1.0 mol% $[RhH(CO)(PPh_3)_3]$, 20 bar CO/$H_2$ (1:1), 0.1 equiv piperidine, 0.1 equiv AcOH, toluene, 90 °C, 24 h (41%).

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stereogenic center and with high levels of regio- and acyclic stereocontrol. Additionally, a synthetically useful $\beta$-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, $1 \times 10^{-2}$ 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 $\beta$-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 $\beta$-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, →$\alpha,\beta$-unsaturated $\beta$-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**

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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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