Evidence for Competing *syn* and *anti* Pathways in Palladium-Catalyzed Eliminations of Acyclic Allylic Carbonates

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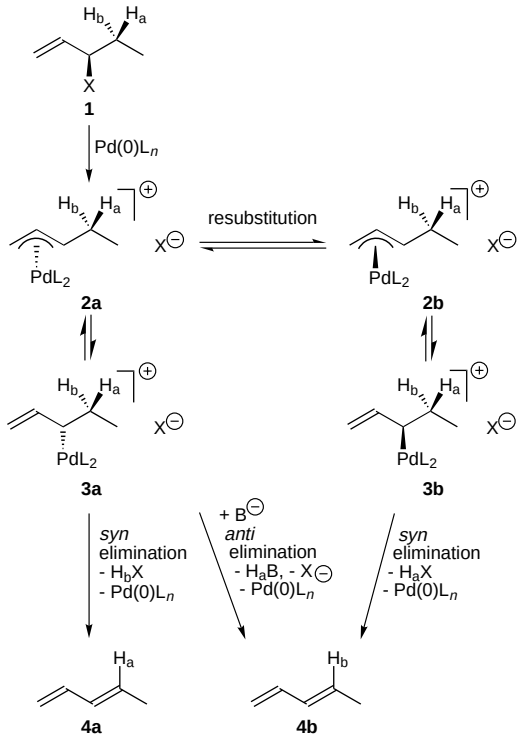
Abstract: *Syn*- and *anti*-configured carbonates **6a** and **6b**, available from stereoselective aldol additions and subsequent protection with methyl chloroformate, serve as probes for the elucidation of the stereochemistry of the β-Pd–H elimination. Upon treatment with $[Pd(PPh_3)_4]$, the carbonates **6a** and **6b** give the dienes **7a** and **7b** in different ratios; the latter stereoisomer **7b** is formed as a result of $\pi-\sigma-\pi$ conversions. Both *syn* and *anti* eliminations are shown to occur as competing reactions, the former one being the strongly preferred pathway. The highly reactive $[Pd\{P(n\text{Bu})_3\}_4]$ catalyst, generated in situ from $Pd(OAc)_2$ and $P(n\text{Bu})_3$ causes thermodynamic control in the elimination; thus, it serves as a smooth reagent for *Z*–*E* isomerization.

Keywords: allyl complexes · eliminations · olefinations · palladium · reaction mechanisms

Introduction

The β-Pd–H elimination, a well-known and thoroughly investigated process, is usually considered to be a limitation of organopalladium compounds that leads to their thermal instability.[1] More recently, however, this reaction has been found to be an essential step in the catalytic cycles of Heck-type reactions,[2] isomerizations of alkynes to dienes,[3] cyclizations of enynes,[4] and alkene methyl acrylate polymerizations.[5] As shown by the fundamental work of Trost[6] and Tsuji,[7] smooth access to 1,3-dienes is opened when allylic acetates are submitted to palladium-catalyzed eliminations. Allylic carbonates were found to undergo this reaction under even milder conditions[8] and $Pd(OAc)_2/P(n\text{Bu})_3$ turned out to be the catalyst of choice in this case.[9] According to a widely accepted mechanism, the allylic substrate **1** is first converted into an η^3-allylpalladium intermediate **2a**, which exists in an equilibrium with an η^1-complex **3a**.[10, 11] As shown in Scheme 1, the latter then undergoes a β-Pd–H elimination[12] to give the diene **4a**. Simultaneously, the catalyst is regenerated and H_bX is liberated, the atom H_b having been in a *syn* position relative to palladium in the complexes **2a** and **3a**. Thus, the last step was commonly believed to occur as a *syn*-elimination process. However, this stereochemical outcome has been challenged more recently, when palladium complexes **2a** lacking a *syn*-β-hydrogen atom H_b were found by the groups of Tsuji, Anderson, and Takacs to undergo at least a formal *anti* elimination.[8, 9, 13, 14]



Scheme 1. Pathways of *syn* and *anti* eliminations in allyl palladium complexes.

The explanation offered by Tsuji is based on a resubstitution of the metal in **2a** by free Pd^0 under inversion. The isomeric complex **2b** formed thereby undergoes a conven-

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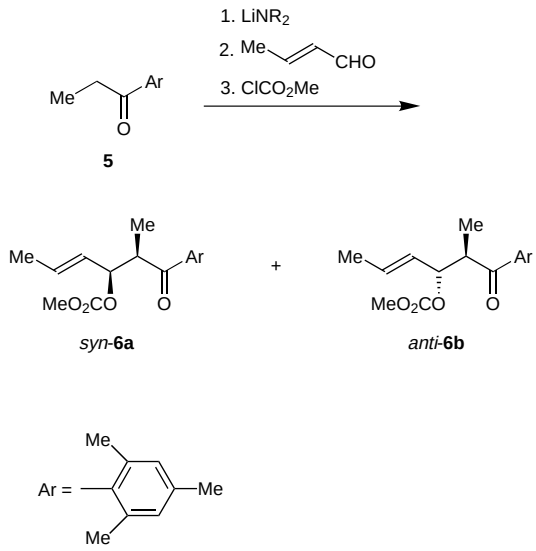
tional *syn* elimination via the σ-complex **3b**. Thus, H_aX is liberated under the formation of **4b**.[6, 7] On the other hand, a base-induced abstraction of the *β*-hydrogen in **3a** has been postulated to account for the *anti* elimination of allyl palladium complexes.[13, 14] Thus the base B^- attacks the hydrogen atom H_a, which is in an *anti* orientation relative to the palladium in the complex **3a**. This type of elimination, which follows essentially an E_2 mechanism, leads to the formation of the diene **4b**, whereby the protonated base H_aB is liberated and the catalyst is regenerated. In all cases, the substrate was incorporated in a cyclohexyl ring system, whereas in acyclic allylic carbonates an *anti* elimination mechanism has been postulated only on the base of isotope effects.[14] In this paper, we report for the first time on evidence of competing *syn* and *anti* pathways in *β*-Pd–H eliminations of acyclic substrates.

Results and Discussion

Recently, we have shown that methyl carbonates, generated in situ from lithium aldolates, undergo an extremely smooth elimination upon treatment with 1 to 5 mol% of $[Pd(PPh_3)_4]$.[15] In this context, the idea came up to use carbonates derived from diastereomeric aldols as a suitable probe for the elucidation of the stereochemical outcome in palladium-catalyzed eliminations. For this purpose, lithium enolates derived from 2′,4′,6′-trimethylpropiophenone **5** were added to (*E*)-crotonaldehyde, and the lithium alkoxide formed thereby was converted in situ into the diastereomeric carbonates **6a** and **6b** upon treatment with methyl chloroformate (Scheme 2). A controlled and predictable access to the racemic diastereomers **6a** or **6b** was possible, based on established aldol methodology that provides simple diastereoselection.[16]

Thus, *syn*-carbonate **6a** was obtained predominantly from ketone **5** by deprotonation with lithium hexamethyldisilazide[17] and subsequent addition of the enolate to (*E*)-crotonaldehyde. As shown in Table 1 (entries 1 and 2) the diastereoselectivity in favor of **6a** could be enhanced when lithium (*N*-phenyl)trimethylsilazide was chosen for enolate generation.[18] On the other hand, the *anti* product **6b** was

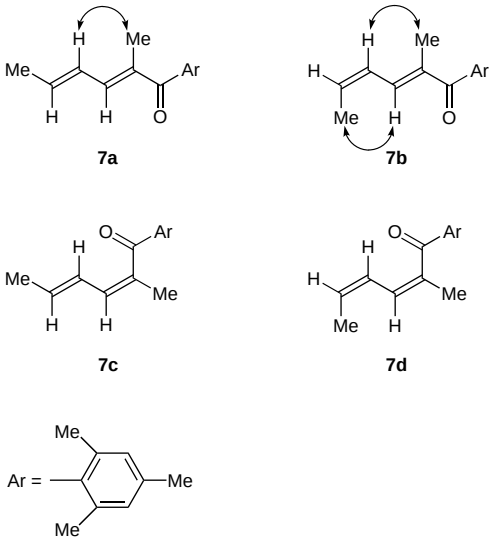


Scheme 2. Reaction scheme for the formation of **6a** and **6b**.

Table 1. Yield and *syn*/*anti* ratios of carbonates **6a**/**6b** prepared from ketone **5**.

	$LiNR_2$	Yield **6a**/**6b**	Ratio **6a**:**6b**
1	$LiN(SiMe_3)_2$	48%	87:13
2	$LiN(Ph)SiMe_3$	41%	95:5
3	$LiN(iPr)_2$	56%	2:98

accessible in a highly diastereoselective manner by using lithium diisopropylamide for the deprotonation of the ketone **5** (entry 3). The three different diastereomeric mixtures of the carbonates **6a**/**6b** were submitted to the elimination process. For this purpose, a solution of the starting material **6a**/**6b** in tetrahydrofuran was stirred with 5–20 mol% of the corresponding palladium catalyst at room temperature. At a glance, two conjugated dienes, (2*E*,4*E*)-**7a** and (2*Z*,4*E*)-**7c**, isomeric with respect to this new bond, were the expected products. The double bond between the carbon atoms 4 and 5, which was already present in the precursors **6a**/**6b** was not expected to be isomerized. Indeed, all runs of the elimination



Abstract in German: *Syn- und anti-Carbonate **6a** und **6b** sind durch diastereoselektive Aldoladdition und anschließendes Schützen mit Chlorameisensäuremethylester erhältlich. Sie dienen als Sonde zur Untersuchung der Stereochemie der β-Pd–H-Eliminierung. Bei der Umsetzung mit $Pd(PPh_3)_4$ entstehen aus den Carbonaten **6a** und **6b** die Diene **7a** und **7b** in unterschiedlichen Verhältnissen. Das unerwartet gebildete Stereoisomer **7b** geht aus einer π–σ–π-Umwandlung hervor. Es zeigt sich, daß syn- und anti-Eliminierung als konkurrierende Reaktionen ablaufen, wobei der syn-Verlauf deutlich bevorzugt ist. Der hochreaktive $Pd[P(nBu)_3]_4$-Katalysator, der in-situ aus $Pd(OAc)_2$ und $P(nBu)_3$ erzeugt wird, führt zur thermodynamisch kontrollierten Eliminierung und dient als mildes Reagens zur Z–E-Isomerisierung.*

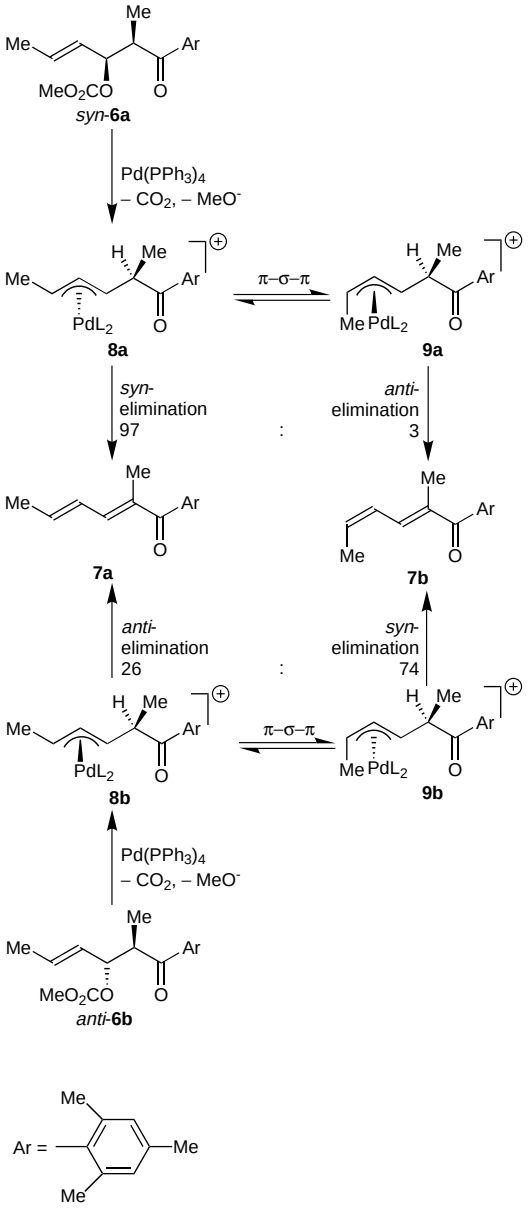
shown in Table 2 gave only two isomeric dienes, the structures of which were assigned by ^{1}H NMR spectroscopy from H,H-COSY and NOESY experiments. As expected, one of the isomers turned out to have the 2*E*,4*E* configuration **7a**, which

Table 2. *E*/*Z* ratios of dienes **7a**/**7b** prepared from diastereomeric mixtures of **6a**/**6b** by palladium-catalyzed elimination.

	Palladium catalyst	Catalytic amount [mol%]	Carbonates ratio **6a**:**6b**	Dienes ratio **7a**:**7b**
1	$[Pd(PPh_3)_4]$	5	87:13	87:13
2	$[Pd(PPh_3)_4]$	10	87:13	87:13
3	$[Pd(PPh_3)_4]$	20	87:13	86:14
4	$[Pd(PPh_3)_4]$	5	95:5	93:7
5	$[Pd(PPh_3)_4]$	5	2:98	27:73
6	$[Pd(PPh_3)_4]$	10	2:98	28:72
7	$[Pd(PPh_3)_4]$	20	2:98	28:72
8	$Pd(OAc)_2/4P(n\mathrm{Bu})_3$	5	87:13	91:9
9	$Pd(OAc)_2/4P(n\mathrm{Bu})_3$	20	87:13	91:9
10	$Pd(OAc)_2/4P(n\mathrm{Bu})_3$	10	2:98	91:9

is proven by the *trans* 4-H, 5-H coupling constant and by the NOE effect between 4-H and the methyl group at C-2 of the diene moiety. Quite unexpectedly, the NMR spectra of the second isomer did not display an *E* configuration of the double bond between the carbon atoms 4 and 5, but a *Z* geometry according to the 4-H, 5-H coupling constant. Furthermore, the NOESY experiment correlated the methyl group at C-2 with 4-H and the terminal methyl substituent with 3-H. As a consequence, the structure of 2*E*,4*Z*-**7b** had to be assigned to the second isomer formed in the elimination reaction, whereas the stereoisomers **7c** and **7d** were not formed at all.

In a series of experiments shown in Table 2, the influence of the palladium compound, the molar ratio of the catalyst, and the diastereomeric ratio of the carbonates **6a**/**6b** on the composition of the mixture of dienes **7a**/**7b** was investigated. In all cases studied, the elimination products **7a**/**7b** were formed in quantitative crude yield, and the conversion was found to be complete. First, there was a distinct influence of the type of catalyst on the distribution of products. Comparison of entries 8–10 with 1–7 clearly shows that there was a constant product ratio of 91:9 when a mixture of palladium acetate and four equivalents of tributylphosphine was used. Obviously, the ratio of dienes **7a**:**7b** *is completely independent* of the *syn*:*anti* ratio of the precursors in this case. The starting material containing mainly the *syn* diastereomer **6a** (entries 8 and 9) as well as that consisting predominantly of the *anti* diastereomer **6b** gave the dienes **7a**/**7b** in a ratio of 91:9. On the other hand, the tetrakis(triphenylphosphine)palladium catalyst displayed a completely different result (entries 1–7). There was a distinct tendency of *syn* carbonate **6a** to deliver the *E*,*E*-isomer **7a** predominantly (entries 1–4). When the *syn*–*anti* ratio was enhanced (entry 4), a higher amount of the *E*,*E*-diene **7a** was formed. On the other hand, the *anti* carbonate **6b**, being the predominant isomer in entries 5–7, afforded mainly the unexpected *E*,*Z*-diene **7b**, although in a lower selectivity. In all cases studied, the relative amount of the catalyst had—within experimental error—no influence on the distribution of the isomeric dienes **7a**/**7b**. It was not possible to separate the diastereomeric carbonates **6a** and **6b** in order to use the pure stereoisomers for the elimination protocol. Fortunately, the data given in entries 1–7 allowed us to calculate the ratio of dienes **7a**:**7b** that would have formed if either pure *syn* or *anti* carbonate **6a** or **6b** had been used.[19] These ratios are given in Scheme 3, and the following discussion is based thereon.



Scheme 3. Formation of dienes **7a** and **7b** from carbonates *syn*-**6a** and *anti*-**6b**.

The correlation between the configuration of the carbonates **6a**/**6b** and the dienes **7a**/**7b** obtained by means of $[Pd(PPh_3)_4]$ (entries 1–7) is interpreted as follows. When *syn*-**6a** is chosen as the starting material, the palladium complex **8a** forms as a first intermediate. Obviously, it is the suitable precursor for the favored *syn* elimination because the hydrogen atom 2-H is in *syn* position relative to the palladium.

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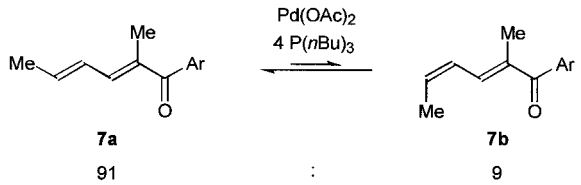
Thus, the *E*,*E*-diene **7a** arises as the highly predominant product. Being aware of the π–σ–π interconversion,[11a] however, one has to take into account that there is an equilibrium between the complexes **8a** and **9a**. Owing to the rotation about the C-4–C-5 bond in an intermediate complex with a Pd–C-5 σ-bond, the palladium switches from the rear side in **8a** to the front side in **9a**. As a consequence, the only hydrogen atom available for the elimination (2-H) is in an *anti* position, relative to the palladium atom. Thus, the unfavored *anti* elimination takes place, of course to a very small extent, with the ratio of *syn*–*anti* elimination being 97:3. This experiment excludes the resubstitution pathway, which would postulate an equilibrium between **8a** and **8b**, and would not be able to explain the isomerization of the original double bond (C-4/C-5).

On the other hand, the palladium complex **8b** is considered to be the first intermediate formed upon treatment of the *anti*-carbonate **6b** with $[Pd(PPh_3)_4]$. Since there is no hydrogen atom in a *syn* orientation at C-2, the unfavored *anti* elimination occurs, giving **7a** as the minor product. The major pathway, in this case, follows the π–σ–π mechanism that converts the allyl complex **8b** into its diastereomer **9b**. In a final step, the *syn* elimination takes place which gives the *E*, *Z* alkene **7b** as the main product (the ratio of **7a**:**7b** being 26:74). In order to avoid, at least partly, the *anti* elimination, the allyl complex **8b** undergoes a themodynamically unfavored conversion to **9b**. Again, this result is in a strict contradiction to the resubstitution pathway. In the case of resubstitution, the isomer **8a** would be generated from **8b**, and, as a consequence, the alkene **7a** would be the main product. The fact that the molar ratio of the catalyst does not influence the ratio of the products **7a**/**7b** serves as another argument against the resubstitution mechanism, at least in this particular case, when $[Pd(PPh_3)_4]$ is used as catalyst. The difference in the activation enthalpies of *syn* and *anti* elimination might be estimated from the conversion of *syn*-**6a** into the alkenes **7a** and **7b**, the mechanism of which is proposed above. When a rapid reversible π–σ–π interconversion of the allyl complexes **8a** and **9a** is assumed, the Curtin–Hammett principle should apply so that the ratio of the dienes **7a** and **8a** formed is determined by the difference in the transition state enthalpies of the steps **8a**→**7a** and **9a**→**7b**. Based on the 97:3 ratio of the dienes **7a** and **7b** formed at room temperature, the activation barrier of an *anti* Pd–H elimination combined with a contrathermodynamic π–σ–π conversion is estimated to be higher than that of the *syn* elimination by 2 kcal mol^{-1}.

The elimination procedures using a mixture of palladium acetate and tributylphosphine $[Pd(OAc)_2/4\,P(n\mathrm{Bu})_3]$ obviously follow a different mechanism. The formation of **7a** and **7b** in a constant ratio of 91:9 which is independent of the choice of the starting material, either diastereomer **6a** or **6b** (Table 1, entries 8–10), suggests the idea of thermodymamic control. Thus, the ratio of 91:9 in the mixture of dienes **7a** and **7b** formed should reflect the product distribution in the equilibrium. This assumption was proven by the following experiment: mixtures of the dienes **7a** and **7b** with different ratios were treated with $Pd(OAc)_2/4\,P(n\mathrm{Bu})_3$ at room temperature. In all cases, isomerization of the dienes was observed, and the mixture obtained consisted of **7a**/**7b** in a ratio of 91:9 (Scheme 4). Obviously, this is identical with the ratio of the thermodynamic equilibrium also found in the elimination of **6a** and **6b** upon treatment with $Pd(OAc)_2/4\,P(n\mathrm{Bu})_3$.[20] The equilibrium ratio of **7a** and **7b** corresponds to a difference of



Scheme 4. Equilibrium between **7a** and **7b**.

1.3 kcal mol^{-1} in the enthalpy of both dienes. MM2 calculations of both compounds reveal a difference in energy of 1.0 kcal mol^{-1}. A slightly higher value (1.14 kcal mol^{-1}) was obtained from an AM1 calculation based on optimized geometries of **7a** and **7b**. Thus, there is acceptable accordance between the calculated and the experimental data.

Conclusion

The treatment of diastereomeric carbonates **6a** and **6b** with catalytic amounts of $[Pd(PPh_3)_4]$ leads to the formation of the dienes **7a** and **7b**, isomeric with respect to the C-4/C-5 double bond, in kinetically controlled reactions. In all cases the *syn* elimination of the allyl complex **8a** is found to be the preferred stereochemical outcome; it leads to the predominant formation of *E*,*E*-configured diene **7a** from *syn* carbonate **6a**, which also gives a small amount of *E*,*Z*-diene **7b** by an *anti* elimination pathway. The latter is combined with a π-σ–π conversion. The *anti* elimination occurs to a larger extent when the *anti* carbonate **6b** serves as the starting material. Nevertheless, the *anti* elimnation of the intermediate **8b**, arising from **6b**, is a clearly disfavored process. In order to avoid the *anti* elimination as much as possible, the allyl complex **8b** prefers to undergo a π–σ–π conversion followed by a *syn* elimination, so that the thermodynamically less stable diene **7b** is formed in a distinctly predominant manner. As a consequence, clear evidence of an *anti* elimination pathway is given. The abstraction of the *β*-hydrogen might follow an E2-type mechanism, in the course of which the methoxide liberated may serve as a base. On the other hand, the resubstitution of η^3-palladium complexes can be excluded for eliminations mediated by $[Pd(PPh_3)_4]$.

When the elimination is brought about by a reactive catalyst, generated in situ from $Pd(OAc)_2$ and $P(n\mathrm{Bu})_3$, thermodynamic control is provided. As this catalyst has been shown to be able to equilibrate dienes **7a** and **7b**, it might serve as a suitable smooth reagent for *Z*–*E* isomerizations in dienes and polyenes.

Experimental Section

The following spectrometers were used: NMR spectra: Varian VXR300 and Bruker DRX500; $CDCl_3$ solutions and TMS as internal standard. Mass

spectra: Hewlett – Packard 5890/5870. IR spectra: Bruker Vector 22. Chromatography: TLC: Silica gel 60 F_{254} (Merck). Column chromatography: Silica gel 60, mesh size 0.04 – 0.063 mm (Merck). Elemental analyses were carried out by Institut für Pharmazeutische Chemie, Universität Düsseldorf and Mikroanalytisches Labor Beller, Göttingen. All reactions were carried out under an atmosphere of dry nitrogen. Tetrahydrofuran (THF) was predried with KOH and distilled under N_2 from sodium/benzophenone. Reactions at temperatures below $-20\,^{\circ}C$ were monitored by a thermocouple connected to a resistance thermometer (Ebro). General remarks concerning the handling of lithium enolates and other organolithium compounds are given in ref. [21]. (*N*-phenyl)trimethylsilazane[22] and 2′,4′,6′-trimethylpropiophenone[23] (**5**) were prepared according to literature procedures.

Deprotonation of 2′,4′,6′-trimethylpropiophenone (5): Generation of the *Z*-enolate: A 100 mL two-necked flask, connected to a combined nitrogen/vacuum line, was equipped with a magnetic stirrer and a septum. A thermocouple was introduced through the septum. Anhydrous THF (25 mL) and either hexamethyldisilazane (2.3 mL, 11 mmol) or (*N*-phenyl)trimethylsilazane (1.94 mL, 11 mmol) were injected through the septum by syringes. The mixture was stirred at $-5\,^{\circ}C$, and a solution of *n*-butyllithium in hexane (1.6 M, 6.5 mL, 10.75 mmol) was added in such a way that the temperature did not exceed $0\,^{\circ}C$. After stirring for 30 min at $20\,^{\circ}C$, the mixture was cooled to $-78\,^{\circ}C$. In a 50 mL two-necked flask, connected to the combined nitrogen/vacuum line, a solution of **5** (1.76 g, 10 mmol) in anhydrous THF (25 mL) was stirred at $-78\,^{\circ}C$. This mixture was added dropwise by a cannula to the slightly evacuated 50 mL flask containing the solution of the lithium amide and the mixture was stirred at $-78\,^{\circ}C$ for 2 h.

Deprotonation of 2′,4′,6′-trimethylpropiophenone (5): Generation of the *E*-enolate: A 50 mL two-necked flask, connected to a combined nitrogen/vacuum line, was equipped with a magnetic stirrer and a septum. A thermocouple was introduced through the septum. Anhydrous THF (5 mL) and diisopropylamine (1.55 mL, 11 mmol) were injected through the septum by syringes. The mixture was stirred at $-78\,^{\circ}C$, and a solution of *n*-butyllithium in hexane (1.6 M, 6.5 mL, 10.75 mmol) was added in such a way that the temperature did not exceed $-70\,^{\circ}C$. After stirring for 30 min at $0\,^{\circ}C$, the mixture was cooled to $-78\,^{\circ}C$. In a 25 mL two-necked flask, connected to the combined nitrogen/vacuum line, a solution of **5** (1.76 g, 10 mmol) in anhydrous THF (10 mL) was stirred at $-78\,^{\circ}C$. This mixture was added dropwise by a cannula to the slightly evacuated 50 mL flask containing the solution of the lithium amide and the mixture was stirred at $-78\,^{\circ}C$ for 30 min.

3-(Methoxycarbonyloxy)-2-methyl-1-[(2,4,6-trimethyl)phenyl]hex-4-en-1-one (6a/6b): (*E*)-Crotonaldehyde (0.91 mL, 11 mmol) was added dropwise by syringe to the solution of the lithium enolate prepared as described above so that the temperature did not exceed $-70\,^{\circ}C$, and stirring was continued for 30 min at $-78\,^{\circ}C$. Methyl chloroformate (1.7 mL, 22 mmol) was injected and the mixture was allowed to reach room temperature overnight. A saturated aqueous solution of NH_4Cl (20 mL) was added. The mixture was transferred into a separatory funnel and the organic layer was separated. The aqueous phase was extracted with diethyl ether (2×50 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), and concentrated in a rotary evaporator. The residue was purified by column chromatography; $R_f = 0.4$ (hexane/ethyl acetate 6:1) to give **6a/6b** as a light yellow oil. Yields and diastereomeric ratios are given in Table 1.

Compound ***syn*-6a:** ^{1}H NMR (500 MHz): $\delta = 1.20$ (d, $^3J = 7.3$ Hz, 3H; CH_3CHCO), 1.71 (dd, $^3J = 6.5$ Hz, $^4J = 1.6$ Hz, 3H; CH_3CH=), 2.19 (s, 6H; ArCH_3), 2.27 (s, 3H; ArCH_3), 3.14 (qd, $^3J = 7.3$ Hz, $^3J = 5.2$ Hz, 1H; C*H*CO), 3.73 (s, 3H; OCH_3), 5.46 (ddd, $^3J = 7.5$ Hz, $^3J = 5.2$ Hz, $^4J = 0.7$ Hz, 1H; OC*H*), 5.55 (qdd, $^4J = 1.6$ Hz, $^3J = 15.2$ Hz, $^3J = 7.5$ Hz, 1H; CH_3CH=C*H*), 5.84 (qdd, $^3J = 6.5$ Hz, $^3J = 15.2$ Hz, $^4J = 0.7$ Hz, 1H; CH_3C*H*=), 6.83 (s, 2H; H_{arom}); ^{13}C NMR (75 MHz): $\delta = 11.38$, 17.80, 19.65, 21.03, 51.00, 54.63, 78.34, 126.96, 128.83, 131.07, 133.60, 137.92, 138.70, 154.92, 209.83; IR (film): $\tilde{\nu} = 2956$, 1752, 1695, 1611, 1442, 1379, 1263, 970, 852, 790 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 304 (1) [M^+], 228 (8), 213 (10), 148 (11), 147 (100), 119 (15); $C_{18}H_{24}O_4$ (304.4): calcd C 71.03, H 7.95; found: C 71.14, H 8.06.

Compound ***anti*-6b:** ^{1}H NMR (500 MHz): $\delta = 1.07$ (d, $^3J = 7.3$ Hz, 3H; CH_3CHCO), 1.73 (dd, $^3J = 6.6$ Hz, $^4J = 1.6$ Hz, 3H; CH_3CH=), 2.24 (s, 6H; ArCH_3), 2.27 (s, 3H; ArCH_3), 3.26 (qd, $^3J = 7.3$ Hz, $^3J = 8.2$ Hz, 1H; C*H*CO), 3.73 (s, 3H; OCH_3), 5.43 (qdd, $^4J = 1.6$ Hz, $^3J = 14.7$ Hz, $^3J = 8.3$ Hz, 1H; CH_3CH=C*H*), 5.49 (dd, $^3J = 8.3$ Hz, $^3J = 8.2$ Hz, 1H; OC*H*), 5.90 (qd, $^3J = 6.6$ Hz, $^3J = 14.7$ Hz, 1H; CH_3C*H*=), 6.83 (s, 2H; H_{arom}); ^{13}C NMR (75 MHz): $\delta = 12.98$, 17.88, 19.74, 21.05, 50.79, 54.55, 79.21, 126.30, 128.89, 132.71, 134.06, 137.71, 138.87, 154.82, 209.63; IR (film): $\tilde{\nu} = 2957$, 1752, 1697, 1611, 1442, 1379, 1263, 970, 852, 790 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 304 (1) [M^+], 228 (5), 213 (6), 148 (12), 147 (100), 119 (18); $C_{18}H_{24}O_4$ (304.4): calcd C 71.03, H 7.95; found: C 70.79, H 7.93.

(2*E*,4*E*)- and (2*E*,4*Z*)-2-Methyl-1-(2,4,6-trimethylphenyl)hexa-2,4-dien-1-one (7a/7b): A 10 mL two-necked flask was equipped with a magnetic stirrer, connected to a combined nitrogen/vacuum line, and was charged with either $[Pd(PPh_3)_4]$ (0.029 g – 0.116 g, 0.025 – 0.1 mmol, 5% – 20%) or $Pd(OAc)_2$ (0.006 g – 0.023 g, 0.025 – 0.1 mmol, 5% – 20%) with PBu_3 (0.020 g – 0.080 g, 0.1 – 0.4 mmol) and anhydrous THF (4 mL) was added. A 10 mL two-necked flask was equipped with a magnetic stirrer, connected to a combined nitrogen/vacuum line, and was charged with the carbonate (0.15 g, 0.5 mmol) to which anhydrous THF (1 mL) was added. This mixture was added by a cannula to the slightly evacuated flask containing the solution of the catalyst, and the resulting solution was stirred under N_2 at ambient temperature overnight. The solvent was distilled off in a rotary evaporator, and the residue was subjected to column chromatography, $R_f = 0.27$ (hexane/ethyl acetate 20:1), to give oily, yellowish **7a/7b**. Yield: 0.095 g, 83%. Product ratio are given in Table 2.

Compound **(2*E*,4*E*)-7a**: ^{1}H NMR (500 MHz): $\delta = 1.84$ (dd, $^3J = 6.9$ Hz, $^4J = 1.6$ Hz, 3H; CH_3CH=), 2.02 (s, 3H; CH_3CCO), 2.08 (s, 6H; ArCH_3), 2.29 (s, 3H; ArCH_3), 5.97 (qd, $^3J = 6.9$ Hz, $^3J = 14.7$ Hz, 1H; CH_3C*H*=), 6.48 (qdd, $^4J = 1.6$ Hz, $^3J = 14.7$ Hz, $^3J = 11.1$ Hz, 1H; CH_3CH=C*H*), 6.60 (d, $^3J = 11.1$ Hz, 1H; CH_3C=C*H*), 6.82 (s, 2H; H_{arom}); ^{13}C NMR (125 MHz): $\delta = 10.71$, 19.01, 19.14, 21.09, 128.10, 128.16, 134.12, 134.91, 137.46, 137.73, 139.59, 143.30, 202.93.

Compound **(2*E*,4*Z*)-7b**: ^{1}H NMR (500 MHz): $\delta = 1.63$ (dd, $^3J = 7.2$ Hz, $^4J = 1.8$ Hz, 3H; CH_3CH=), 2.02 (s, 3H; CH_3CCO), 2.10 (s, 6H; ArCH_3), 2.29 (s, 3H; ArCH_3), 5.92 (qd, $^3J = 7.2$ Hz, $^3J = 10.9$ Hz, 1H; CH_3C*H*=), 6.42 (qdd, $^4J = 1.8$ Hz, $^3J = 10.9$ Hz, $^3J = 11.7$ Hz, 1H; CH_3CH=C*H*), 6.83 (s, 2H; H_{arom}), 7.00 (d, $^3J = 11.7$ Hz, 1H; CH_3C=C*H*); ^{13}C NMR (125 MHz): $\delta = 10.64$, 13.99, 19.23, 21.11, 125.47, 128.08, 134.08, 135.64, 136.56, 137.17, 137.36, 137.79, 203.14.

Compounds **7a/7b**: IR (film): $\tilde{\nu} = 2920$, 1651, 1627, 1440, 1384, 1339, 1295, 1266, 1185, 1003, 895 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 229 (9) [M^++1], 228 (50) [M^+], 214 (16), 213 (93), 185 (13), 171 (19), 147 (100); $C_{16}H_{20}O$ (228.3): calcd C 84.16, H 8.83; found: C 84.05, H 8.83.

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