Mild and Stereoconvergent Palladium-Catalyzed Carbonyl Alkenation Reaction of α,β-Unsaturated Aldehydes

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Received 30 May 1997

Dedicated to Professor D. Seebach on the occasion of his 60th birthday

The addition of preformed ketone and ester enolates to α,β-unsaturated aldehydes **1** followed by in situ protection leads to the carbonates **3**, **7**, **8**, **11**, and **13**. They are converted into sensitive functionalized dienes **4**, **9**, **12**, and **14** by a smooth palladium-catalyzed elimination. Both *syn*- and *anti*-carbonates **7** and **8** lead to *E*-dienes **9** in a stereoconvergent manner.

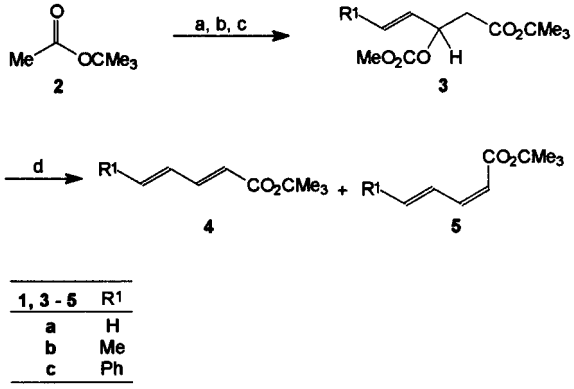
Although the β-elimination in organopalladium compounds is usually considered to be a limitation of their versatility,[1] the reaction is advantageous for the preparation of 1,3-dienes starting from alllylic acetates,[2] carbonates,[3] amines,[4] and vinyl epoxides.[5] Generally, rather vigorous conditions and the presence of strong bases are necessary in order to bring about this palladium-catalyzed reaction and fragmentation of the carbon skeleton can also occur.[6] In this paper, we report on a sequence which involves aldol addition to α,β-unsaturated aldehydes **1**, in situ protection of the alkoxides formed thereby and smooth elimination, thus leading to sensitive functionalized dienes. The stereochemical outcome of the reaction might give new insights into the mechanism of the β-elimination in organopalladium compounds.

R1 = H, Me, Ph; R2 = H, Me

E = CO_2R, COR, CN, 2-pyridyl

Scheme 1

First, *t*-butyl acetate (**2**) was deprotonated[7] with lithium diisopropylamide or hexamethyldisilazanide and subsequently treated with the aldehydes **1a**–**c**. The alkoxide formed thereby was quenched by reaction with methyl chloroformate to give the carbonates **3a**–**c**, which were either submitted to distillation or column chromatography or used without purification in the following step. When lithium diisopropylamide was used for deprotonation, *N*,*N*-(diisopropyl)methyl carbamate formed which was stable under the conditions of the aqueous workup, and had to be removed by chromatography. Thus, lithium hexamethyldisilazanide was found to be the reagent of choice, avoiding these complications. Treatment of the esters **3a**–**c** thus obtained in 76–86% yield with $Pd(PPh_3)_4$ either at room temperature or upon gentle warming to 35°C led to spontaneous evolution of carbon dioxide, and the dienes **4**/**5** formed (Scheme 2). The reaction was run neat and usually 1–5 mol% of the catalyst were used. Under those conditions, the dienes **4**/**5** were obtained in 86–93% yield, and a substantial preference for the formation of the *E* isomers **4a**–**c** was observed (Table 1, entries 1–3).



1, 3 - 5	R1
a	H
b	Me
c	Ph

Reagents and Conditions: (a) $LiN(SiMe_3)_2$, THF, 0 °C, 20 min, r. t.; (b) 1, THF, –78 °C, 30 min; (c) $ClCO_2Me$, –78 °C too20 °C overmight; (d) 1–5 mol% $Pd(PPh_3)_4$, neat, r. t. to 35 °C

Scheme 2

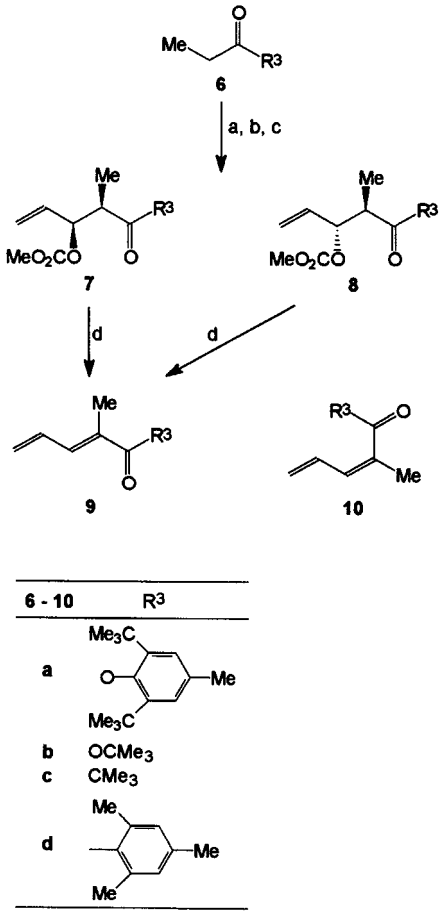
Table 1. Yield of Carbonates **3**, **7**, and **8** and Dienes **4/5** and **9/10** Prepared. *E*:*Z* Ratios of Dienes **4/5** and **9/10**

Entry	Carbonate(s) **3**, **7**, **8**	Yield (%)	Dienes **4**, **5**, **9**, **10**	Yield (%)	*E*:*Z* Ratio
1	**3a**[a]	86	**4a/5a**	93	86:14
2	**3b**[a]	80	**4b/5b**	91	88:12
3	**3c**[a]	76	**4c/5c**	86	94:6
4	**8a**[b] .	61	**9a/10a**	87	95:5
5	**7b/8b**[b,c]	52	**9b/10b**	92	95:5
6	**7c**[a]	55	**9c/10c**	87	96:4
7	**7d**[a]	61	**9d/10d**	90	97:3
	8d[b]	52	**9d/10d**	90	97:3

[a] Deprotonation by $LiN(SiMe_3)_2$.
[b] Deprotonation by $LiN(i\text{-}Pr)_2$.
[c] Mixture of *syn*- and *anti*-diastereomer (50:50).

When α-substituted ester or ketone enolates were submitted to an aldol addition followed by in situ protection of the alkoxides formed, diastereomeric carbonates, *syn*-**7** and *anti*-**8** resulted. The fact that, in principle, either *syn*-*Z*, *anti*-*E* or *syn*-*E*, *anti*-*Z* correlation or stereoconvergence are conceivable raises the question whether the configuration of dienes obtained by palladium-catalyzed elimination reflects the configuration of the carbonates **7** and **8**. Simple diastereoselection is effected by reliable protocols for aldol additions of preformed lithium enolates.[8] Taking advantage of these methods, *syn*-ketones **7c**,**d** and *anti*-aldols **8a**,**d** were obtained in high diastereomeric purity (>95% de) after purification by chromatography or distillation. On the other hand, the propionate **7b**/**8b** was prepared as a 1:1-mixture. When this mixture (**7b**/**8b**) or the *syn*-carbonates **7c** and **7d** or the *anti*-diastereomers **8a**

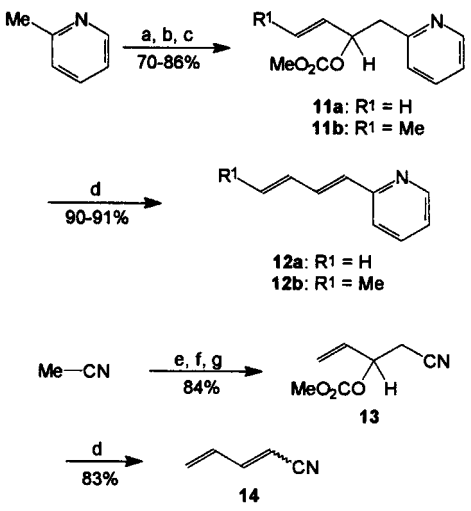
and **8c** were treated with $Pd(PPh_3)_4$ at room temperature, the predominant formation of *E*-dienes **9a**–**d** resulted in all cases (Scheme 3). This result clearly indicates a stereoconvergent outcome of the elimination process which strongly favors the formation of *E*-dienes **9a**–**d** (Table 1 entries 4–8). The *E* : *Z* ratio is determined by ^1H and ^{13}C NMR measurements and the assignment of *E* or *Z* configuration is based on nuclear Overhauser effects observed between the methyl group at C-2 and the vinylic 4-H.



Reagents and conditions: (a) LiN(*i*-Pr)$_2$ or LiN(SiMe$_3$)$_2$, THF, -78°C, 30 min, 0°C; (b) **1**, -78°C, 30 min; (c) $ClCO_2Me$, -78°C to 0°C, overnight; (d) 1-5 mol% $Pd(PPh_3)_4$, neat, r. t. to 35°C

Scheme 3

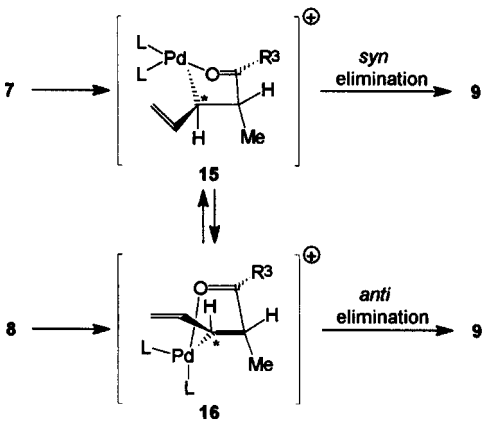
Due to the stereoconvergence, the isolation of pure *syn*- and *anti*-isomers **7** and **8** is not necessary under synthetic aspects, as mixtures of **7** and **8** can also be submitted to the palladium-catalyzed elimination to give *E*-dienes **9** predominantly. Besides enolates, other CH-acidic compounds have been found to be suitable starting materials for the alkenation protocol as well. When carbonates **11a**,**b** and **13**, originating from additions of lithiated α-picoline and acetonitrile followed by in situ protection, were allowed to react with the palladium catalyst, *E*-dienes **12a**,**b** and *E*/*Z*-mixture of **14** (2:1) resulted (Scheme 4).



Reagents and conditions: (a) *n*-BuLi, THF, -50 to -20°C, (b) **1a**, **b**, -50°C, 5 min; (c) $ClCO_2Me$, -50°C, 60 min r. t.; (d) 2 mol% $Pd(PPh_3)_4$, neat, 30°C; (e) *n*-BuLi, THF, -78 to -50°C; (f) **1a**, -78 to -20°C; (g) $ClCO_2Me$, -20°C to r.t.

Scheme 4

Any method which effects the conversion of a carbonyl compound into an alkene undoubtedly has to compete with the established alkenation reactions of Wittig, Horner–Wadsworth–Emmons, Julia and Peterson.[9] Some advantages of the procedure disclosed here should be emphasized: The sensitive dienes are liberated in a neutral, solvent-free medium and they are formed with substantial to high preference of the *E*-isomer. Compared to the alkenations based on phosphorus ylides, phosphonates and sulfones, this protocol avoids not only the tedious removal of phosphine oxides but also the use of toxic phosphonates and sodium amalgam, the common reducing agent in the Julia reaction. Furthermore, the Horner–Wadsworth–Emmons alkenation of α,β-unsaturated carbonyl compounds encounters the difficulty of competing 1,4-addition[10] – a drawback which is also avoided here by using hard nucleophiles.



Scheme 5

Although η^3 palladium complexes have been shown to be the initial intermediates formed by the reaction of Pd(0) reagents with allyl carbonates, η^1complexes have been postulated to be the precursors of the β-elimination.[2,3] Based on a recent structure determination of a σ-bonded palladium reagent containing a carbonyl group,[11] the diastereomeric complexes **15** and **16** are postulated to be the intermediates arising from *syn*-**7** and *anti*-**8**, respectively. In order to explain the stereoconvergence, one has to assume that **15** can react in a *syn*-elimination whereas **16** has to undergo an *anti*-elimination (Scheme 5). It remains to be established whether both mechanisms occur, as suggested recently,[12] or whether the configuration at the carbon center *C undergoes inversions[13] due to resubstitutions or σ-π-σinterconversions.

The following spectrometers were used to record physical data: ^{1}H NMR and ^{13}C NMR spectra: Varian VXR 300 and Bruker DRX 500. Mass spectra: Varian MAT CH5 and Varian MAT 8200 (HRMS). IR spectra: Perkin Elmer 1420 and 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 f. Pharmazeutische Chemie, Universität Düsseldorf and Beller, Mikroanalytisches Laboratorium, Göttingen. Spectroscopic data of the new compounds are given in Table 2. THF was predried with KOH and distilled under N_2 from Na/benzophenone. It was taken from the receiving flask, which was closed by a septum, using syringes or cannulas. Reactions performed at temperatures lower than –20°C were monitored by introducing a thermocouple, connected to a resistance thermometer (Ebro), through a septum into the reaction mixture. General remarks concerning the handling of lithium enolates and other organolithio compounds are given in Ref. 14.

1-[2,6-Bis(1,l-dimethylethyl)-4-methyl]phenyl propanoate (**6a**) was prepared according to Ref.15, 2,2-dimethylpentan-3-one (**6c**) according to Ref.16, 1-(2,4,6-Trimethylphenyl)propan-1-one (**6d**) according to Ref.17.

Carbonates 4, 7, and 8; General Procedure A:
A 250-mL two-necked flask, connected to a combined N_2/vacuum line, was equipped with a magnetic stirrer, a thermocouple, and a septum. During the following manipulations, N_2 atmosphere was maintained in all flasks. Anhyd THF (50 mL) and hexamethyldisilazane (4.6 mL, 22 mmol) were injected through the septum by syringes. The mixture was stirred at –20 °C, and a 1.6 M solution of BuLi in hexane (13.0 mL, 21.5 mmol) was added in such a way that the temperature did not exceed 0 °C. After stirring for 20 min at r.t., the mixture was cooled to –78 °C. In a 100 mL two-necked flask, connected to the combined N_2/vacuum line and equipped with a magnetic stirrer, a septum, and a thermocouple, a solution of the carbonyl compound **2** or **6** (20.0 mmol) in anhyd THF (50 mL) was stirred at –78°C. This mixture was added by a cannula to the slightly evacuated 250 mL flask containing the solution of LiHMDS. After stirring for 30 min at –78°C the aldehyde **1** was added slowly by syringe so that the temperature did not exceed –70 °C, and stirring was continued for 30 min at –78 °C. Methyl chloroformate (1.7 mL, 22 mmol) was injected and the mixture was allowed to reach r.t. overnight. A sat. aqueous solution of NH_4Cl (40 mL) and 1 M HCl (20 mL) were added. The mixture was transferred into a separatory funnel and the organic layer was separated. The aqueous phase was extracted with Et_2O (2 × 50 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$) and concentrated in a rotary evaporator. The crude product thus obtained was either used without purification in the following step or purified by distillation or column chromatography.

3-(Methoxycarbonyloxy)pent-4-enoic Acid 1′,1′-Dimethylethyl Ester (**3a**):
Yield: 3.96 g (86%); purified by distillation; bp 67 °C (0.07 mbar).
Anal. calc. for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.37; H, 7.84.

(E)-3-(Methoxycarbonyloxy)hex-4-enoic Acid 1′,1′-Dimethylethyl Ester (**3b**):
Yield: 3.90 g (80%); purified by column chromatography; R_f 0.6 ($CHCl_3$).
Anal. calc. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 58.95; H, 8.39.

(E)-3-(Methoxycarbonyloxy)-5-phenylpent-4-enoic Acid 1′,1′-Dimethylethyl Ester (**3c**):
Yield: 4.78 g (78%); purified by distillation; bp 125°C (0.14 mbar).
Anal. calc. for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.57; H, 7.28.

5-(Methoxycarbonyloxy)-2,2,4-trimethylhept-6-en-3-one (**7c**):
Yield: 2.54 g (55%); purified by distillation; bp 56°C (0.07 mbar).
Anal. calc. for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.17; H, 8.88.

2-Methyl-1-(2,4,6-trimethyl)pent-4-en-1-one (**7d**):
Yield: 3.45 g (61%); purified by column chromatography; R_f 0.35 (hexane/EtOAc, 6 : 1).
Anal. calc. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.28; H, 7.82.

Carbonates 7 and 8; General Procedure B
A 100 mL two-necked flask, connected to a combined N_2/vacuum line, was equipped with a magnetic stirrer and a septum. A thermocouple was introduced through the septum. During the following manipulations, N_2 atmosphere was maintained in all flasks. Anhyd THF (3.5 mL) and diisopropylamine (3.5 mL, 22 mmol) were injected through the septum by syringes. The mixture was stirred at –78 °C, and a 1.6 M solution of BuLi in hexane (13.0 mL, 21.5 mmol) was added in such a way that the temperature did not exceed –70 °C. After stirring for 30 min at 0 °C, the mixture was again cooled to –78 °C. In a 50 mL two-necked flask, connected to the combined N_2/vacuum line, a solution of the carbonyl compound **6** (20.0 mmol) in anhyd THF (17 mL) was stirred at –78 °C . This mixture was added by a cannula to the slightly evacuated 100 mL flask containing the solution of LDA. After stirring for 30 min at –78°C the aldehyde **1** was added slowly by syringe so that the temperature did not exceed –70 °C, and stirring was continued for 30 min at –78 °C. Methyl chloroformate (3.4 mL, 44 mmol) was injected, the mixture was allowed to reach r.t. overnight and worked up according to Procedure A.

syn- and anti-3-(Methoxycarbonyloxy)-2-methylpent-4-enoic Acid 1′,1′-Dimethylethyl Ester **(7b/8b)**:
Yield: 2.55 g (52%); purified by distillation, bp 64 °C (0.05 mbar).
Anal. calc. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 59.14; H, 8.32.

3-(Methoxycarbonyloxy)-2-methylpent-4-enoic Acid [2′,6′-Bis(1′′,1′′-dimethylethyl)-4′-methyl]phenyl Ester (**8a**):
Yield: 4.76 g (61%); purified by distillation, bp 138 °C (0.015 mbar).
Anal. calc. for $C_{23}H_{34}O_5$: C, 70.73; H, 8.78. Found: C, 70.50; H, 8.80.

3-(Methoxycarbonyloxy)-2-methyl-1-[(2,4,6-trimethyl)phenyl]-pent-4-en-1-one (**8d**):
Yield: 2.98 g (52%); purified by column chromatography, R_f 0.25 (hexane / EtOAc 6 : 1)
Anal. calc. for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.60; H, 7.54.

Carbonates 11; General Procedure C:
A 100 mL two-necked flask, equipped with a magnetic stirrer, a thermocouple and a pressure-equalizing dropping funnel, was connected to the combined N_2/vacuum line and the air in the flask was replaced by N_2. A 1.6 M solution of BuLi in hexane (13.0 mL, 21.5 mmol) was added by a syringe and diluted with anhyd THF (15 mL) at –20 °C. The mixture was cooled to –50 °C, and a solution of 2-methylpyridine (2.0 mL, 20 mmol) in anhyd THF (2 mL) was injected at such a rate that the temperature did not exceed –45 °C. The cooling bath was removed so that the stirred mixture could reach –20 °C. The deep red solution was cooled again to –50 °C and the aldehyde **1a** or **1b** (22 mmol) was added by a syringe. After stirring for 15 min at –50 °C, methyl chloroformate (1.7 mL, 22 mmol) was injected. The cooling bath was removed and the mixture was stirred at r.t. for 1 h. Sat. aq NH_4Cl (10 mL) and H_2O (10 mL) were added and the mixture was extracted with Et_2O (2 × 20 mL). The combined organic layers were washed with H_2O (20 mL) and brine (20 mL) and dried ($MgSO_4$). The solvent was removed in a rotary evaporator and the residue was purified by distillation.

2-[2-(Methoxycarbonyloxy)but-3-enyl]pyridine (**11a**):
Yield: 3.55 g (86%); purified by distillation, bp 67 °C (0.07 mbar).
Anal. calc. for $C_{11}H_{13}O_3N$: C, 63.74; H, 6.33. Found: C, 63.86; H, 6.58.

(E)-2-[2-(Methoxycarbonyloxy)pent-3-enyl]pyridine (**11b**):
Yield: 3.08 g (70%); purified by distillation, bp 84°C (0.05 mbar).
Anal. calc. for $C_{12}H_{15}O_3N$: C, 65.14; H, 6.83. Found: C, 65.29; H, 6.97.

3-(Methoxycarbonyloxy)pent-4-enenitrile (**13**):
Under N_2 atmosphere, a 1.6 M solution of BuLi in hexane (6.6 mL, 10.5 mmol) was stirred in a 50 mL two-necked flask, equipped with a magnetic stirrer, a septum, and a thermocouple. After cooling to –20 °C, anhyd THF (8 mL) was added, and the mixture was cooled to –78 °C. In a second flask, a solution of MeCN (0.52 mL, 10 mmol) in anhyd THF (2 mL) was prepared under N_2 and also cooled to –78 °C. The solution of MeCN was transferred by a cannula into the slightly evacuated flask containing the solution of BuLi. The temperature was allowed to reach –50 °C, and a white precipitate formed gradually. The mixture was cooled to –78 °C, and aldehyde **1a** (0.8 mL, 12 mmol) was injected in one portion whereby the temperature reached –50 °C. The cooling bath was removed, so that the mixture warmed up to –20 °C. Methyl chloroformate (0.92 mL, 12 mmol) was injected rapidly, and the temperature rose to 15 °C within 1 min. After stirring for 18 h at r.t., the mixture was worked up according to Procedure C. Yield: 1.30 g (84%) after column chromatography; R_f 0.6 ($CHCl_3$). The product was submitted to Procedure D without further purification.

Dienes 4, 9, 12, and 14 by Palladium-Catalyzed Elimination; General Procedure D:
A 5 mL two-necked flask was equipped with a magnetic stirrer and charged with either purified or crude carbonate **3**, **7**, **8**, **11**, or **13** (5.0 mmol). $Pd(PPh_3)_4$ (0.058–0.289 g; 0.05–0.25 mmol) was added, and the mixture was stirred under N_2 at 25 to 35 °C until the evolution of CO_2 ceased. The crude product was purified by distillation or column chromatography.

(E)-Penta-2,4-dienoic Acid 1′,1′-Dimethylethyl Ester **(4a)**:
Yield: 0.71 g (93%); purified by distillation, bp 44°C (13 mbar). The physical and spectroscopic data are in accordance with those described in the literature.[18]

(2E,4E)-Hexa-2,4-dienoic Acid 1′,1′-Dimethylethyl Ester **(4b)**:
Yield: 0.76 g (91%); purification by distillation, bp 45 °C (4 mbar). The physical and spectroscopic data are in accordance with those described in the literature.[19]

(2E,4E)-5-Phenylpenta-2,4-dienoic Acid 1′,1′-Dimethylethyl Ester **(4c)**:
Yield: 1.03 g (90%); purified by column chromatography; R_f 0.8 ($CHCl_3$). The physical and spectroscopic data are in accordance with those described in the literature.[20]

(2E,4E)-2-Methylpenta-2,4-dienoic Acid [2′,6′-Bis(1′′,1′′-dimethylethyl)-4′-methyl]phenyl Ester **(9a)**:
Yield: 1.37 g (87%); purified by distillation, bp 60°C (2 mbar).
Anal. calc. for $C_{21}H_{30}O_2$: C, 80.20; H, 9.62. Found: C, 80.06; H, 9.70.

Table 2. Spectroscopic Properties of Carbonates **3**, **7**, **8**, **11**, **13** and Dienes **9** Prepared

Product	IR (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ	MS m/z (%)
3a	1760 1745	1.44 (s, 9H, CCH_3), 2.50–2.72 (m, 2H, CH_2), 3.79 (s, 3H, OCH_3), 5.23–5.90 (m, 4H, CH_2=CHCH)	28.11, 40.58, 54.78, 75.07, 81.27, 118.15, 134.64, 154.85, 168.71	174 (12), 157 (15), 128 (19), 99 (21), 81 (53), 57 (100)
3b	1752 1733	1.43 (s, 9H, CCH_3), 1.69 (d, J=1.3, CH_3), 2.45–2.71 (m, 2H, CH_2), 3.76 (s, 3H, OCH_3), 5.40–5.90 (m, 3H, CH=CHCH)	17.72, 28.01, 40.94, 54.63, 75.36, 81.05, 127.66, 130.98, 154.89, 168.86	188 (15), 171 (6), 142 (19), 130 (34), 57 (100)
3c	1760 1735	1.44 (s, 9H, CCH_3), 2.63 (dd, J=6, 15.5, 1H, CH_2CO), 2.79 (dd, J=8, 15.5, 1H, CH_2CO), 3.78 (s, 3H, OCH_3), 5.62–5.65 (m, 1H, CH), 6.17 (dd, J=7.5, 16, 1H, CH), 6,73 (d, J=16, 1H, CHPh), 7.25–7.40 (m, 5H, H_{arom})	28.00, 40.97, 54.78, 75.26, 81.30, 125.36, 126.75, 128.28, 128.61, 133.90, 135.85, 154.85, 168.65	306 (M^+, 3), 250 (12), 204 (83), 174 (24), 157 (53), 130 (100)
7b/8b	1725 1750	1.11; 1.18 (d, J=7, 3H, CH_3), 1.444; 1.436 (s, 9H, CCH_3), 2.62–2.70 (m, 1H, CH), 3.768; 3.783 (s, 3H, OCH_3), 5.22–5.44 (m, 3H, CH_2=CCH), 5.69–5.83 (m, 1H, CH)	12.82, 29.97, 44.52, 54.70, 80.00, 80.92, 120.08, 133.72, 154.79, 172.33, 12.32, 27.97, 44.61, 54.77, 79.29, 80.98, 118.70, 132.99, 155.07, 172.04	188 (4), 171 (9), 142 (18), 112 (10), 95 (26), 57 (100)
7c	1710 1760	1.13 (s, 9H, CCH_3), 1.15 (d, J=7, 3H, CH_3), 3.32–3.37 (m, 1H, CH), 3.79 (s, 3H, OCH_3), 5.16–5.32 (m, 3H, CH_2=CCH), 5.72–5.83 (m, 1H, CH)	15.61, 26.13, 43.89, 44.89, 54.80, 80.79, 119.01, 134.05, 155.07, 216.00	228 (M^+, 0.5), 171 (19), 152 (6), 95 (100)
7d	1700 1760	1.20 (d, J=7.3, 3H, CH_3), 2.19 (s, 6H, CH_3), 2.27 (s, 3H, CH_3), 3.11–3.15 (m, 1H, CH), 3.75 (s, 3H, OCH_3), 5.26–5.38 (m, 2H, CH_2), 5.55–5.59 (m, 1H, CH), 6.83 (s, 2H, H_{arom})	11.02, 19.63, 21.03, 50.72, 54.76, 77.83, 118.02, 128.82, 133.51, 134.26, 137.70, 138.74, 154.88, 209.60	290 (M^+, 3), 214 (6), 147 (100)
8a	1751	1.30 (s, 9H, CCH_3), 1.32 (s, 9H, CCH_3), 1.45 (d, J=3, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.12–3.22 (m, 1H, CH), 3.77 (s, 3H, OCH_3), 5.32–5.48 (m, 2H, CH_2), 5.57–5.62 (m, 1H, CH), 5.82–5.95 (m, 1H, CH), 7.09–7.13 (m, 2H, H_{arom})	12.15, 21.45, 31.33, 31.47, 35.17, 35.21, 43.93, 54.71, 78.10, 120.00, 126.94, 127.26, 132.35, 134.66, 142.00, 142.04, 146.02, 154.65, 172.64	276 (2), 220 (93), 204 (77), 95 (15), 57 (100)

Table 2. (continued)

Product	IR (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ	MS m/z (%)
8d	1705 1762	1.08 (d, J=7.4, 3H, CH_3), 2.25 (s, 6H, CH_3), 2.27 (s, 3H, CH_3), 3.26–3.31 (m, 1H, CH), 3.75 (s, 3H, OCH_3), 5.31–5.47 (m, 2H, CH_2), 5.52–5.57 (m, 1H, CH), 5.78–5.90 (m, 1H, CH), 6.84 (s, 2H, H_{arom})	12.69, 19.72, 21.04, 50.61, 54.66, 78.80, 119.84, 128.90, 133.26, 133.99, 137.59, 138.92, 154.77, 209.38	290 (M^+, 2), 214 (3), 147 (46), 28 (100)
9a	1730	1.33 (s, 18H, CCH_3), 2.12 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 5.53–5.71 (m, 2H, CH_2), 6.70–6.84 (m, 1H, CH), 7.12 (s, 2H, H_{arom}), 7.40 (d, J=12, 1H, CH)	13.03, 21.54, 31.51, 31.60, 125.21, 126.97, 132.22, 134.29, 140.47, 142.05, 146.06, 168.54	314 (M^+, 8), 220 (15), 205 (20), 95 (100)
9b	1600 1640 1710	1.50 (s, 9H, CCH_3), 1.91 (s, 3H, CH_3), 5.40–5.56 (m, 2H, CH_2), 6.58–6.70 (m, 1H, CH), 7.08 (d, J=11.3, 1H, CH)	12.71, 28.11, 80.26, 123.45, 129.69, 132.43, 137.41, 167.58	168 (M^+, 32), 112 (90), 95 (91), 67 (42), 57 (100)
9c	1600 1665	1.27 (s, 9H, CCH_3), 1.93 (s, 3H, CH_3), 5.35–5.47 (m, 2H, CH_2), 6.60–6.68 (m, 2H, CHCH)	14.52, 28.14, 44.02, 122.08, 132.19, 133.50, 136.56, 210.96	152 (M^+, 9), 124 (6), 95 (100)
9d	1615 1640 1655	1.93 (s, 3H, CH_3), 2.25 (s, 6H, CH_3), 2.27 (s, 3H, CH_3), 5.35–5.47 (m, 2H, 134. 11, CH_2), 6.60 (d, J=11.5, 1H, CH), 6.75–6.81 (m, 1H, CH), 6.84 (s, 2H, H_{arom})	10.88, 19.15, 21.09, 125.55, 128.15, 132.83, 134.11, 137.63, 137.92, 142.67, 203.01	214 (M^+, 51), 199 (34), 171 (20), 156 (15), 147 (100)
11a	1753	3.07–3.23 (m, 2H, CH_2), 3.71 (s, 3H, OCH_3), 5.19–5.34 (m, 2H, CH_2), 5.51–5.58 (m, 1H, CH), 5.84–5.96 (m, 1H, CH), 7.12–7.21, 7.58–7.63, 8.54–8.56 (m, 5H, H_{arom})	43.12, 54.64, 78.26, 117.76, 121.75, 124.05, 135.31, 136.31, 149.50, 154.92, 156.90	207 (M^+, 2), 148 (46), 132 (100)
11b	1750	1.67 (d, J=5.2, 3H, CH_3), 3.04–3.12 (m, 2H, CH_2), 3.69 (s, 3H, OCH_3), 5.46–5.83 (m, 3H, CHCH=CH), 7.1 l–7.20, 7.56–7.62, 8.53–8.56 (m, 5H, H_{arom})	17.76, 43.38, 54.50, 78.49, 121.65, 124.02, 128.31, 130.56, 136.27, 149.38, 154.94, 157.94	221 (M^+, 6), 162 (41), 146 (100)
13	2265 1760	2.7l–2.80 (m, 2H, CH_2), 3.82 (s, 3H, OCH_3), 5.27–5.33 (m, 1H, CH), 5.40–5.54 (m, 2H, CH_2), 5.84–5.95 (m, 1H, CH)	23.55, 55.23, 73.06, 115.73, 120.34, 132.49, 154.46	155 (M^+, 1), 128 (56), 115 (24), 96 (11), 80 (66), 53 (83)

(2E,4E)-2-Methylpenta-2,4-dienoic Acid 1′,1′-Dimethylethyl Ester (**9b**):
Yield: 0.77 g (92%); purified by distillation, bp 45 °C (7 mbar).
Anal. calc. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.31; H, 9.53.

(4E,6E)-2,2,4-Trimethylhepta-4,6-dien-3-one (**9c**):
Yield: 0.66 g (87%); purified by distillation, bp 41 °C (10 mbar).

(2E,4E)-2-Methyl-1-(2,4,6-trimethylphenyl)penta-2,4-dien-1-one (**9d**):
Yield: 0.97 g (90%); purified by column chromatography: R_f 0.3 (hexane / EtOAc 20 : 1).
HRMS: *m/z*= 214.1350 (calc. for $C_{15}H_{18}O$: 214.1358).

E-2-(Buta-1,3-dienyl)pyridine (**12a**):
Yield: 0.59 g (91%); purified by distillation, bp 52 °C (0.25 mbar). The physical and spectroscopic data are in accordance with those described in the literature.[21]

(1E,3E)-2-(Penta-1,3-dienyl)pyridine (**12b**):
Yield: 0.60 g (90%); purified by distillati/n, bp 65 °C (0.7 mbar). The physical and spectroscopic data are in accordance with those described in the literature.[22]

E-2,4-Pentadienenitrile (**14**):
Yield: 0.33 g (83%); purified by distillation, bp 55 °C (25 mbar). The physical and spectroscopic data are in accordance with those described in the literature.[23]

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The latter institution also kindly provided doctoralfellowships to S. M. and I. S.

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