A Convenient Method for the Synthesis of Terminal (*E*)-1,3-Dienes

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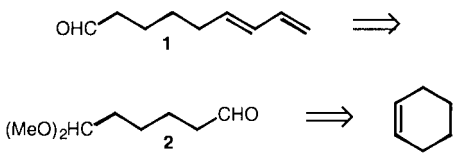
Received 22 August 2001

Dedicated to Professor Edwin Vedejs in recognition of his important contributions to phosphorus-based methods in organic synthesis

Abstract: Lithiated allylic phosphonates undergo efficient olefination reactions with a variety of aldehydes in the presence of HMPA to give terminal 1,3-dienes with high selectivity for the *E*-isomer. This method is general and procedurally simple.

Key words: aldehydes, alkenation, phosphorus, Wittig reactions, ylides

We recently described the Lewis acid-catalyzed cycloisomerization of tetraenones via 4+3 trapping of the Nazarov oxyallyl intermediate.[1] This methodology called for the efficient preparation of 1,4-dien-3-ones bearing pendant 1,3-diene moieties. Our studies required the dienal **1** (Scheme 1), a compound whose preparation has been previously described several times.[2] However, use of the existing routes was not attractive in conjunction with the subsequent multistep preparation of the eventual substrates needed. Instead, we focused on the development of a more direct and high-yield strategy. Ideally, the 1,3-diene moiety would be installed in one step with high stereoselectivity. Many methods for the synthesis of 1,3-dienes are known, including elimination of allylic alcohols or halides, reductive elimination of dihalogenated compounds, or transition metal catalyzed coupling reactions of vinylic compounds.[3] However, most of these procedures require precursors whose preparation can be nontrivial. Direct synthesis of the 1,3-diene via aldehyde olefination was attractive, as it would permit the use of monoprotected dial **2**, which is available in a one-pot process from ozonolysis of cyclohexene via Schreiber's protocol.[4]



Scheme 1

One aldehyde → diene approach that has enjoyed considerable attention involves a Peterson olefination following addition of a γ-silyl-substituted allylmetal reagent to an aldehyde. For example, silylated allylboronates,[5] allyltitanates[6] and allylzirconium reagents[7] have all been used in additions to a variety of aliphatic or aromatic aldehydes. Subsequent treatment with protic acid or $BF_3{\cdot}OEt_2$ effects eliminative desilylation to furnish the diene with high *E*-selectivity. The need for a multistep sequence with isolation of at least one intermediate in each case is a potential drawback to these silyl-mediated methods.

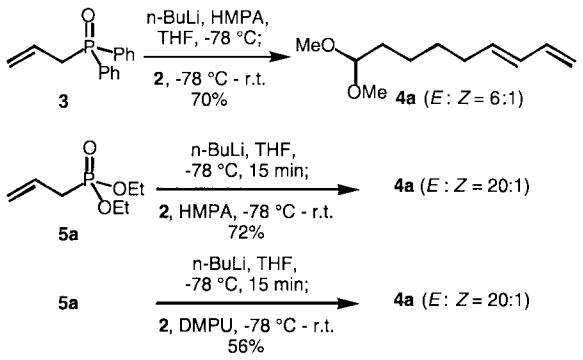
The Wittig reaction has long been recognized as a convenient method for olefination of carbonyl compounds.[8] Use of the Wittig reaction for construction of 1,3-dienes requires the use of modified phosphorus ylides, $Ph_3P{=}CHCH{=}CHR$, which typically furnish impractical *E*/*Z*-mixtures.[9] An important exception to this generalization is the 1984 report by Vedejs and Huang that phosphoranes $Ph_2R^1P{=}CHCH{=}CHR$ (R^1 = Me or $CH_2CH{=}CHR$) provide (*E*)-dienes in useful ratios when used under salt-free conditions.[10] A subsequent report by Tamura using allylidene tributylphosphoranes confirmed the value of *P*-alkyl substituents for increasing the *E*-selectivity of this process.[11] The selectivity of these methods was found to be dependent upon the degree of substitution on the allylidene fragment and the steric demand of the aldehyde, with more congested partners favoring greater *E*-selectivity.

For construction of simple terminal dienes, the Wittig–Horner reaction of lithiated allyldiphenylphosphine oxide described by Yamamoto and co-workers appeared to be the most convenient and general method.[12,13] The starting phosphine oxide **3** is easily prepared, and reacts smoothly with a variety of aldehydes under mild conditions to provide the desired dienes in high yield and acceptable *E*-selectivity. However, in the specific case of aldehyde **2** we obtained a rather low *E*/*Z* ratio of diene **4a** (6:1; Scheme 2). Efforts to obtain greater *E*-selectivity led to the present study, in which we have found lithiated allylphosphonates to provide dienes in good yield and with consistently high stereoselectivity.[14]

Phosphonate anions substituted with electron-withdrawing groups are known to react with aldehydes (Horner–Wadsworth–Emmons reaction; HWE) to furnish alkenes with high *E*-selectivity.[16] There have been a number of applications of the HWE reaction to diene or polyene construction using substituted allylphosphonates.[17] However, apart from Schlosser's report,[15] this process has not been used as a general method for synthesis of terminal (*E*)-dienes. Diethyl allylphosphonate (**5a**) is commercially available and easily prepared,[18] and in the event it furnished the desired terminal diene with high *E*-selectivity (≥20:1). Notably, we found that the yield was very sensi-

Synthesis 2002, No. 1, 28 12 2001. Article Identifier:
1437-210X,E;2002,0,01,0099,0103,ftx,en;M03901SS.pdf.

ISSN 0039-7881



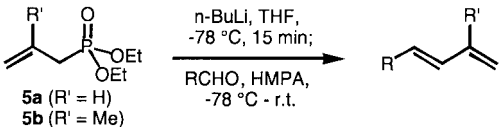
Scheme 2

tive to reaction time and order of addition. Under the optimal conditions, phosphonate **5a** was treated with BuLi at –78 °C, then after 15 min, a mixture of aldehyde **2** and HMPA (2.4 equiv) was added and the reaction mixture was allowed to warm to room temperature. Deviation from this procedure led to greatly reduced yields of **4a**, with the remainder of the material isolated as a complex mixture of phosphorus-containing products.[19] Other bases (e.g., KOBu-*t*, NaH, LDA) gave poor yields (<20%), and omission of HMPA gave only traces of **4a**. Substitution of *N*,*N*′-dimethylpropyleneurea (DMPU) for HMPA led to somewhat lower yields as well (56%). There is ample evidence for the lithiation of phosphonates such as **5a** by BuLi in the absence of HMPA, and for addition of the resulting phosphoryl-stabilized allyl anion to aldehydes[20] and other electrophiles.[21] However, the presence of HMPA is clearly essential in this case, presumably due to its perturbation of the aggregation state of the intermediate organolithium species.[22]

The optimum conditions used with **2** were applied to several other aldehydes, and the results were compared with those from analogous literature examples utilizing the Yamamoto procedure (Table). In general, dienes **4** were obtained in comparable yields and with higher *E*-selectivity. Moreover, the method can be easily adapted to the preparation of substituted dienes, as illustrated by the use of diethyl methallylphosphonate (**5b**). In these cases, the *E*-selectivity was uniformly excellent: any (*Z*)-diene formed was present in quantities below the limits of detection using ^{1}H NMR.

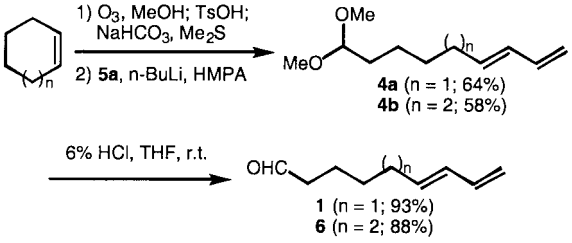
The original impetus for this study was the need for an efficient route to dienals such as **1**. In fact, aqueous hydrolysis of **4a** furnished **1** in 93% yield, and its homologue **4b** gave dienal **6** in comparable yield (Scheme 3). Thus, this methodology permits access to the versatile dienals **1** and **6** in 3 steps and 60% or 52% overall yields, respectively, from cyclohexene or cycloheptene. In a more general sense, this study describes a convenient method for terminal diene synthesis, using readily available aldehydes and allylphophonates, which proceeds with high *E*-selectivity.

Table Terminal Diene Synthesis via Allylphosphonates **5a** and **5b**



Entry	R	Phosphonate	Yield (%)[a]	*E*:*Z*[b]	Yamamoto Procedure
1	$(MeO)_2CH(CH_2)_4$	**5a**	72	20:1	70%, 6:1[c]
2	$(MeO)_2CH(CH_2)_5$	**5a**	69	16:1	-
3	$(MeO)_2CH(CH_2)_6$	**5a**	62	18:1	-
4	$THPO(CH_2)_4$	**5a**	65	20:1	-
5	Ph	**5a**	60	40:1[d]	79%, 19:1[d,e]
6	$CH_3(CH_2)_8$	**5a**	66	20:1	88%, 19:1[e]
7	*c*-C_6H_{11}	**5a**	76	15:1	82%, 9:1[e]
8	$(MeO)_2CH(CH_2)_4$	**5b**	65	>98:2	-
9	$(MeO)_2CH(CH_2)_6$	**5b**	69	>98:2	-
10	$THPO(CH_2)_4$	**5b**	63	>98:2	-
11	Ph	**5b**	57	>98:2	-
12	$CH_3(CH_2)_8$	**5b**	71	>98:2	-
13	*c*-C_6H_{11}	**5b**	75	>98:2	-

[a] Isolated yields.
[b] Ratios were determined by ^{1}H NMR integration unless otherwise specified.
[c] From this work.
[d] Ratios determined by GC analysis.
[e] See Ref.[12]



Scheme 3

All air or moisture sensitive reactions were carried out in oven dried (120 °C) or flame dried glassware under N_2, unless otherwise noted. Reactive liquids were transferred by syringe and were added into the reaction flask through rubber septa. Et_2O and THF were freshly distilled from sodium-benzophenone ketyl. Purchased reagents were used as received unless otherwise indicated. TLC was performed on glass plates coated with 0.25 mm Kieselgel 60 F_{254} (Merck). Flash columns were packed with 230–400 mesh silica gel (Merck or Baxter). All solvents were distilled before use. ^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Varian Unity-300, Varian XL-300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) or Varian VXR-500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometer. IR spectra were measured with a Mattson FTIR 3000 infrared spectrometer. Mass spec-

tra were determined on a Finnigan Mat 95 high resolution gas chromatograph/mass spectrometer with Finnigan Mat ICIS II operating system. GC analyses of product *E*/*Z* ratios were determined on a Hewlett-Packard 5890 Series II Gas Chromatograph equipped with a 30 m × 0.53 mm HP-5 capillary column and a flame ionization detector.

Terminal (*E*)-Dienes ; General Procedure

To a solution of diethyl allylphosphonate (**5a**;[18] 1.07 g, 6.0 mmol) or diethyl (2-methylallyl)phosphonate (**5b**;[23] 1.15 g, 6.0 mmol) in anhyd THF (15 mL) was added dropwise BuLi (2.5 M in hexanes, 2.4 mL, 6.0 mmol) at –78 °C. After stirring for 15 min, a solution of the aldehyde (see below for individual cases) (5.0 mmol) in HMPA (2.1 mL, 12 mmol) was added dropwise via cannula. The resulting solution was stirred for 2 h at –78 °C, and then allowed to warm to r.t. Stirring was continued for an additional 12 h at r.t. before quenching with sat. aq NH_4Cl solution. The mixture was extracted with Et_2O (3 × 15 mL). The combined organic phases were washed with brine (30 mL) , dried ($MgSO_4$) and concentrated to afford the crude product. Purification by flash chromatography (EtOAc–hexanes) gave the desired dienes (Table).

(*E*)-9,9-Dimethoxynona-1,3-diene (4a)

The diene was prepared from lithiated **5a** and 6,6-dimethoxyhexanal (**2**)[4] according to the general procedure and was obtained as a colorless oil in 72% yield (*E*/*Z* = 20:1, determined by integration of ^{1}H NMR signals of H-2); R_f 0.36 (1:9 EtOAc–hexanes).

IR (film): 3086, 2988, 2857, 1651, 1602 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.30 (ddd, 1 H, *J* = 17.0, 10.4, 10.4 Hz), 6.05 (dd, 1 H, *J* = 15.3, 10.5 Hz), 5.69 (dt, 1 H, *J* = 15.2, 7.0 Hz), 5.08 (ddd, 1 H, *J* = 17.0, 1.1, 0.5 Hz), 4.95 (ddd, 1 H, *J* = 10.1, 1.1, 0.5 Hz), 4.36 (t, 1 H, *J* = 5.8 Hz), 3.31 (s, 6 H), 2.09 (br q, 2 H, *J* = 7.0 Hz), 1.63–1.57 (m, 2 H), 1.46–1.31 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.46, 135.31, 131.29, 114.96, 104.64, 52.81, 32.64, 32.53, 29.22, 24.37.

HRMS: *m*/*z* calcd for $C_{10}H_{17}O$ (M^+ – OCH_3) 153.1280; found 153.1280.

(*E*)-10,10-Dimethoxydeca-1,3-diene (4b)

The diene was prepared from lithiated **5a** and 7,7-dimethoxyheptanal[4] according to the general procedure and was obtained as a colorless oil in 69% yield (*E*/*Z* = 16:1, determined by integration of ^{1}H NMR signals of H-2); R_f 0.35 (1:9 EtOAc–hexanes).

IR (film): 3086, 2991, 2858, 1650, 1602 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.30 (ddd, 1 H, *J* = 16.9, 10.2, 10.2 Hz), 6.04 (dd, 1 H, *J* = 15.2, 10.3 Hz), 5.69 (dt, 1 H, *J* = 15.1, 7.0 Hz), 5.08 (br d, 1 H, *J* = 16.4 Hz), 4.95 (br d, 1 H, *J* = 10.2 Hz), 4.35 (t, 1 H, *J* = 5.7 Hz), 3.31 (s, 6 H), 2.08 (br q, 2 H, *J* = 7.0 Hz), 1.62–1.55 (m, 2 H), 1.42–1.29 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.48, 135.53, 131.16, 114.86, 104.67, 52.77, 32.61, 32.60, 29.26, 29.19, 24.64.

HRMS: *m*/*z* calcd for $C_{11}H_{19}O$ (M^+ – OCH_3) 167.1436; found 167.1429.

(*E*)-11,11-Dimethoxyundeca-1,3-diene

The diene was prepared from lithiated **5a** and 8,8-dimethoxyoctanal[4] according to the general procedure and was obtained as a colorless oil in 62% yield (*E*/*Z* = 18:1, determined by integration of ^{1}H NMR signals of H-2); R_f 0.38 (1:9 EtOAc–hexanes).

IR (film): 3088, 2956, 1650, 1603 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.30 (ddd, 1 H, *J* = 17.1, 10.3, 10.2 Hz), 6.04 (dd, 1 H, *J* = 15.4, 10.5 Hz), 5.69 (dt, 1 H, *J* = 15.1, 6.9 Hz), 5.07 (d, 1 H, *J* = 16.4 Hz), 4.94 (d, 1 H, *J* = 10.2 Hz), 4.35 (t, 1 H, *J* = 5.8 Hz), 3.31 (s, 6 H), 2.07 (q, 2 H, *J* = 7.1 Hz), 1.61–1.55 (m, 2 H), 1.43–1.27 (m, 8 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.40, 135.50, 131.01, 114.69, 104.59, 52.64, 32.59, 32.55, 29.40, 29.18, 29.16, 24.63.

HRMS: *m*/*z* calcd for $C_{12}H_{20}O$ (M^+ – OCH_3) 180.1515; found 180.1525.

(*E*)-8-(2-Tetrahydropyranyloxy)octa-1,3-diene

The diene[24] was prepared from **5a** and 5-(2-tetrahydropyranyloxy)pentanal[24a,25] according to the general procedure and was obtained as a colorless oil in 65% yield (*E*/*Z* = 20:1, determined by integration of ^{1}H NMR signals of H-2); R_f 0.48 (1:9 EtOAc–hexanes).

IR (film): 3004, 2941, 1651, 1601 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.30 (ddd, 1 H, *J* = 17.1, 10.1, 10.1 Hz), 6.06 (dd, 1 H, *J* = 15.1, 10.5 Hz), 5.71 (dt, 1 H, *J* = 15.1, 7.1 Hz), 5.07 (d, 1 H, *J* = 17.0 Hz), 4.95 (d, 1 H, *J* = 10.1 Hz), 4.57 (dd, 1 H, *J* = 4.3, 2.8 Hz), 3.90–3.83 (m, 1 H), 3.74 (ddd, 1 H, *J* = 9.6, 6.7, 6.7 Hz), 3.53–3.47 (m, 1 H), 3.39 (ddd, 1 H, *J* = 9.7, 6.4, 6.4 Hz), 2.12 (br q, 2 H, *J* = 7.1 Hz), 1.87–1.79 (m, 1 H), 1.75–1.68 (m, 1 H), 1.65–1.45 (m, 8 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.47, 135.33, 131.34, 114.98, 99.04, 67.59, 62.52, 32.55, 30.97, 29.49, 26.06, 25.71, 19.87.

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.00; H, 10.64.

(*E*)-1-Phenylbuta-1,3-diene

The diene[12] was prepared from lithiated **5a** and benzaldehyde according to the general procedure and was obtained as a colorless oil in 60% yield (*E*/*Z* = 40:1, determined by GC); R_f 0.85 (hexanes).

IR (film): 3086, 2930, 1601 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41–7.37 (m, 2 H), 7.32–7.28 (m, 2 H), 7.23–7.19 (m, 1 H), 6.78 (dd, 1 H, *J* = 15.6, 10.2 Hz), 6.54 (d, 1 H, *J* = 15.6 Hz), 6.50 (ddd, 1 H, *J* = 16.6, 10.7 10.6 Hz), 5.32 (d, 1 H, *J* = 17.4 Hz), 5.16 (d, 1 H, *J* = 10.8 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.36, 137.29, 133.04, 129.79, 128.79, 127.81, 126.63, 117.82.

(*E*)-Trideca-1,3-diene

The diene[12] was prepared from lithiated **5a** and decanal according to the general procedure and was obtained as a colorless oil in 66% yield (*E*/*Z* = 20:1, determined by integration of ^{1}H NMR signals of H-2); R_f 0.88 (hexanes).

IR (film): 3088, 2958, 1635, 1642 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.31 (ddd, 1 H, *J* = 16.9, 10.5, 10.5 Hz), 6.05 (dd, 1 H, *J* = 15.3, 10.5 Hz), 5.71 (dt, 1 H, *J* = 15.3, 7.0 Hz), 5.08 (d, 1 H, *J* = 17.0 Hz), 4.94 (d, 1 H, *J* = 10.1 Hz), 2.07 (q, 2 H, *J* = 7.0 Hz), 1.42–1.23 (m, 14 H), 0.88 (t, 3 H, *J* = 7.2 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.59, 135.89, 131.02, 114.02, 32.79, 32.13, 29.79, 29.74, 29.56, 29.44, 29.42, 22.91, 14.35.

(*E*)-1-Cyclohexylbuta-1,3-diene

The diene[12] was prepared from lithiated **5a** and cyclohexanecarbaldehyde according to the general procedure and was obtained as a colorless oil in 76% yield (*E*/*Z* = 15:1 by GC); R_f 0.90 (hexanes).

IR (film): 3038, 2927, 1650, 1603 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.30 (ddd, 1 H, *J* = 17.0, 10.3, 10.3 Hz), 6.02 (dd, 1 H, *J* = 15.4, 10.3 Hz), 5.66 (dd, 1 H, *J* = 15.3, 6.8 Hz), 5.09 (d, 1 H, *J* = 16.9 Hz), 4.95 (d, 1 H, *J* = 10.2 Hz), 2.04–1.96 (m, 1 H), 1.78–1.62 (m, 5 H), 1.32–1.02 (m, 5 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.52, 137.85, 128.49, 114.92, 40.85, 32.95, 26.36, 26.21.

(*E*)-9,9-Dimethoxy-2-methylnona-1,3-diene
The diene was prepared from lithiated **5b** and 6,6-dimethoxyhexanal according to the general procedure and was obtained as a colorless oil in 65% yield (single isomer by ^{1}H NMR); R_f 0.39 (1:9 EtOAc–hexanes).

IR (film): 3082, 2950, 1609, 1456, 1382, 1128, 1076, 964 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.14 (d, 1 H, *J* = 15.7 Hz), 5.64 (dt, 1 H, *J* = 15.6, 6.9 Hz), 4.86 (br s, 2 H), 4.36 (t, 1 H, *J* = 5.8 Hz), 3.31 (s, 6 H), 2.11 (q, 2 H, *J* = 6.7 Hz), 1.83 (br s, 3 H), 1.65–1.56 (m, 2 H), 1.49–1.30 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.34, 133.14, 130.82, 114.47, 104.64, 52.80, 32.85, 32.54, 29.46, 24.41, 18.91.

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.55; H, 11.30.

(*E*)-11,11-Dimethoxy-2-methylundeca-1,3-diene
The diene was prepared from lithiated **5b** and 8,8-dimethoxyoctanal according to the general procedure and was obtained as a colorless oil in 69% yield (single isomer by ^{1}H NMR); R_f 0.42 (1:9 EtOAc–hexanes).

IR (film): 3081, 2987, 1608, cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.12 (d, 1 H, *J* = 15.6 Hz), 5.64 (dt, 1 H, *J* = 15.6, 7.9 Hz), 4.85 (s, 2 H), 4.35 (t, 1 H, *J* = 5.9 Hz), 3.31 (s, 6 H), 2.09 (q, 2 H, *J* = 7.0 Hz), 1.83 (s, 3 H), 1.62–1.56 (m, 2 H), 1.44–1.28 (m, 8 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.39, 132.95, 131.17, 114.34, 104.74, 52.81, 32.92, 32.68, 29.54, 29.52, 29.34, 24.76, 18.92.

(*E*)-8-(2-Tetrahydropyranyloxy)-2-methylocta-1,3-diene
The diene was prepared from lithiated **5b** and the corresponding aldehyde according to the general procedure and was obtained as a colorless oil in 63% yield (single isomer by ^{1}H NMR); R_f 0.48 (1:9 EtOAc–hexanes).

IR (film): 3082, 2966, 1608 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.13 (d, 1 H, *J* = 15.6 Hz), 5.64 (dt, 1 H, *J* = 15.6, 7.0 Hz), 4.85 (s, 2 H), 4.57 (dd, 1 H, *J* = 4.4, 3.0 Hz), 3.90–3.84 (m, 1 H), 3.78–3.71 (m, 1 H), 3.53–3.47 (m, 1 H), 3.42–3.36 (m, 1 H), 2.14 (q, 2 H, *J* = 6.3 Hz), 1.83 (s, 3 H), 1.74–1.45 (m, 10 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.28, 133.21, 130.76, 114.45, 99.01, 67.60, 62.49, 32.73, 30.95, 29.49, 26.26, 25.69, 19.86, 18.87.

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.79; H, 10.63.

(*E*)-1-Phenyl-3-methylbuta-1,3-diene
The diene[10,26] was prepared from **5b** and benzaldehyde according to the general procedure and was obtained as a colorless oil in 57% yield (single isomer by ^{1}H NMR); R_f 0.84 (hexanes).

IR (film): 3081, 2949, 1603 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.41–7.37 (m, 2 H), 7.30–7.25 (m, 2 H), 7.20–7.16 (m, 1 H), 6.85 (d, 1 H, *J* = 16.1 Hz), 6.50 (d, 1 H, *J* = 16.3 Hz), 5.09 (s, 1 H), 5.05 (s, 1 H), 1.94 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.16, 137.53, 131.81, 128.85, 128.75, 127.56, 126.63, 117.52, 18.75.

(*E*)-2-Methyltrideca-1,3-diene
The diene was prepared from **5b** and decanal according to the general procedure and was obtained as a colorless oil in 71% yield (single isomer by ^{1}H NMR); R_f 0.85 (hexanes).

IR (film): 3082, 2958, 1609 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.13 (d, 1 H, *J* = 15.7 Hz), 5.66 (dt, 1 H, *J* = 15.6, 7.0 Hz), 4.85 (s, 2 H), 2.09 (q, 2 H, *J* = 6.9 Hz), 1.83 (s, 3 H), 1.42–1.24 (m, 14 H), 0.88 (t, 3 H, *J* = 7.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.47, 132.86, 131.38, 114.27, 33.00, 32.13, 29.79, 29.76, 29.67, 29.56, 29.49, 22.92, 18.94, 14.35.

(*E*)-1-Cyclohexyl-3-methylbuta-1,3-diene
The diene[10,27] was prepared from lithiated **5b** and cyclohexanecarbaldehyde according to the general procedure and was obtained as a colorless oil in 75% yield (single isomer by ^{1}H NMR); R_f 0.90 (hexanes).

IR (film): 3081, 2926, 1607 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.10 (d, 1 H, *J* = 15.8 Hz), 5.60 (dd, 1 H, *J* = 15.9, 7.0 Hz), 4.87 (br s, 2 H), 2.06–1.98 (m, 1 H), 1.83 (s, 3 H), 1.77–1.62 (m, 5 H), 1.34–1.05 (m, 5 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 142.61, 136.99, 130.38, 114.47, 41.08, 33.22, 26.39, 26.29, 18.90.

(*E*)-Nona-6,8-dienal (1); Typical Procedure
To a solution of **4a** (1.0 g, 5.43 mmol) in THF (20 mL) was added 6% aq HCl (15 mL). After stirring for 8 h at r.t., the mixture was extracted with Et_2O (3 × 30 mL). The organic phases were combined, washed with sat. aq $NaHCO_3$ (25 mL), and brine (2 × 25 mL), dried ($MgSO_4$) and concentrated to give 0.70 g (93%) of known aldehyde **1**[2] as a clear, colorless oil; R_f 0.33 (1:9 EtOAc–hexanes).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.71 (t, 1 H, *J* = 1.8 Hz), 6.25 (ddd, 1 H, *J* = 17.1, 10.2, 10.2 Hz), 6.00 (dd, 1 H, *J* = 15.1, 10.3 Hz), 5.62 (dt, 1 H, *J* = 15.1, 6.8 Hz), 5.05 (br d, 1 H, *J* = 17.0 Hz), 4.91 (br d, *J* = 10.1 Hz), 2.39 (td, 2 H, *J* = 7.2, 1.8 Hz), 2.07 (br q, 2 H, *J* = 6.4 Hz), 1.66–1.55 (m, 2 H), 1.46–1.34 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.48, 137.17, 134.46, 131.48, 115.06, 43.73, 32.25, 28.65, 21.60.

(*E*)-Deca-7,9-dienal (6)
Aldehyde **6** was prepared from **4b** by following the typical procedure for the preparation of **1** and was obtained as a colorless oil in 88% yield; R_f 0.34 (1:9 EtOAc–hexanes).

IR (film): 3093, 2931, 2858, 1725, 1650, 1601 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.76 (t, 1 H, *J* = 1.8 Hz), 6.30 (ddd, 1 H, *J* = 17.0, 10.2, 10.2 Hz), 6.45 (br dd, 1 H, *J* = 15.1, 10.4 Hz), 5.68 (dt, 1 H, *J* = 15.1, 6.9 Hz), 5.08 (br d, 1 H, *J* = 16.9 Hz), 4.96 (br d, 1 H, *J* = 10.1 Hz), 2.42 (td, 2 H, *J* = 7.3, 1.8 Hz), 2.09 (br q, 2 H, *J* = 7.1 Hz), 1.64 (tt, 2 H, *J* = 7.5, 7.3 Hz), 1.46–1.30 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.90, 137.37, 135.13, 131.34, 115.04, 44.01, 32.45, 29.06, 28.84, 22.08.

HRMS: *m*/*z* calcd for $C_{10}H_{16}O$ (M^+) 152.1201; found 152.1209.

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