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Reaction of 4-methyl, 4-phenyl, and 4-hydrogen substituted 1-lithio-1,3-butadienes with aldehydes: preparation of multiply substituted cyclopentadienes

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Abstract—Reaction of aldehydes with 1-lithio-1,3-butadiene reagents possessing a methyl substituent, a phenyl substituent or a hydrogen at position 4 of the butadienyl skeletons was studied. Polysubstituted cyclopentadiene derivatives were obtained in high yields upon hydrolysis using strong acidic solution. Reaction mechanism study revealed that these cyclopentadienes were formed via an acid-promoted cyclization of conjugated dienols. Thus, stereodefined all-*cis* substituted dienols or a wide diversity of substituted cyclopentadienes can be obtained from the same 1-lithio-1,3-butadiene reagent and aldehyde by adjusting the hydrolysis conditions.

1. Introduction

We have recently demonstrated that 1-lithio-1,3-butadienes **I**–**IV** (Fig. 1) are useful reagents for the preparation of a wide variety of linear and cyclic compounds through their direct addition onto nitriles,[1] CO,[2] CO_2,[3] aldehydes, and ketones.[4,5] Results have shown that the substitution patterns at position 4 of 1-lithio-1,3-butadienes **I** (alkenyl lithium),[1–4] **II** (silyl group),[6] **III** (naphthyl group),[7] and **IV** (hydrogen)[1–4] have remarkable influences on the reactivity of these organolithium reagents. In the case of 1-lithio-1,3-butadienes **IV** (hydrogen), their reaction with aldehydes afforded stereodefined all-*cis* substituted dienols or multiply substituted cyclopentadienes depending on the nature of substituents and work up procedures.[4c] Prompted by the different types of results obtained from 1-lithio-1,3-butadienes **I**–**IV**, we prepared 1-lithio-1,3-butadiene reagent **V** and **VI** possessing a methyl substituent and a phenyl substituent at position 4 of the butadienyl skeletons, respectively, expecting new reaction patterns and synthetically useful methodology. We found that reactions of these organolithium reagents with aldehydes afforded fully substituted cyclopentadienes, via the acid-promoted cyclization of conjugated dienols. This type of reaction provides an alternative method for the preparation of useful cyclopentadiene derivatives[8] and conjugated butadienols.[9,10]

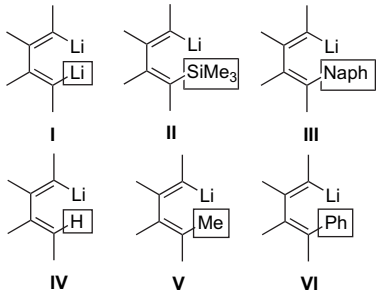

Figure 1. A variety of 1-lithio-1,3-butadienes of different substitution patterns at position 4.

2. Results and discussion

1-Bromo-4-methyl-1,2,3,4-tetraethyl-1,3-butadiene **2a** was successfully obtained in 67% isolated yield via selective lithiation of **1a** followed by treatment with Me_2SO_4 (Eq. 1).[11] Bromotriene **2b** was prepared similarly via selective lithiation of **1a** followed by treatment with LTMP and 1,2-epoxyoctane.[12] 1-Iodo-4-phenyl-1,2,3,4-tetraethyl-1,3-butadiene **2c** and 1-iodo-1,3-butadienes **2d**–**g** were conveniently prepared according to known procedures.[13,14] These halobutadienes and halotrienes are interesting and useful

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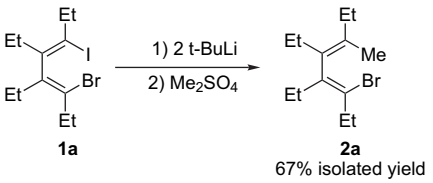
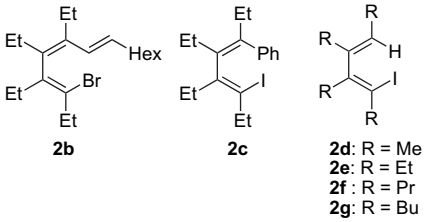
compounds but have not been much utilized in organic synthesis.

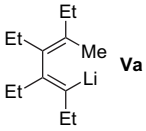
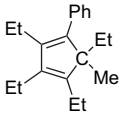
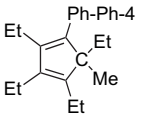
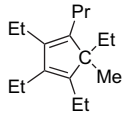
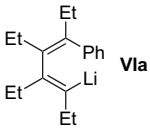
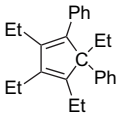
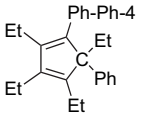
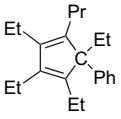
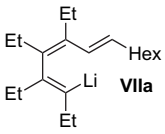
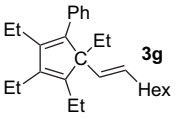


(1)



Lithiation of **2a** with 2 equiv of *t*-BuLi afforded 1-lithio-4-methyl-1,2,3,4-tetraethyl-1,3-butadiene **Va** quantitatively (Eq. 2). Reaction of thus generated **Va** with benzaldehyde went smoothly. However, quenching the reaction mixture with 3 N HCl resulted in two products, which were determined to be the corresponding butadienyl alcohol and a cyclopentadiene derivative. Because the cyclopentadiene derivative might be formed via the known acid-catalyzed cyclization of butadienyl alcohols,[4c,15] we decided to treat the reaction mixture with strong aqueous acidic solution (12 N HCl). Fully substituted cyclopentadiene **3a** was obtained as the sole product in 74% isolated yield. Results are given in Table 1. Both aromatic and aliphatic aldehydes could be applied for this reaction to afford the fully substituted cyclopentadienes in good isolated yields. This type of cyclopentadienes, which are otherwise difficult to prepare, can be expected to have applications as building units for conjugated organic materials. Reaction of the conjugated triene **VIIa** with benzaldehyde generated the cyclopentadiene derivative **3g** in a low yield, probably due to the competitive intramolecular carbo-lithiation of **VIIa**. The structure of product **3e** was determined by single-crystal X-ray structural analysis (Fig. 2).[16]

Table 1. Formation of cyclopentadiene derivatives by acidic quenching of the reaction mixture of **Va**, **VIa**, and **VIIa** with aldehydes[a]

Lithiobutadiene reagent	Aldehyde	Product **3**	Yield of **3** (%)[b]
 **Va**	PhCHO	 **3a**	74
Va	4-Ph–PhCHO	 **3b**	54
Va	PrCHO	 **3c**	56
 **VIa**	PhCHO	 **3d**	65
VIa	4-Ph–PhCHO	 **3e**	77
VIa	PrCHO	 **3f**	62
 **VIIa**	PhCHO	 **3g**	26

[a] Reaction conditions are given in Eq. 2.
[b] Isolated yields.

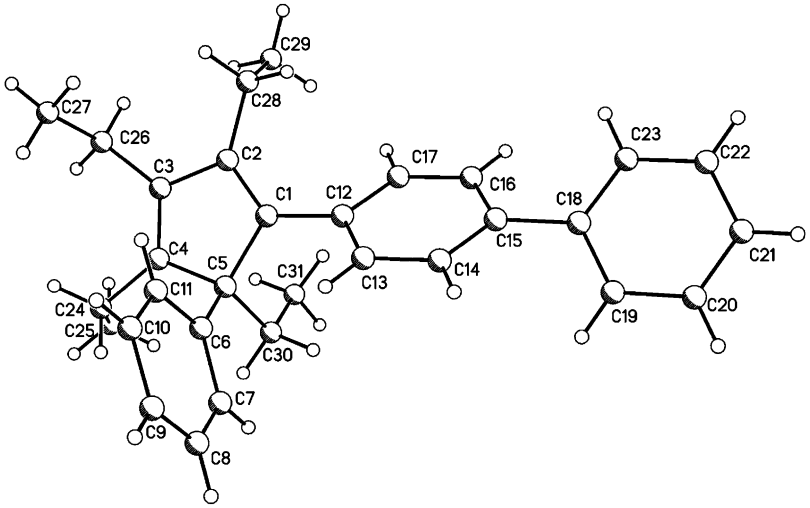
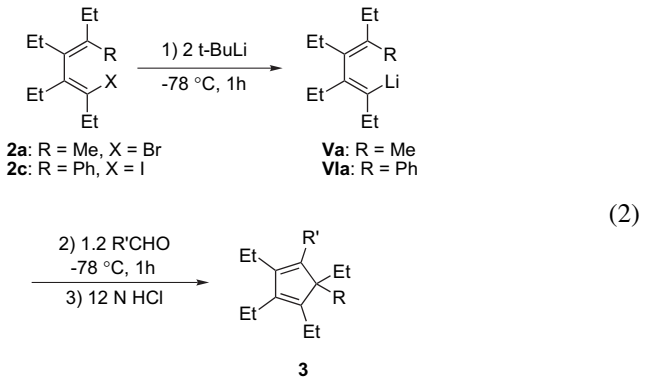
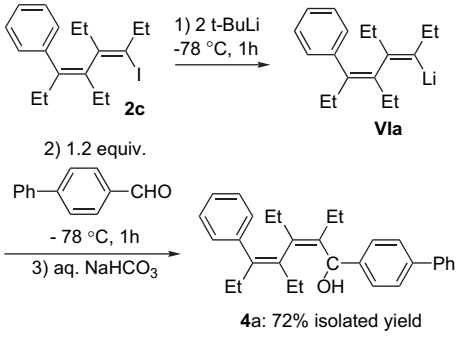


Figure 2. X-ray structure of **3e**.



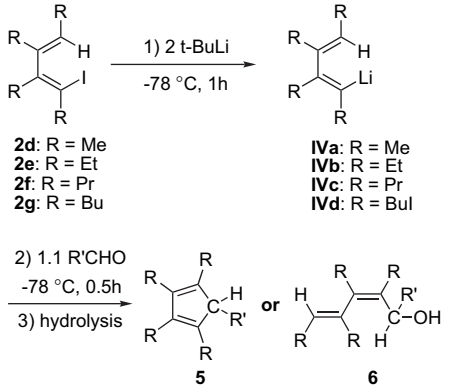
(2)

As discussed above, these cyclopentadienes might be generated via the acid-catalyzed cyclization of their corresponding butadienyl alcohols.[4c,15] In fact, when the reaction mixture of **VIa** with 4-phenylbenzaldehyde was quenched with aqueous $NaHCO_3$ instead of acidic solution, an alcohol **4a** was obtained in 72% isolated yield (Eq. 3). Treatment of the isolated pure butadienyl alcohol **4a** with 12 N HCl afforded the cyclopentadiene derivative **3e** in 77% isolated yield.



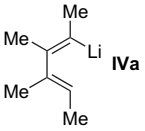
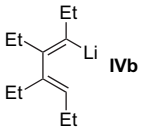
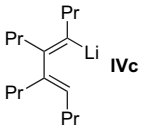
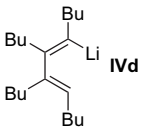
(3)

Similarly, conjugated dienols or cyclopentadiene derivatives could be prepared highly selectively in excellent yields by hydrolysis of the reaction mixtures of 1-lithiobutadienes **IV** (a hydrogen substituent at position 4) with aldehydes (Eq. 4). Results are given in Table 2. As indicated by the hydrolysis conditions shown in Table 1 and Table 2, when there was substituent such as a methyl group (**V**) or a phenyl group (**VI**) at position 4 of the butadienyl skeletons, stronger acid (12 N HCl) was required for the formation of cyclopentadiene derivatives from their corresponding dienols. In the cases of **6a** (run 6 of Table 2) and **6b** (run 8 of Table 2) without substituents at position 4, weaker acid (3 N HCl) was good enough to promote the cyclization. These isolated dienols **6a** and **6b** could be quantitatively transformed to their corresponding cyclopentadiene derivatives when treated with 3 N HCl.



(4)

Table 2. Formation of cyclopentadiene derivatives and dienols by acidic quenching of the reaction mixture of **IV** with aldehydes[a]

Run	Reagent **IV**	Aldehyde	Hydrolysis condition	Product **5** or **6**	Yield (%)[b]
1	 **IVa**	4-OMePhCHO	3 N HCl	**5a**	(53)
2	 **IVb**	PhCHO	3 N HCl	**5b**[c]	(75)
3	**IVb**	2-FurylCHO	3 N HCl	**5c**[c]	(71)
4	**IVb**	4-BrPhCHO	3 N HCl	**5d**[d]	(86)
5	**IVb**	2-ThienylCHO	3 N HCl	**5e**[e]	(78)
6	 **IVc**	PhCHO	Satd aq $NaHCO_3$	**6a**	99 (95)
7	**IVc**	PhCHO	3 N HCl	**5f**[f]	99 (86)
8	**IVc**	PrCHO	Satd aq $NaHCO_3$	**6b**	82 (65)
9	**IVc**	PrCHO	3 N HCl	**5g**[g]	85 (70)
10	 **IVd**	4-OMePhCHO	3 N HCl	**5h**	(81)

[a] Reaction conditions: shown in Eq. 4.
[b] GC yields. Isolated yields are given in parentheses.
[c] Two isomers in 3:1.
[d] Three isomers in 1:1:1.
[e] Three isomers in 2:1:1.
[f] Two isomers in 5:2.
[g] Two isomers in 4:3.

3. Conclusions

We have investigated the preparation and reaction of the useful 1-lithio-1,3-butadiene reagents possessing a phenyl substituent, a methyl substituent, and a hydrogen at position 4 of the butadienyl skeletons. Results of these organolithium reagents with aldehydes show that they are versatile synthetic building units. Cyclopentadiene derivatives thus formed are expected to have useful applications for conjugated organic materials' synthesis.

4. Experimental

4.1. General methods

All reactions were conducted under a slightly positive pressure of dry, pre-purified nitrogen using standard Schlenk line techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and used without further purification. Diethyl ether was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. *t*-BuLi was obtained from Acros Organics.

^{1}H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in $CDCl_3$ or C_6D_6 solution on JEOL JNM-AL300 NMR spectrometer.

4.1.1. A typical procedure for the formation of multiply substituted cyclopentadienes. To a solution of **2a** (1.0 mmol) in Et_2O (10 ml) was added *t*-BuLi (1.5 M pentane solution, 2.0 mmol) slowly at −78 °C and the mixture was stirred for 1 h at the same temperature. PhCHO (1.2 mmol) was added and stirring was continued for 1 h at −78 °C. HCl (12 N, 5 ml) was added to the reaction mixture, and it was stirred for 5 h at room temperature. The reaction mixture was extracted with diethyl ether and washed with aqueous $NaHCO_3$, brine, and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by chromatography on silica gel to afford the corresponding product **3a**.

Compound **3a**: colorless liquid, isolated yield 74% (198 mg). ^{1}H NMR ($CDCl_3$): δ 0.53 (t, J=7.2 Hz, 3H), 0.95 (t, J=7.5 Hz, 3H), 1.02 (s, 3H), 1.07–1.14 (m, 6H), 1.46–2.35 (m, 8H), 7.09–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 8.23, 14.36, 15.19, 15.35, 18.26, 18.88, 19.26, 21.95, 27.53, 58.20, 126.10, 127.86, 129.64, 138.67, 140.66, 143.40, 145.07, 147.04. HRMS calcd for $C_{20}H_{28}$: 268.2191; found: 268.2193.

Compound **3b**: colorless liquid, isolated yield 54% (186 mg). ^{1}H NMR ($CDCl_3$): δ 0.55 (t, J=7.2 Hz, 3H), 0.99 (t, J=7.5 Hz, 3H), 1.07 (s, 3H), 1.09–1.15 (m, 6H), 1.46–2.41 (m, 8H), 7.16–7.64 (m, 9H). ^{13}C NMR ($CDCl_3$): δ 8.26, 14.36, 15.20, 15.41, 18.28, 18.90, 19.34, 22.05, 27.64, 58.32, 126.56, 126.94, 127.00, 128.70, 129.96, 137.77, 138.76, 140.73, 141.09, 143.72, 144.66, 147.29. HRMS calcd for $C_{26}H_{32}$: 344.2504; found: 344.2508.

Compound **3c**: colorless liquid, isolated yield 56% (66 mg). ^{1}H NMR ($CDCl_3$): δ 0.31 (t, J=7.5 Hz, 3H), 0.92–1.07 (m, 15H), 1.40–2.28 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 7.96, 14.58, 15.09, 15.16, 15.25, 18.06, 18.81, 18.90, 22.19, 23.21, 27.94, 28.27, 57.08, 140.58, 140.96, 143.81, 145.25. HRMS calcd for $C_{17}H_{30}$: 234.2348; found: 234.2351.

Compound **3d**: colorless liquid, isolated yield 65% (215 mg). ^{1}H NMR ($CDCl_3$): δ 0.58 (t, J=7.2 Hz, 3H), 0.75 (t, J=7.5 Hz, 3H), 1.09–1.19 (m, 6H), 1.77–2.47 (m, 8H), 6.71–7.24 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 7.34, 13.79, 15.07, 15.16, 18.90, 19.00, 19.45, 22.84, 65.60, 125.75, 125.96, 126.72, 127.64, 127.99, 128.54, 137.32, 141.85, 142.60, 145.56, 145.76, 149.66. HRMS calcd for $C_{25}H_{30}$: 330.2348; found: 330.2344.

Compound **3e**: colorless solid, mp 131–132 °C, isolated yield 77% (313 mg). ^{1}H NMR ($CDCl_3$): δ 0.59 (t, J=7.2 Hz, 3H), 0.75 (t, J=7.8 Hz, 3H), 1.17 (t, J=7.8 Hz, 6H), 1.83–2.54 (m, 8H), 6.80–7.54 (m, 14H). ^{13}C NMR ($CDCl_3$): δ 7.37, 13.83, 15.11, 15.20, 18.89, 18.97, 19.59, 22.99, 65.56, 125.82, 126.32, 126.69, 126.76, 126.90, 128.09, 128.61, 128.74, 136.30, 138.40, 140.88, 141.95, 142.60, 145.20, 145.97, 150.07. HRMS calcd for $C_{31}H_{34}$: 406.2661; found: 406.2658. Anal. Calcd for $C_{31}H_{34}$: C, 91.57; H, 8.43. Found: C, 91.53; H, 8.48.

Compound **3f**: colorless liquid, isolated yield 62% (184 mg). ^{1}H NMR ($CDCl_3$): δ 0.52 (t, J=7.2 Hz, 3H), 0.66–0.74 (m, 6H), 1.06–1.13 (m, 6H), 1.84–2.34 (m, 12H), 7.04–7.16 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 7.38, 14.05, 14.94, 15.07, 15.15, 18.89, 18.95 (2C), 22.53, 22.86, 28.68, 64.54, 125.46, 126.60, 127.64, 142.41, 142.65, 142.83, 145.75, 147.13. HRMS calcd for $C_{22}H_{32}$: 296.2504; found: 296.2505.

Compound **3g**: colorless liquid, isolated yield 26% (47 mg). ^{1}H NMR ($CDCl_3$): δ 0.45 (t, J=7.2 Hz, 3H), 0.89 (t, J=6.9 Hz, 3H), 1.01–1.13 (m, 9H), 1.28–2.38 (m, 18H), 5.02 (d, J=15.9 Hz, 1H), 5.42 (dt, J=15.6, 6.9 Hz, 1H), 7.17–7.27 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 7.42, 14.13, 14.50, 15.17, 15.23, 18.54, 19.00, 19.43, 22.28, 22.69, 28.95, 29.70, 31.82, 33.02, 64.65, 125.87, 127.58, 128.44, 129.01, 133.55, 137.96, 142.56, 143.50, 145.08, 146.46. HRMS calcd for $C_{27}H_{40}$: 364.3130; found: 364.3133.

4.1.2. A typical procedure for the formation of dienol 4a and the acid-promoted cyclization. To a solution of **2c** (0.5 mmol) in Et_2O (10 ml) was added *t*-BuLi (1.5 M pentane solution, 1.0 mmol) slowly at −78 °C and the mixture was stirred for 1 h at the same temperature. 4-Phenylbenzaldehyde (0.6 mmol) was added and stirring was continued for 1 h at −78 °C. The reaction mixture was quenched with aqueous $NaHCO_3$ and extracted with diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by chromatography on Al_2O_3 to afford the corresponding alcohol **4a**. Colorless liquid, isolated yield 72% (153 mg). ^{1}H NMR (C_6D_6): δ 0.70 (d, J=2.7 Hz, 1H), 0.79 (t, J=7.5 Hz, 3H), 0.88 (t, J=7.2 Hz, 3H), 1.09 (t, J=7.8 Hz, 3H), 1.17 (t, J=7.5 Hz, 3H), 1.84–2.54 (m, 8H), 5.71 (d, J=2.7 Hz, 1H), 6.98–7.67 (m, 14H). ^{13}C NMR (C_6D_6): δ 13.39, 13.85, 13.98, 14.71, 21.27, 25.83, 26.34, 26.84, 74.22, 126.84, 126.95, 127.08, 127.19, 127.34, 128.22, 128.96, 129.32, 137.11, 138.48, 138.90, 139.66, 140.61, 141.56, 142.89, 143.37. HRMS calcd for $C_{31}H_{36}O$: 424.2766; found: 424.2762.

HCl (12 N, 5 ml) was added to the pure alcohol product **4a** with 1 ml Et_2O as solvent, and stirring was continued for 5 h at room temperature. The reaction mixture was extracted with diethyl ether and washed with aqueous $NaHCO_3$, brine, and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by chromatography on silica gel to afford **3e** in 77% isolated yield.

4.1.3. A typical procedure for the preparation of dienols and cyclopentadiene derivatives from reactions of 1-lithio-1,3-butadienes IV with aldehydes. 1-Lithio-1,3-butadiene derivative **IVa** was generated in situ by lithiation of its corresponding 1-iodo-1,3-butadiene **2d**. 4-Methoxybenzaldehyde (1.1 mmol) was then added to **IVa** at −78 °C and the reaction mixture was stirred at the same temperature for 0.5 h. The reaction mixture was then quenched with saturated aqueous 3 N HCl and extracted with ether. The extract was washed with water and brine, and dried over $MgSO_4$. The solvent was evaporated in vacuum to give a brown oil, which was purified by column chromatography (silica gel, hexane/CH_2Cl_2=1:1) to afford **5a** as a colorless liquid in 53% isolated yield.

Compound **5a**: colorless liquid, isolated yield 53% (120 mg). ^{1}H NMR ($CDCl_3$): δ 1.08 (d, J=3.6 Hz, 3H), 2.00 (s, 3H), 2.06 (s, 3H), 2.14 (s, 3H), 3.28 (q, J=11.4 Hz, 1H), 3.96 (s, CH_3, 3H), 7.04 (d, J=4.5 Hz, 2H), 7.31 (d, J=4.5 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 11.07, 11.84, 12.57, 14.87, 50.13, 55.18, 113.59, 129.46, 130.40, 134.91, 135.89, 139.95, 142.35, 157.51. HRMS calcd for $C_{16}H_{20}O$: 228.1514; found: 228.1513.

Compound **5b**: colorless liquid, isolated yield 75% (192 mg), two isomers in 3:1. ^{1}H NMR ($CDCl_3$) of the main product: δ 0.54–0.88 (m, 12H), 1.19–2.35 (m, 8H), 3.05–3.30 (m, 1H), 6.77–7.14 (m, 5H). ^{13}C NMR ($CDCl_3$) of the main product: δ 6.81, 15.21, 15.44, 15.55, 18.53, 19.46, 19.66, 20.74, 52.45, 125.47, 128.09, 128.37, 137.61, 140.63, 141.98, 144.24, 145.04. HRMS calcd for $C_{19}H_{26}$: 254.2034; found: 254.2037.

Compound **5c**: brown liquid, 3:1 mixture of positional double bond isomers, combined isolated yield 71% (175 mg). ^{1}H NMR ($CDCl_3$) of the mixture: δ 0.37 (t, J=7.5 Hz, 3H), 0.85–1.19 (m, 10H), 1.61–2.67 (m, 10H), 3.43 (t, J=4.4 Hz, 1H), 5.46 (q, J=11.1 Hz, 1H), 6.19 (d, J=1.8 Hz, 1H), 3.10 (d, J=1.6 Hz, 0.3H), 6.40–6.46 (m, 1.3H), 7.37 (d, J=0.9 Hz, 1H), 7.42 (d, J=0.9 Hz, 0.3H). ^{13}C NMR ($CDCl_3$) of the mixture: δ 6.68, 11.23, 11.25, 13.30, 14.30, 14.59, 15.14, 15.36, 18.32, 18.74, 19.59, 20.01, 22.01, 27.62, 27.86, 46.06, 50.54, 51.15, 104.74, 107.58, 110.93, 111.02, 113.16, 129.68, 132.14, 140.21, 140.38, 141.29, 142.00, 145.36, 145.49, 150.89, 152.89, 153.23. HRMS calcd for $C_{17}H_{24}O$: 244.1827; found: 244.1822.

Compound **5d**: colorless liquid, three isomers in 1:1:1, isolated yield 86% (284 mg). ^{1}H NMR ($CDCl_3$) of the mixture: δ 0.30 (t, J=7.2 Hz, 3H), 0.81–1.19 (m, 27H), 1.25–1.78 (m, 14H, including 1.43 (d, J=3.6 Hz, 3H) and 1.70 (d, J=3.6 Hz, 3H)), 2.00–2.60 (m, 14H), 3.37 (s, 1H), 3.14 (t, J=4.2 Hz, 1H), 3.52 (s, 1H), 5.29–5.43 (m, 2H), 6.95 (d, J=4.2 Hz, 2H), 7.01 (d, J=4.2 Hz, 2H), 7.11 (d, J=4.2 Hz, 2H), 7.34 (d, J=4.2 Hz, 2H), 7.46 (d, J=4.2 Hz, 2H). ^{13}C NMR ($CDCl_3$) of the mixture: δ 6.76, 10.85, 10.90, 12.79, 12.90, 13.81, 14.17, 14.26, 15.02, 15.18, 15.36, 15.48, 17.79, 17.83, 18.49, 18.68, 19.44, 19.56, 19.66, 19.94, 20.37, 20.68, 26.31, 28.08, 49.81, 50.40, 52.46, 56.08, 56.82, 111.04, 111.77, 118.96, 119.27, 119.50, 128.64, 128.99, 129.90, 131.25, 131.38, 131.41, 136.50, 139.22, 139.39, 140.11, 142.08, 145.05, 145.22, 145.36, 145.53, 146.14, 146.46, 149.77. HRMS calcd for $C_{19}H_{25}Br$: 332.1140; found: 332.1134.

Compound **5e**: colorless liquid, three isomers in 2:1:1, isolated yield 78% (203 mg). ^{1}H NMR ($CDCl_3$) of the mixture: δ 0.35 (t, J=7.2 Hz, 3H), 0.97–1.32 (m, 27H), 1.59 (d, J=3.6 Hz, 3H), 1.71(d, J=3.6 Hz, 3H), 1.76–2.02 (m, 6H), 2.12–2.71 (m, 14H), 3.39 (t, J=4.2 Hz, 1H), 3.74 (s, 0.5H), 3.90 (s, 0.5H), 5.36 (q, J=7.2 Hz, 1H), 6.73 (d, J=2.7 Hz, 1H), 6.78 (d, J=2.7 Hz, 1H), 6.80–6.95 (m, 3H), 7.02–7.08 (m, 3H), 7.18 (d, J=2.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) of the mixture: δ 6.62, 10.84, 11.09, 12.76, 12.82, 13.60, 13.66, 14.17, 14.28, 14.43, 15.16, 15.41, 17.81, 18.44, 19.67, 19.88, 20.00, 20.29, 21.91, 26.16, 27.90, 45.54, 51.06, 51.30, 53.04, 57.20, 111.43, 112.19, 122.25, 122.34, 122.76, 122.85, 123.33, 125.98, 126.46, 126.94, 133.43, 138.17, 139.51, 139.80, 142.18, 145.04, 145.32, 145.40, 145.61, 149.11, 149.50, 150.41, 150.98. HRMS calcd for $C_{17}H_{24}S$: 260.1599; found: 260.1604.

Compound **6a**: quenched with saturated $NaHCO_3$. Colorless liquid, isolated yield 95%, GC yield 99%. ^{1}H NMR ($CDCl_3$, TMS): δ 0.72–0.98 (m, 14H), 1.31–1.43 (m, 8H), 2.03–2.10 (m, 6H), 5.19 (t, J=7.2 Hz, 1H), 5.78 (s, 1H), 7.21–7.39 (m, 5H). ^{13}C NMR ($CDCl_3$, TMS): δ 13.91, 14.22, 14.65, 14.84, 21.54, 21.82, 23.11, 24.41, 29.91, 30.02, 32.15, 32.57, 73.85, 126.06, 126.48, 127.90, 129.22, 135.74, 139.04, 143.47. HRMS calcd for $C_{23}H_{36}O$: 328.2766; found: 328.2757.

Compound **5f**: colorless liquid as a mixture of two double bond positional isomers (5:2) in 99% combined GC yield (combined isolated yield 86%). The NMR data of **5f** were consistent with those reported.[17]

Compound **6b**: colorless liquid, isolated yield 65%, GC yield 82%. ^{1}H NMR ($CDCl_3$, TMS): δ 0.85–0.97 (m, 17H), 1.25–1.59 (m, 10H), 1.93–2.11 (m, 8H), 4.57 (t, J=4.8 Hz, 1H), 4.96 (t, J=7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, TMS): δ 13.97, 14.18, 14.23, 14.60, 15.00, 19.69, 21.57 ($2CH_2$), 23.18, 24.79, 29.18, 29.89, 31.97, 32.46, 37.87, 72.71, 128.73, 136.77, 139.05, 141.78. HRMS calcd for $C_{20}H_{38}O$: 294.2923; found: 294.2929.

Compound **5g**: colorless liquid as a mixture of two double bond positional isomers (4:3) in 85% combined GC yield (combined isolated yield 70%). The NMR data of **5g** were consistent with those reported.[17]

Compound **5h**: colorless liquid, isolated yield 81% (321 mg). ^{1}H NMR ($CDCl_3$): δ 0.65–0.70 (m, 5H), 0.86–1.04 (m, 9H), 1.17–1.60 (m, 14H), 1.99–2.59 (m, 8H), 3.23–3.47 (br, 1H), 3.81 (s, 3H), 6.88 (d, J=4.2 Hz, 2H), 7.14 (d, J=4.2 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 13.92, 14.00, 14.07, 22.94, 23.07 ($2CH_2$), 23.09, 24.82, 25.46, 26.30, 27.89, 32.68, 33.06, 33.20, 52.52, 55.14, 113.50, 129.45, 130.58, 140.59, 141.08, 141.57, 143.56, 157.52. HRMS calcd for $C_{28}H_{44}O$: 396.3392; found: 396.3386.

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References and notes

1. Chen, J.; Song, Q.; Wang, C.; Xi, Z. *J. Am. Chem. Soc.* **2002**, *124*, 6238–6239.
2. (a) Song, Q.; Chen, J.; Jin, X.; Xi, Z. *J. Am. Chem. Soc.* **2001**, *123*, 10419–10420; (b) Song, Q.; Li, Z.; Chen, J.; Wang, C.; Xi, Z. *Org. Lett.* **2002**, *4*, 4627–4629.

3. Xi, Z.; Song, Q. *J. Org. Chem.* **2000**, *65*, 9157–9159.
4. (a) Xi, Z.; Song, Q.; Chen, J.; Guan, H.; Li, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 1913–1915; (b) Chen, J.; Song, Q.; Li, P.; Guan, H.; Jin, X.; Xi, Z. *Org. Lett.* **2002**, *4*, 2269–2271; (c) Fang, H.; Song, Q.; Wang, Z.; Xi, Z. *Tetrahedron Lett.* **2004**, *45*, 5159–5162; (d) Fang, H.; Li, G.; Mao, G.; Xi, Z. *Chem.—Eur. J.* **2004**, *10*, 3444–3450; (e) Mao, G.; Lu, J.; Xi, Z. *Tetrahedron Lett.* **2004**, *45*, 8095–8098; (f) Mao, G.; Wang, C.; Chen, J.; Muramatsu, A.; Xi, Z. *Tetrahedron Lett.* **2005**, *46*, 5369–5372; (g) Xi, Z.; Zhang, W.; Song, Z.; Zheng, W.; Kong, F.; Takahashi, T. *J. Org. Chem.* **2005**, *70*, 8785–8789; (h) Wang, C.; Lu, J.; Mao, G.; Xi, Z. *J. Org. Chem.* **2005**, *70*, 5150–5156.
5. (a) Xi, Z. *Eur. J. Org. Chem.* **2004**, 2773–2781; see also: (b) Varela, J. A.; Saa, C. *Chem. Rev.* **2003**, *103*, 3787–3801; (c) Langer, P.; Freiberg, W. *Chem. Rev.* **2004**, *104*, 4125–4149; (d) Foubelo, F.; Yus, M. *Curr. Org. Chem.* **2005**, *9*, 459–490.
6. Wang, Z.; Fang, H.; Xi, Z. *Tetrahedron Lett.* **2005**, *46*, 499–501.
7. Wang, Z.; Xi, Z. *Synlett.* **2006**, 1275–1277.
8. Xi, Z. *Top. Catal.* **2005**, *35*, 63–71.
9. (a) Huang, Y.; Mo, X. *Tetrahedron Lett.* **1995**, *36*, 3539–3542; (b) Hill, J. E.; Balaich, G.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2911–2924; (c) Reich, H. J.; Shah, S. K.; Chow, F. *J. Am. Chem. Soc.* **1979**, *101*, 6648–6656.
10. For examples of tethered dienols as starting materials in intramolecular Diels–Alder reactions: (a) Bols, M.; Skrydstrup, T. *Chem. Rev.* **1995**, *95*, 1253–1277; (b) Stork, G.; Kim, G. *J. Am. Chem. Soc.* **1992**, *114*, 1087–1088; (c) Stork, G.; Chan, T. T.; Breault, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 7578–7579; (d) Sieburth, S. M.; Fensterbank, L. *J. Org. Chem.* **1992**, *57*, 5279–5281.
11. For preparation of mixed dihalobutadienes, see: Ubayama, H.; Xi, Z.; Takahashi, T. *Chem. Lett.* **1998**, 517–518.
12. Hodgson, D. M.; Fleming, M. J.; Stanway, S. J. *J. Am. Chem. Soc.* **2004**, *126*, 12250–12251.
13. Takahashi, T.; Sun, W.; Xi, C.; Ubayama, H.; Xi, Z. *Tetrahedron* **1998**, *54*, 715–726.
14. For preparative methods of 1-iodo-1,3-diene derivatives, see: (a) Takahashi, T.; Kondakov, D. Y.; Xi, Z.; Suzuki, N. *J. Am. Chem. Soc.* **1995**, *117*, 5871–5872; (b) Ubayama, H.; Sun, W.; Xi, Z.; Takahashi, T. *Chem. Commun.* **1998**, 1931–1932.
15. (a) Xi, Z.; Guo, R.; Mito, S.; Yan, H.; Kanno, K.; Nakajima, K.; Takahashi, T. *J. Org. Chem.* **2003**, *68*, 1252–1257; See also: (b) Olah, G. A.; Asensio, G.; Mayr, H. *J. Org. Chem.* **1978**, *43*, 1518–1520; (c) Deno, N. C.; Pittman, C. U., Jr.; Turner, J. O. *J. Am. Chem. Soc.* **1965**, *87*, 2153–2157.
16. The deposition number of **3e** at the Cambridge Crystallographic Data Centre: CCDC 295391.
17. Zhao, C.; Li, P.; Cao, X.; Xi, Z. *Chem.—Eur. J.* **2002**, *8*, 4292–4298.