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Transformation of 1,5- and 1,6-dienes to carbocycles by hydrozirconation and oxidation with cerium(IV) compounds

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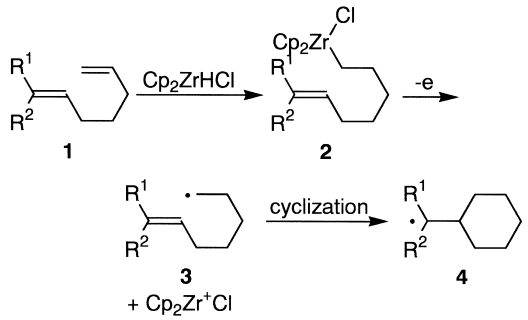
Abstract—Cyclopentane and cyclohexane derivatives are prepared from 1,5- and 1,6-dienes in a one pot procedure by hydrozirconation, then oxidation of the generated 5- and 6-alkenylzirconocene chlorides with ammonium hexanitratocerate.

1. Introduction

Radical addition to the olefinic moiety is recognized as one of the general tools to construct molecular skeletons, particularly cyclopentane derivatives.[1] To generate radical species, one-electron oxidation of organometallic compounds has attracted considerable attention and has been utilized mostly to generate α-keto and β-keto radical species.[2] For example, Mn(III)-based oxidation is applied to the generation of keto radicals and the successive intra- and intermolecular addition to alkenes.[2a–e] Such oxidative methods, however, have found a quite limited application for the generation of alkyl radicals from organometallics. The dimerization of alkyl groups occurs by oxidation probably due to the aggregation of alkyl metals, as being exemplified by the dimerization of phenyl Grignard reagent by electrode oxidation.[3] Accordingly, the choice of alkyl metals seems to be crucial to prevent such a dimerization of alkyl groups to generate radical species by oxidation of organometals. Alkylzirconocenes are easily prepared by hydrozirconation of alkenes[4,5] and scarcely aggregate due to steric effects by of the cyclopentadienyl groups. We planed to examine the oxidation of alkylzirconocenes **2** having an internal olefinic moiety with the expectation that alkyl radical species **3** would be generated by oxidation and add to the olefinic moiety to give cyclization product **4** as shown in Scheme 1. The 6-alkenylzirconocenes **2** are readily prepared by the regioselective hydrozirconation of the less-hindered terminal vinyl group of 1,6-dienes **1**.[6]

Concerning the oxidation of alkylzirconocenes, the formation of alcohols was reported by the reaction of alkylzirconocenes with peroxides and peracids.[4a] The oxidation of benzylarylzirconocene with Cp_2FePF_6 caused the dimerization of benzyl groups to 1,2-diphenylethane.[7] The intramolecular cross-coupling of organic substituents on zirconium was accomplished by the oxidation of the alkenyl-alkynylzirconocenes with an oxovanadium(V) compound, giving the corresponding enynes.[8] In contrast, there has been no example for oxidative cyclization reaction of organozirconocenes.



Scheme 1. Oxidative cyclization of alkenylzirconocenes.

2. Results and discussion

6-Heptenylzirconocene chloride **2a** was prepared in situ by hydrozirconation of 1,1-diphenyl-1,6-heptadiene (**1a**) with a slight excess of Cp_2ZrHCl. In fact, the quench of the generated alkenylziconocene with CD_3COOD gave only 7-deuterio-1,1-diphenyl-1-heptane. The in situ generated 6-alkenylzirconocene intermediate **2a** was submitted for the oxidation with Ce(IV) complexes as shown in Scheme 2. When a DMF solution of ammonium hexanitratocerate (CAN) was added to a THF solution of **2a**, the expected cyclization product **5a** was obtained in 60% yield whereas **5a** was not obtained by the oxidation with Cp_2FePF_6, $Mn(pic)_3$, $Ag(pic)_2$ (pic=2-pyridinecarboxylato), or

Keywords: 1,5- and 1,6-Dienes; Radical cyclization; Alkyl zirconocene; Cerium(IV).
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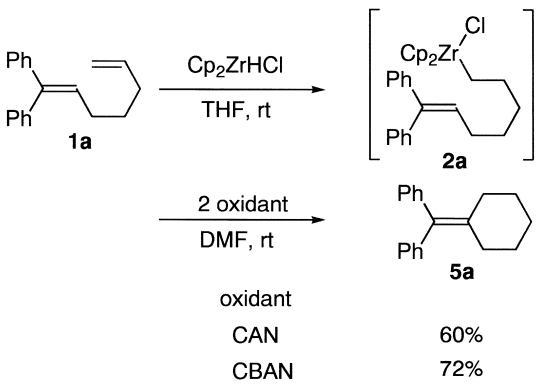
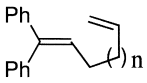
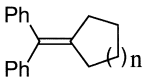
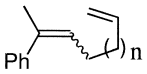
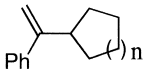
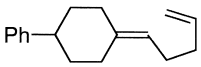
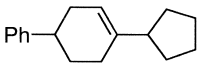
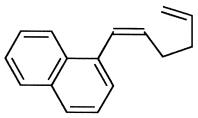
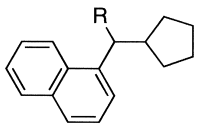
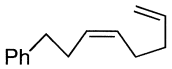
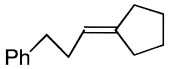
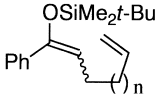
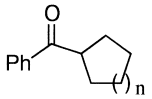
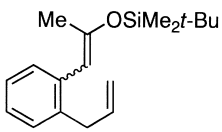
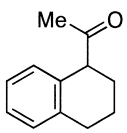
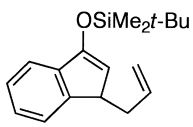
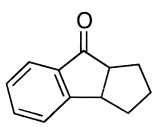


Scheme 2. Oxidation of alkenylzirconocene **2a** by using Ce(IV) salts.

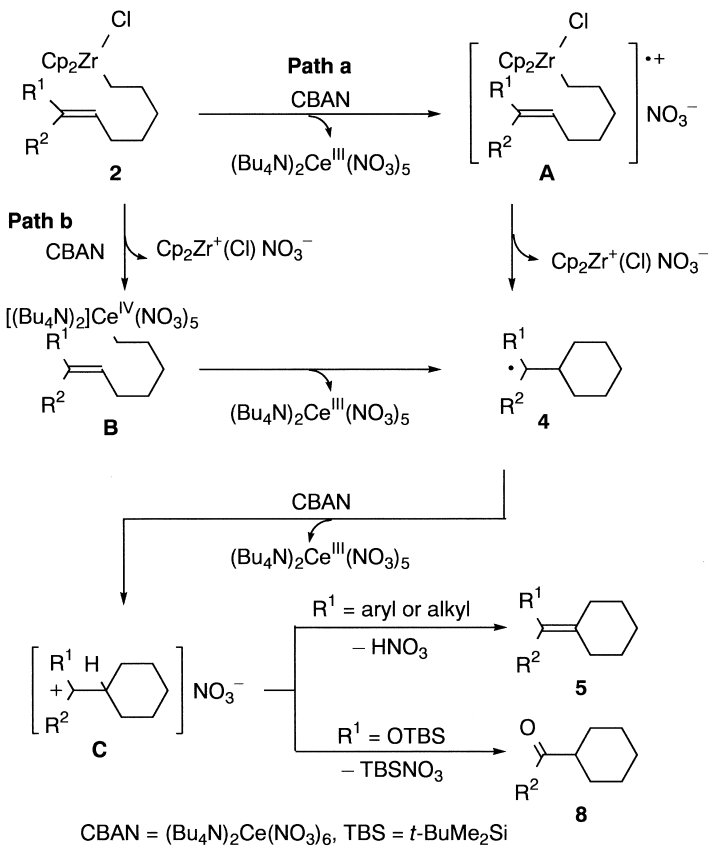
$Cu(OAc)_2$.[9] The yield of **5a** was increased to 72% by use of tetrabutylammonium hexanitratocerate (CBAN).

This oxidative method was applied to the cyclization of various 1,5- and 1,6-dienes, and the results are summarized in Table 1. Prior to the oxidation, the hydrozirconation of the teminal vinyl group of dienes (**1a**–**k**) was confirmed by quenching the in situ generated 5-or 6-alkenylzirconocene with CD_3COOD or D_2O, which gave the terminal monodeuterated alkenes in 76–92% yield. As compared to the formation of 6-membered ring derivatives from 1,6-dienes, 1,5-pentadienes are converted to the corresponding cyclopentane derivatives in better yields (run 1 vs. 2 and 3 vs. 4). Within the radical addition process, the 5-membered cyclization tend to proceed more efficiently than the 6-membered cyclization.[10] Diene having trialkyl substituted olefinic moiety **1e** gave the desired cyclopentane **5e** in 76% yield. In the case of naphthyl substituted 1,5-diene **1f**, alcohol **6** and formate **7** were formed exceptionally in 56% total yield. These compounds were formed by trapping the benzylic cation intermediate (vide infra: **C** in Scheme 3) with DMF. Dialkyl substituted alkene **1g** is not suitable for a radical accepter and the reduction product of **1g**, 1-phenyl-3-octene, was obtained in 83% yield (run 7). Thus, trisubstituted or aryl substituted olefinic moiety was found to be suitable as a radical acceptor. Particularly noteworthy is that various carbonyl compounds were prepared by this cyclization method from dienes bearing a siloxy olefinic moiety **1h**–**k**. For example, the cyclization of 1-phenyl-1-siloxy-1,6- and 1,5-dienes **1h** and **1i** proceeded smoothly to afford the corresponding cyclohexyl ketone **8h** and cyclopentyl ketone **8i** in high yield (runs 8 and 9). Bicyclic

Table 1. The oxidative intramolecular cycloaddition of various 1,5- and 1,6-dienes with CBAN[a]

Run	Substrates		Products		Yield (%)
1		n=2 **1a**		n=2 **5a**	72
2		n=1 **1b**		n=1 **5b**	83
3		n=2 **1c**[b]		n=2 **5c**	39
4		n=1 **1d**[b]		n=1 **5d**	72
5		**1e**		**5e**	76
6[c]		**1f**		R=OH **6** R=OCOH **7**	42 14
7[d]		**1g**			0
8		n=2 **1h**[e]		n=2 **8h**	71
9		n=1 **1i**[f]		n=1 **8i**	78
10		**1j**[b]		**8j**	36
11		**1k**		**8k**[g]	75

[a]*Reaction and conditions*: (1) diene, Cp_2ZrHCl (1 equiv.), THF, rt, 1 h, (2) CBAN (2 equiv.), DMF, rt, 12 h; [b]*E*, *Z* mixture. The stereochemistry is not determined; [c]Hydrozirconation was carried out at −10 °C for 5 h; [d]Hydrozirconation was carried out at −10 °C for 4 h; [e]*E*/*Z*=13:1; [f]*E*/*Z*=10:1; [g]Single diastereomer. The stereochemsitry is not determined.



Scheme 3. A plausible mechanism of the cyclization of alkenylzirconocene **2** with CBAN.

and tricyclic ketones **8j** and **8k** could be also synthesized from olefinic silyl enol ethers **1j** and **1k**, respectively (runs 10 and 11).

A plausible mechanism of the present cyclization of alkenylzirconocene **2** with CBAN is depicted in Scheme 3. Alkenylzirconocene **2** is oxidized with CBAN to give cation radical species **A** and the successive radical cyclization occurs to give radical intermediate **4** (Path a). **4** might be formed via alkenylcerium(IV) intermediate **B** generated by the transmetallation between **2** and CBAN (Path b). Further oxidation of the radical intermediate **4** with CBAN gives the corresponding cation species **C** and the successive deprotonation or desilylation from **C** affords cycloalkenes **5** or cycloalkyl ketones **8**.

In conclusion, we developed the method of the synthesis of cyclopentane and cyclohexane derivatives from 1,5- and 1,6-dienes in a one pot procedure by hydrozirconation, and the successive oxidation of the generated 5- and 6-alkenylzirconocene chlorides with Ce(IV) compounds.

3. Experimental

3.1. General

IR spectra were measured with a Horiba FT 300-S spectrometer. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded on a Bruker DRX 500 or an Avance 500 spectrometer with $CHCl_3$ (δ=7.24 for ^{1}H NMR) and $CDCl_3$ (δ=77.0 for ^{13}C NMR) as an internal standard. High-resolution mass spectra were recorded on a JEOL MS-700P mass spectrometer (EI: operating at 70 eV). All melting points were uncorrected. Yields quoted are based on isolated mass. All reactions were carried out under an argon atmosphere. Et_2O and THF were dried by distillation from sodium and benzophenone. Dimethylformamide (DMF) was dried over by P_2O_5 for 24 h followed by distillation, then was distilled from CaH_2 and subsequently stored over 4 Å molecular sieves. Cp_2ZrHCl was purchased from Aldrich and was used as received. Ammonium hexanitratocerate [$(NH_4)_2Ce(NO_3)_6$, (CAN)] was dried under pressure (0.5 mmHg) for 6 h at 80 °C. Tetrabutylammonium hexanitratocerate [$(n\text{-}Bu_4N)_2Ce(NO_3)_6$, (CBAN)] was prepared according to the literature procedure.[11] Flash column chromatography was carried out on silica-gel [Kanto Chemical Co., Inc. Silica gel 60N (spherical, neutral)]. Preparative TLC was performed on silica-gel (Wakogel B-5F).

3.2. General procedure for oxidation of alkenyl-zirconocene

Freshly distilled dienes (0.20 mmol) were added to a THF suspension (2.0 mL) of Cp_2ZrHCl (114 mg, 0.21 mmol) under argon atmosphere at rt, and the suspension was stirred for 1 h (a white suspension turned to a yellow solution). To this solution was added CBAN (439 mg, 0.42 mmol) in DMF (4.5 mL) at rt, and the mixture was allowed to stir for 12 h. After the reaction was quenched with water, the mixture was filtered through a Celite pad. The filtrate was extracted with EtOAc, and the combined organic extracts were washed with water and brine, and dried over Na_2SO_4.

The solvent was evaporated in vacuo to give a crude product, which was purified by preparative TLC.

3.2.1. (Diphenylmethylene)cyclohexane (5a).[12] 72% Yield; mp 73–74 °C; ^{1}H NMR ($CDCl_3$) δ 1.56–1.60 (m, 6H), 2.23–2.25 (m, 4H), 7.10–7.29 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 26.8, 28.7, 32.4, 126.0, 127.8, 129.8, 134.5, 139.1, 143.1.

3.2.2. (Diphenylmethylene)cyclopentane (5b).[13] 83% Yield; mp 61–63 °C; ^{1}H NMR ($CDCl_3$) δ 1.65–1.71 (m, 4H), 2.23–2.25 (m, 4H), 7.15–7.31 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 26.8, 33.2, 126.0, 127.9, 129.2, 134.3, 138.9, 143.5.

3.2.3. 1-Cyclohexyl-1-phenylethene (5c).[14] 39% Yield; ^{1}H NMR ($CDCl_3$) δ 1.19–1.38 (m, 6H), 1.80–1.88 (m, 4H), 2.42–2.48 (m, 1H), 5.04 (s, 1H),?5.16 (s, 1H), 7.28–7.37 (m, 5H).

3.2.4. 1-Cyclopentyl-1-phenylethene (5d).[15] 72% Yield; ^{1}H NMR ($CDCl_3$) δ 1.23–2.02 (m, 7H), 2.18–2.36 (m, 1H), 2.94 (q, J=8.1 Hz, 1H), 5.05 (d, J=1.1 Hz, 1H), 5.15 (d, J=1.1 Hz, 1H), 7.15–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 24.8, 32.0, 44.5, 110.0, 126.5, 126.9, 128.0, 143.1, 152.8.

3.2.5. (4-Cyclopentyl-3-cyclohexenyl)benzene (5e). 76% Yield; ^{1}H NMR ($CDCl_3$) δ 1.37–2.36 (m, 15H), 2.64–2.83 (m, 1H), 5.52 (d, J=5.1 Hz, 1H), 7.16–7.33 (m, 5H).

3.2.6. Cyclopentyl-(1-naphthyl)methanol (6). 42% Yield; IR (neat) 3390, 2950, 2870, 800, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.23–1.28 (m, 1H), 1.41– 1.68 (m, 6H), 1.86–1.96, (m, 1H), 2.49–2.57 (m, 1H), 5.20 (d, J=7.6 Hz, 1H), 7.40–7.52 (m, 3H), 7.58 (d, J=7.0 Hz, 1H), 7.77 (d, J=8.2 Hz, 1H), 7.83–7.86 (m, 1H), 8.20–8.24 (m, 1H); ^{13}C NMR δ 25.6, 25.7, 29.0, 29.7, 46.5, 75.3, 123.6, 123.9, 125.3, 125.4, 125.8, 128.0, 128.8, 130.8, 133.9; FAB HRMS $(M+H)^+$ calcd for $C_{16}H_{19}O$ 227.1437, found 227.1428.

3.2.7. Cyclopentyl-(1-naphthyl)methylformate (7). 14% Yield; oil; IR (neat) 2960, 2870, 1720, 1170, 800, 780; ^{1}H NMR ($CDCl_3$) δ 1.15–1.87 (m, 8H), 2.65–2.73 (m, 1H), 6.45 (d J=8.6 Hz, 1H), 7.42–7.55 (m, 4H), 7.80 (d, J=8.0 Hz, 1H), 7.86 (d, J=8.1 Hz, 1H), 8.14 (s, 1H), 8.26 (d, J=8.1 Hz, 1H); ^{13}C NMR δ 25.2, 25.3, 29.4, 29.5, 45.1, 123.6, 125.0, 125.2, 125.6, 126.2, 128.6, 128.9, 130.6, 133.8, 135.8, 160.6; FAB HRMS $(M+H)^+$ calcd for $C_{17}H_{19}O_2$ 255.1380, found 255.1386.

3.2.8. Cyclohexyl phenyl ketone (8h).[16] 71% Yield; ^{1}H NMR ($CDCl_3$) δ 1.24–1.90 (m, 10H), 3.26 (m, 1H), 7.41 (m, 3H), 7.94 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.8, 25.9, 29.4, 45.6, 128.2, 128.5, 132.7, 136.3, 203.9.

3.2.9. Cyclopentyl phenyl ketone (8i).[17] 78% Yield; ^{1}H NMR ($CDCl_3$) δ 1.58–1.72 (m, 4H), 1.76–1.94 (m, 4H), 3.70 (q, J=7.8 Hz, 1H), 7.41–7.59 (m, 3H), 7.94–7.97 (m, 2H).

3.2.10. 1-(1,2,3,4-Tetrahydro-1-naphthyl)ethanone (8j).[18] 36% Yield; ^{1}H NMR ($CDCl_3$) δ 1.72–1.80 (m, 1H), 1.88–2.08 (m, 3H), 2.12 (s, 3H), 2.76–2.82 (m, 2H), 3.83 (t, J=6.8 Hz, 1H), 6.97–6.99 (m, 1H), 7.06–7.21 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 20.8, 26.2, 27.7, 29.2, 53.7, 125.9, 126.8, 129.2, 129.5, 133.6, 137.4, 210.6.

3.2.11. 1,2,3,3a,8a-Pentahydrocyclopenta[*a*]inden-8-one (8k).[19] 75% Yield; ^{1}H NMR ($CDCl_3$) δ 1.10–1.13 (m, 1H), 1.55–1.58 (m, 1H), 1.81–1.88 (m, 2H), 1.96–2.00 (m, 2H), 3.01–3.05 (m, 1H), 3.73 (t, J=7.8 Hz, 1H), 7.31 (t, J=7.5 Hz, 1H), 7.44 (dd, J=8.0, 1.0 Hz, 1H), 7.55–7.59 (m, 1H), 7.94 (d, J=8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 24.8, 30.8, 33.1, 43.9, 52.3, 123.1, 125.9, 127.3, 135.1, 137.4, 158.7, 210.2.

3.3. Preparation of starting materials

1,1-Diphenyl-1,5-hexadiene (**1a**),[20] 1,1-diphenyl-1,6-heptadiene (**1b**),[20] *t*-butyldimethyl(1-phenylhexa-1,5-dienyloxy)-silane (**1h**),[21] and *t*-butyldimethyl(1-phenylhepta-1,6-dienyloxy)silane (**1i**),[21] were prepared according to the literature procedures.

3.3.1. 7-Phenyl-1,6-octadiene (1c). Potassium *t*-butoxide (1.0 g, 8.9 mmol) was added to hexenyl triphenylphosphonium bromide[22] (3.8 g, 8.9 mmol) in THF (50 mL). After stirring for 1.5 h at rt, a THF solution (6 mL) of acetophenone (713 mg, 5.94 mmol) was added. After 2 h, the reaction mixture was filtered on a short silica-gel column with ether, and the filtrate was concentrated in vacuo. The crude product was distilled under 1.5 mmHg in Kugelrohr apparatus to give **1c** (1.06 g, 96%) as an oil. *E*, *Z* mixture. Bp 110–120 °C/1.5 mmHg; ^{1}H NMR ($CDCl_3$) δ 1.44–1.56 (m, 2H), 1.97 (s, 3H), 2.02–2.20 (m, 4H), 4.85–4.99 (m, 2H), 5.69–5.83 (m, 2H), 7.12–7.34 (m, 5H),

3.3.2. 6-Phenyl-1,5-heptadiene (1d). Potassium *t*-butoxide (1.40 g, 12.5 mmol) was added to pentenyl triphenylphosphonium bromide[23] (5.13 g, 12.5 mmol) in THF (80 mL). After stirring for 1.5 h at rt, a THF solution (10 mL) of acetophenone (1.00 g, 8.33 mmol) was added. After 2 h, the reaction mixture was filtered on a short silica-gel column with ether, and the filtrate was concentrated in vacuo. The crude product was distilled under 1.5 mmHg in Kugelrohr apparatus to give **1d** (1.36 g, 95%) as an oil. *E*, *Z* mixture. Bp 110–120/1.5 mmHg; ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 3H), 2.07–2.10 (m, 4H), 4.91–4.99 (m, 2H), 5.45–5.48 (m, 1H), 5.72–5.80 (m, 1H), 7.17–7.19 (m, 2H), 7.21–7.25 (m, 1H), 7.31–7.34 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.5, 28.4, 34.1, 114.5, 126.4, 126.8, 127.9, 128.0, 136.5, 138.3, 142.0.

3.3.3. 5-(4-Phenylcyclohexylidene)-1-pentene (1e). Potassium *t*-butoxide (1.49 g, 13.3 mmol) was added to pentenyltriphenylphosphonium bromide[23] (5.47 g, 13.3 mmol) in THF (80 mL). After stirring for 1.5 h at rt, a THF solution (10 mL) of 4-phenylcyclohexanone (1.54 g, 8.87 mmol) was added. After stirring for 2 h, the reaction mixture was filtered on a short silica-gel column with ether, and the filtrate was concentrated in vacuo. The crude product was distilled under 1.5 mmHg in Kugelrohr apparatus gave **1e** (1.99 g, 99%) as an oil. Bp 130–140 °C/1.0 mmHg; IR (neat) 2920, 2360, 1490, 1440, 910, 760, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40–1.53 (m, 2H), 1.85–1.90 (m, 1H), 1.94–1.96 (m, 2H), 2.11–2.21 (m, 5H), 2.28–2.31 (m, 1H), 2.65–2.73 (m, 2H), 4.97–5.06 (m, 2H),

5.16–5.17 (m, 1H), 5.80–5.89 (m, 1H), 7.17–7.21 (m, 3H), 7.26–7.30 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.7, 28.4, 34.3, 35.1, 35.9, 36.8, 44.8, 114.4, 121.3, 125.9, 126.8, 128.3, 138.6, 138.7, 147.1. HRMS calcd for $C_{17}H_{22}$ 226.1721, found 226.1739.

3.3.4. (5*Z*)-6-(1-Naphthyl)-1,5-hexadiene (1f). Potassium *t*-butoxide (1.46 g, 13.0 mmol) was added to pentenyl triphenylphosphonium bromide[23] (5.35 g, 13.0 mmol) in THF (80 mL). After stirring for 1 h at rt, a THF solution (10 mL) of 1-naphthaldehyde (1.35 g, 8.67 mmol) was added. After stirring for 2 h, the reaction mixture was filtered on a short silica-gel column with ether, and the filtrate was concentrated. The crude product was distilled under 1.0 mmHg in Kugelrohr apparatus to give **1f** (1.72 g, 95%) as an oil. Bp 120–130 °C/1.0 mmHg; IR (neat) 3060, 3010, 2920, 2340, 1640, 1510, 910, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.16 (dt, *J*=7.6, 6.6 Hz, 2H), 2.27 (dt, *J*=7.2, 6.6 Hz, 2H), 4.93 (d, *J*=10.2 Hz, 1H), 4.98 (d, *J*=17.2 Hz, 1H), 5.76 (ddt, *J*=17.2, 10.2, 6.6 Hz, 1H), 5.93 (dt, *J*=11.5, 7.2 Hz, 1H), 6.90 (d, *J*=11.5 Hz, 1H), 7.34 (d, *J*=11.5, 7.0 Hz, 1H), 7.43–7.50 (m, 3H), 7.76 (d, *J*=11.5 Hz, 1H), 7.84–7.86 (m, 1H), 7.99 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 28.0, 33.8, 125.0, 125.2, 125.7, 125.8, 126.3, 127.2, 127.4, 128.3, 131.9, 133.4, 133.5, 133.6, 134.7, 138.1; HRMS calcd for $C_{16}H_{16}O$ 208.1252, found 208.1228.

3.3.5. (5*Z*)-8-Phenyl-1,5-octadiene (1g). Potassium *t*-butoxide (1.31 g, 11.7 mmol) was added to pentenyl triphenylphosphonium bromide[23] (4.81 g, 11.7 mmol) in THF (80 mL). After stirring for 1 h at rt, a THF solution (10 mL) of hydrocinnamaldehyde (1.21 g, 9.00 mmol) was added. After stirring for 2 h, the reaction mixture was filtered on a short silica-gel column with ether, and the filtrate was concentrated in vacuo. The crude product was distilled under 1.0 mmHg in Kugelrohr apparatus to give **1 g** (1.68 g, 99%) as an oil. *Z* isomer. Bp 100–110 °C/1.0 mmHg; IR (neat) 3000, 2850, 1640, 1500, 1450, 910, 720, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.01–2.10 (m, 4H), 2.34–2.08 (m, 2H), 2.66 (t, *J*=7.8 Hz, 2H), 4.93–5.01 (m, 2H), 5.36–5.47 (m, 2H), 5.73–5.81 (m, 1H), 7.17–7.20 (m, 3H), 7.25–7.29 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.6, 29.2, 33.7, 35.9, 114.6, 125.8, 128.2, 128.5, 129.1, 129.7, 138.3; HRMS calcd for $C_{14}H_{18}$ 186.1409, found 186.1396, 142.1.

3.3.6. [2-(2-Allylphenyl)-1-methylethenyloxy]-*t*-butyldimethylsilane (1j). *p*-Toluenesulfonic acid monohydrate (38.0 mg, 0.20 mmol) and 1,3-propanediol (4.57 g, 60.0 mmol) were added to a solution of 1-(2-bromophenyl)propan-2-one[24] (4.20 g, 19.7 mmol) in benzene (60 mL). After the reaction mixture was refluxed for 10 h, the reaction was quenched with sat. $NaHCO_3$ aq. The organic materials were extracted with EtOAc, and the organic extract was washed with water followed by brine. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica-gel deactivated by Et_3N (6:1 hexane/EtOAc) to give 2-(2-bromobenzyl)-2-methyl-1,3-dioxane. [97% yield; ^{1}H NMR ($CDCl_3$) δ 1.22 (s, 3H), 1.45–1.55 (m, 1H), 1.67–1.77 (m, 1H), 3.14 (s, 2H), 3.86 (dd, *J*=12.5, 8.5 Hz, 4H), 6.92–6.97 (m, 1H), 7.08–7.14 (m, 1H), 7.30–7.33 (m, 1H), 7.40–7.43; ^{13}C NMR ($CDCl_3$) δ 19.9, 25.4, 43.2, 59.8, 99.6, 126.0, 126.9, 127.9, 132.4, 132.6, 136.7.]

To a solution of 2-(2-bromobenzyl)-2-methyl-1,3-dioxane (2.0 g, 7.0 mmol) in THF (12 mL) was added buthyllithium (7.71 mmol) at −78 °C. After stirring for 1 h, allyl bromide (1.01 g, 8.41 mmol) in THF (5 mL) was added to the reaction mixture at −78 °C. After the reaction mixture was warmed to rt, the reaction was quenched with water. From the mixture organic materials were extracted with EtOAc, and the combined organic extracts were washed with water followed by brine. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. To a solution of the crude product in MeOH (10 mL) was added 1 N HCl (0.5 mL). After stirring for 2 h, the reaction mixture was poured into water and extracted with EtOAc. The combined organic extracts were washed with water followed by brine. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica-gel (6:1:1 hexane/EtOAc/benzene) to give 1-(2-allyl-phenyl)propan-2-one [22% yield; ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 3H), 3.73 (s, 2H), 3.34 (d, *J*=11.5 Hz, 2H), 4.94–5.08 (m, 1H), 5.84–5.96 (m, 1H), 7.12–7.34 (m, 4H).]

To a suspension of NaH (52.1 mg, 2.17 mmol) in THF (2 mL) was added a THF (4 mL) solution of 1-(2-allyl-phenyl)propan-2-one (291 mg, 1.67 mmol) at 0 °C. After the mixture was allowed to warm to rt with stirring, a THF (3 mL) solution of *t*-butyldimethylsilyl chloride (327 mg, 2.17 mmol) was added. After stirring for 2 h, the reaction was quenched with sat. $NaHCO_3$ aq. The organic layer was washed twice with brine and dried over Na_2SO_4. After the solvent was removed in vacuo, the residue was roughly purified by column chromatography deactivated by Et_3N (hexane/EtOAc=9/1) to give **1j**, which was further purified by distillation under 1.0 mmHg to give pure **1j** (0.457 g, 95%) as an oil. *E*, *Z* mixture; Bp 150–160 °C/1.0 mmHg; ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 6H), 0.83 (s, 9H), 1.97 (s, 3H), 3.36–3.38 (m, 2H), 4.96–5.05 (m, 2H), 5.51 (s, 1H), 5.90–6.01 (m, 1H), 7.08–7.16 (m, 3H), 7.60–7.63 (m, 1H).

3.3.7. (3-Allyl-3*H*-1-indenyloxy)-*t*-butyldimethylsilane (1k). To a solution of lithium diisopropylamide [prepared by the reaction of buthyllithium (10.7 mmol) and diisopropylamine (1.08 g, 10.7 mmol) in THF (20 mL)] was added a THF (12 mL) solution of 3-(*t*-butyldimethylsilyloxy)indene[25] (2.49 g, 10.1 mmol) at −78 °C. After stirring for 1 h, allyl bromide (1.32 g, 11.0 mmol) in THF (10 mL) was added to the reaction mixture at −78 °C. After the reaction mixture was warmed to rt, the reaction was quenched with water. From the mixture organic materials were extracted with EtOAc, and the combined organic extracts were washed with water followed by brine. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo. The yellow residue was distilled under 0.1 mmHg to give **1k** (2.20 g, 76%) as a yellow oil. Bp 85–100 °C/0.1 mmHg; ^{1}H NMR ($CDCl_3$) δ −0.02 (s, 1H), 0.83 (s, 1H), 1.97 (s, 3H), 3.37 (d, *J*=6.2 Hz 2H), 4.96–5.05 (m, 2H), 5.90–6.01 (m, 1H), 7.08–7.16 (m, 4H).

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