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Self-cyclization of (*E*)-2-(trimethylsilylmethyl)pentadienol derivative. Synthesis of bicyclo[4.3.0]nonane ring systems

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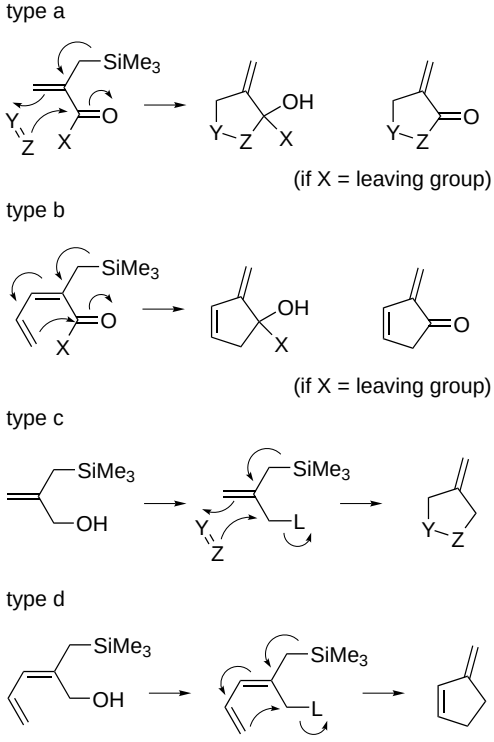
Abstract—Utility and limitation of the title reaction was studied. When (*E*)-3-(4-*t*-butyl- and 4-phenylcyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-en-1-ols were treated with Ms_2O or MsCl, 3-*t*-butyl- and 3-phenyl-8-methylbicyclo[4.3.0]nona-1(6),7-dienes were obtained, respectively. The corresponding (*Z*)-isomer afforded a complex mixture, among which an elimination product was detected. (*E*)-4-(4-*t*-Butylcyclohexylidene)-2-(trimethylsilylmethyl)but-2-en-1-ol afforded only elimination product.

1. Introduction

α,β-Unsaturated carbonyl compounds substituted by trimethylsilylmethyl group at the α-position are unique building blocks in organic synthesis since the β-carbon reacts as an allylsilane[1] but not as an unsaturated carbonyl. Therefore, this moiety acts as a carbon 1,3-dipole based on the nucleophilicity of the β-carbon and the electrophilicity of the carbonyl carbon.[2] This enables to synthesize odd-membered ring compounds[3] via a reaction with the appropriate double-bond compound (Scheme 1, type a). We previously prepared several five-membered ring compounds such as γ-lactones[4] or cyclopentanes[5] via this type of reaction.[6] Further conjugated compounds, that is, α,β,γ,δ-unsaturated carbonyl compounds having α-trimethylsilylmethyl group cyclize themselves to a five-membered ring since the δ-carbon is nucleophilic and reacts with carbonyl carbon (Scheme 1, type b). As an example of this type of reaction, we recently described synthesis of bicyclo[4.3.0]nonane and spiro[4.5]decane carbon skeletons (vide infra).[7]

On the other hand, β-(hydroxymethyl)allylsilane also acts as a carbon-1,3-dipole after conversion of the hydroxy group into an appropriate leaving group. The expected product is a five-membered ring after reaction with a double-bond compound (Scheme 1, type c). This type of reaction was developed by Trost's group and is well documented in review articles.[8] The related [3+4] cycloaddition reaction (homo-Diels–Alder type of reaction) utilizing this unit as the dienophile has also been established.[9] We recently reported a five-carbon ring expansion reaction by replacing



Scheme 1.

Keywords: Bicyclo[4.3.0]nonane; Allylsilane; Pentadienol; Cyclization.
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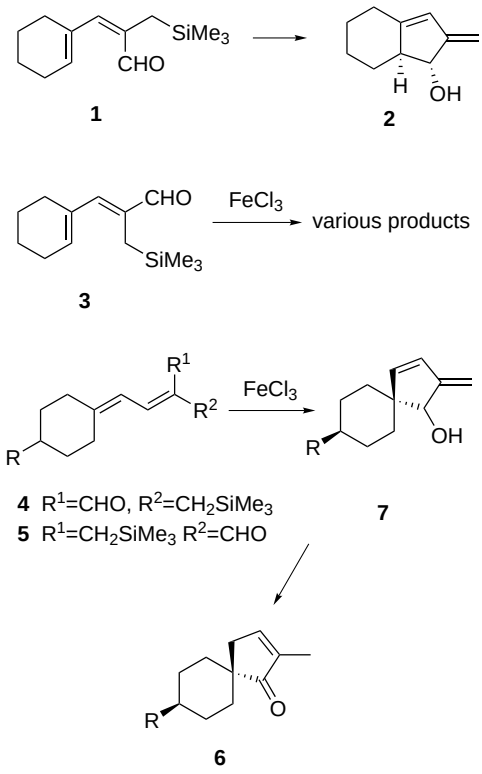
the C=C double bond of the Cope rearrangement with a β-(hydroxymethyl)allylsilane unit (homo-Cope type of reaction).[10]

Further conjugation to β-(hydroxymethyl)allylsilane provides the fourth type of substrate (Scheme 1, type d). Although this type of reaction is an analogue of the 'type b', a problem is expected. Namely, it is for a simple elimination to occur as a competitive reaction, giving a triene if the double bond has some substituents, while this type of elimination reaction is not expected for the 'type b' reaction. The aim of the present study is to clarify the utility and the limitation of this type of reaction.

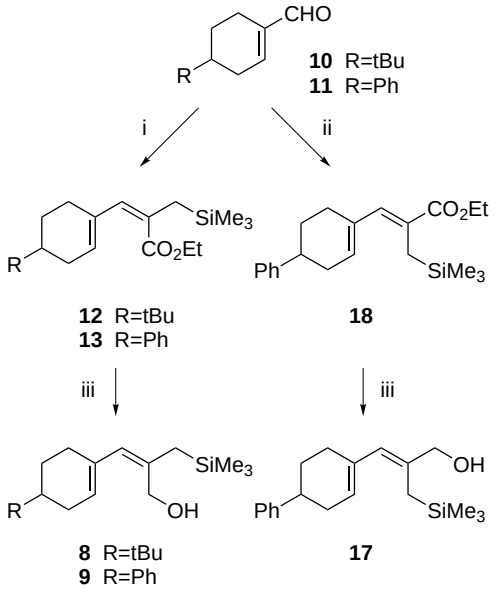
We planned to study the cyclization of 'type d' on the basis of our previous study of the 'type b' reaction,[7a] the outline of which is shown in Scheme 2. In these reactions, the geometry of the cyclization precursor was an important factor for the synthesis of bicyclo[4.3.0]nonane. Namely, (*E*)-precursor **1** cyclized to give the expected product **2** in good yield, while (*Z*)-precursor **3** afforded only a complex mixture. In contrast, in the synthesis of the spiro[4.5]decane carbon framework, both (*E*)- (**4**) and (*Z*)-dienes (**5**) ultimately afforded the same compound **6**, which is the isomerization product of **7**. Here we report that bicyclo[4.3.0]nonane can be synthesized from (*E*)-2-(trimethylsilylmethyl)pentadienol, as in the case of pentadienal, however, spiro[4.5]decane was not obtained.



Scheme 2.

2. Results and discussion

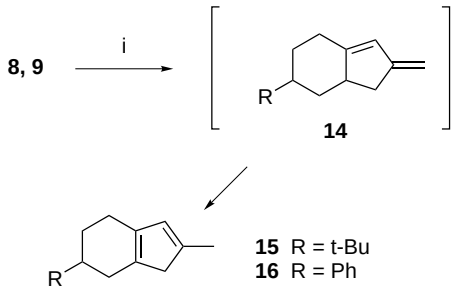
Following the fact that (*E*)-2-(trimethylsilylmethyl)pentadienal **1** cyclized immediately,[7a] we first studied the cyclization of the 3-cyclohexenyl-2-(trimethylsilylmethyl)prop-2-en-1-ol derivative expecting that the cyclization would occur faster than elimination. Since the expected cyclization product is a hydrocarbon, we chose the *t*-butyl- or phenyl-substituted compounds **8** and **9** as the substrates in order to reduce handling problem due to volatility. Compounds **8**[7a] and **9** were synthesized from 4-*t*-butylcyclohex-1-enecarbaldehyde (**10**) and 4-phenylcyclohex-1-enecarbaldehyde (**11**), respectively, via the (*E*)-selective Horner–Wadsworth–Emmons (HWE) reactions[11] followed by DIBAL-H reduction of the ester **12** and **13** (Scheme 3). Compound **11** was prepared from 4-phenylcyclohex-2-en-1-one[12] (see Section 3), which was prepared from 4-phenylcyclohexanone by a standard method.



Scheme 3. Reagents and conditions: (i) $(PhO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, THF, rt; (ii) $(EtO)_2P(O)CH(CO_2Et)CH_2SiMe_3$, NaH, THF, rt; (iii) DIBAL-H, CH_2CH_2, −60 °C.

The 'type d self-cyclization reaction' was then studied. Firstly, following our previous report on the five-carbon ring expansion reaction,[10] **8** was treated with Tf_2O in CH_2Cl_2 at −60 °C in the presence of 2,6-lutidine, however, only a complex product mixture was obtained. Some other bases such as Na_2CO_3, LDA, and BuLi were used instead of 2,6-lutidine but no cyclization product was obtained. Conversion of the hydroxy group into halogen was also tried using halogenation reagents such as PPh_3/CBr_4,[13] but without success.

Then, **8** was converted to its mesylate, which is a less reactive leaving group than triflate. When **8** was treated with Ms_2O in CH_2Cl_2 and pyridine at room temperature, the reaction proceeded within 10 min. The product was not the mesylate but a bicyclic hydrocarbon formed by the 'type d' cyclization reaction (85% yield) (Scheme 4). The product was found not to be the originally expected compound **14** (R = *t*-Bu), but **15**, as characterized from the NMR spectra. Namely, although four olefinic carbons were observed in the ^{13}C NMR, the terminal olefin protons expected for **14** were not found in the ^{1}H NMR, but instead of them, only one alkene proton was

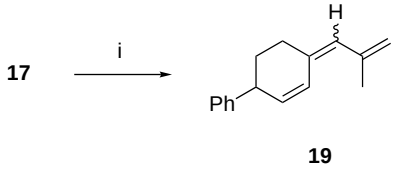


Scheme 4. Reagents and conditions: (i) Ms_2O (for **8**) or MsCl (for **9**), pyridine, CH_2Cl_2, 0 °C.

found at δ 5.90 (br s) together with a pair of methylene protons (δ 2.70 and 2.79) and a methyl group. It is easily expected that **15** is the isomerization product of **14**.

The same reaction was also carried out using **9** as the substrate. The expected product **16** was obtained in only 28% yield via an analogous Ms_2O treatment as above. However, when MsCl was used as the reagent, **16** was afforded in 53% yield, although a longer reaction time (17 h) was required.

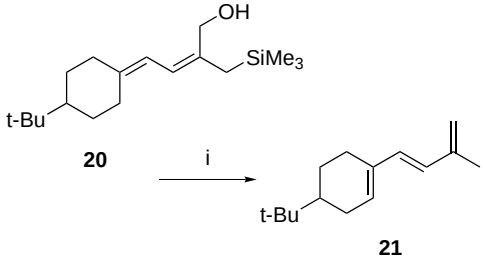
Since the geometry of the allylsilane is considered to be an important factor,[7a] the reaction of the (*Z*)-precursor was also studied using **17** as the substrate, which was prepared via a (*Z*)-selective HWE reaction (**11** to **18**)[14] followed by DIBAL-H reduction (Scheme 3). When **17** was treated with MsCl or Ms_2O in pyridine/CH_2Cl_2, only a complex mixture was afforded among which the presence of triene **19** was detected from ^{1}H NMR spectrum of the reaction mixture (Scheme 5). The geometry of the double-bond in **19** was not determined. Since C-1 and C-5 of the penta-2,4-dien-1-ol unit in **17** are too distant to cyclize, the result indicates that the *Z* to *E* isomerization did not occur, while such an isomerization process occurred partly for the corresponding aldehyde **3**.[7]



Scheme 5. Reagents and conditions: (i) MsCl, pyridine, CH_2Cl_2, 0 °C.

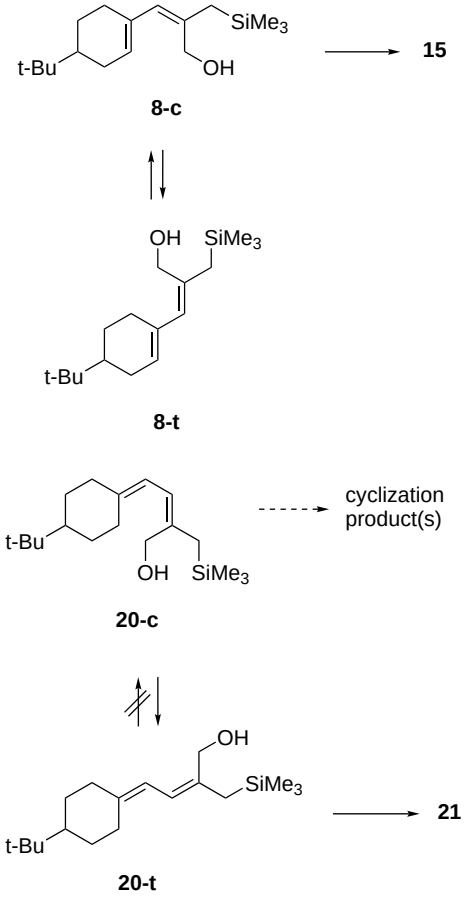
Cyclization of 4-cyclohexylidene-2-(trimethylsilylmethyl)but-2-en-1-ol derivative to the spiro[4.5]decane type of compound was also studied. The substrate **20** was synthesized in accordance with the previously reported procedure.[7] When this compound was treated with Ms_2O and pyridine in CH_2Cl_2, triene **21** was afforded in 77% yield (Scheme 6), together with a small amount of its (*Z*)-isomer. The (*E*)-geometry of **21** was determined from the *J*-value (16.0 Hz) of the olefinic protons. Both compounds **21** and **19** are considered to be the products of simple elimination of mesylate followed by protodesilylation.

The difference in results between **8** and **20** indicates that the substitution pattern of the 2-(trimethylsilylmethyl)pentadienol is an important factor. Namely, C-1 and C-5 of



Scheme 6. Reagents and conditions: (i) Ms_2O, pyridine, CH_2Cl_2, 0 °C.

pentadienol are close to each other for **8** (and **9**) but far for **20**. For **8**, steric congestion of both s-cis (Scheme 7, conformer **8-c**) and s-trans (**8-t**) conformers are almost equal, while s-cis conformer (**20-c**) is highly congested and only s-trans conformer (**20-t**) can be considered for **20**. Also, mesylation is hindered for **20-c** by both the trimethylsilyl group and cyclohexane ring.



Scheme 7.

In conclusion, the utility and limitation of the self-cyclization reaction of 2-(trimethylsilylmethyl)pentadienol in the synthesis of five-memberd ring was revealed. Cyclization of 4,5-disubstituted (*E*)-2-(trimethylsilylmethyl)pentadienol occurred predominantly over the elimination reaction, and was shown to be useful in the synthesis of bicyclo[4.3.0]nonane compounds. In contrast, the elimination reaction giving triene occurred from both 4,5-disubstituted (*Z*)-2-(trimethylsilylmethyl)pentadienol

and 5,5-disubstituted (*E*)-2-(trimethylsilylmethyl)pentadienol. This suggests that both the geometry of the double-bond and the position of the substituents are important factors for the self-cyclization reaction.

3. Experimental

3.1. General procedure

IR spectra were recorded on a Jasco FT/IR-230 spectrometer. Both ^{1}H and ^{13}C NMR spectra were measured on a Jeol GSX-400 (400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer. Chemical shifts were reported on the δ scale (ppm) with solvent ($CHCl_3$=7.26) as an internal standard, unless otherwise noted. The signal of the solvent ($CDCl_3$=77.0) was used as a standard for ^{13}C NMR spectra. Both low-resolution mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained on a Jeol SX-102A, CMATE II, or Shimadzu GCMS-QP5050 mass spectrometer with the EI method. Analytical TLC was done on precoated TLC plates (Kieselgel 60 F254, layer thickness 0.2 mm). Wakogel C-200 or florisil (100–200 mesh) was used for column chromatography. Anhydrous Na_2SO_4 or $MgSO_4$ was used for drying the extracted organic layers. For dry solvent, THF was distilled from $LiAlH_4$, and CH_2Cl_2 was distilled from CaH_2. All new compounds were determined to be >95% pure by ^{1}H and ^{13}C NMR, unless otherwise noted.

3.2. Preparation of the substrates

3.2.1. 4-Phenylcyclohex-1-enecarbaldehyde (11). To a stirred solution of LDA, prepared from *i*Pr_2NH (0.90 cm^3, 5.93 mmol) and BuLi (2.0 cm^3, 3.08 mmol, 1.54 M solution in hexane) in dry THF (3 cm^3) was added a solution of $Ph_2P(O)CH_2OMe$ (730 mg, 2.11 mmol) in THF (13 cm^3) at −60 °C under Ar. A solution of 4-phenylcyclohex-2-en-1-one (255 mg, 1.48 mmol) in THF (6 cm^3) was added, and the mixture was stirred with slow warming to room temperature. After confirming the reaction on TLC, an aqueous solution of HCl (2 M) was added, and the mixture was heated to 80–90 °C for 20 h. This was cooled to room temperature again, $NaHCO_3$ aq. was added, and the product was extracted with Et_2O and dried. Evaporation of the solvent followed by silica gel (15 g) column chromatography using hexane–Et_2O (9/1) as eluent yielded **11** (168.9 mg, 61%) as an oil; IR (neat) 2927, 1682, 1643, 1163, 758, and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si=0.00) δ=1.66–1.78 (1H, m), 2.00–2.08 (1H, m), 2.16–2.28 (1H, m), 2.38–2.55 (2H, m), 2.60–2.70 (1H, m), 2.80–2.90 (1H, m), 6.85–6.89 (1H, m, C=CH), 7.19–7.34 (5H, m, Ph), and 9.48 (1H, s, CHO); ^{13}C NMR ($CDCl_3$) δ=21.79, 28.60, 34.29, 39.68, 126.38, 126.67 (2C), 128.49 (2C), 141.24, 145.45, 150.35, and 193.76; MS *m*/*z* 186 (M^+, 11%), 115 (6), 104 (100), 95 (28), 78 (14), and 51 (13); HRMS [Found: *m*/*z* 186.1074 (M^+). Calcd for $C_{13}H_{14}O$: 186.1045].

3.3. (*E*)-Selective HWE reaction

See our previous paper for the procedure and spectral data of **12**.[7a] By the same procedure, **13** (29.5 mg, 77%) was synthesized from **11** (21.0 mg).

3.3.1. (*E*)-Ethyl 3-(4-phenylcyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-enoate (13). An oil; IR (neat) 2952, 1720, 1248, 1217, and 852 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.10 (9H, s, $SiMe_3$), 1.33 (3H, t, *J*=7.1 Hz, OCH_2CH_3), 1.71–2.48 (8H, m), 2.77–2.87 (1H, m), 4.21 (AB, each q, *J*=7.1 Hz, OCH_2CH_3), 5.76 (1H, br, C=C*H*C$_{ring}$), 5.93 (1H, br s, C*H*=CCO_2Et), and 7.18–7.37 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=−1.67 (3C), 14.01, 25.63, 27.44, 29.72, 33.98, 39.59, 60.21, 125.91, 126.64 (2C), 127.74, 128.23 (2C), 129.20, 132.87, 134.93, 146.64, and 170.56; MS *m*/*z* 342 (M^+, 4%), 297 (3), 223 (11), 195 (6), 117 (14), 91 (31), and 73 (100); HRMS [Found: *m*/*z* 342.2064 (M^+). Calcd for $C_{21}H_{30}O_2Si$: 342.2015].

3.4. (*Z*)-Selective HWE reaction

See our previous paper for the procedure.[7a] Compound **18** (90%) was prepared from **11** but was not characterized at this stage and was subjected to the next reduction step (**18** to **17**) without purification.

3.5. Reduction

See our previous paper for the procedure and the spectral data of **8**. By the same procedure, **13** and **18** afforded **9** (100%) and **17** (90%), respectively.

3.5.1. (*E*)-3-(4-Phenylcyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-en-1-ol (9). An oil; IR (neat) 3338, 2927, 1246, 1018, 852, 756, and 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.07 (9H, s, $SiMe_3$), 1.65–2.45 (9H, m), 2.75–2.84 (1H, m), 4.20 (1H, d, *J*=12.0 Hz, C*H*HOH), 4.29 (1H, d, *J*=12.0 Hz, CH*H*OH), 5.56 (1H, br, C=C*H*C$_{ring}$), 5.60 (1H, br s, C*H*=CCH_2OH), and 7.18–7.34 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=−1.31 (3C), 24.93, 29.84, 30.02, 33.74, 39.71, 62.34, 124.85, 125.93, 126.73 (2C), 128.13, 128.27 (2C), 134.72, 137.47, and 146.82; MS *m*/*z* 300 (M^+, 8%), 271 (55), 210 (7), 195 (7), 181 (8), 167 (7), 155 (7), 117 (17), 91 (48), and 73 (100); HRMS [Found: *m*/*z* 300.1922 (M^+). Calcd for $C_{19}H_{28}OSi$: 300.1910].

3.5.2. (*Z*)-3-(4-Phenylcyclohex-1-en-1-yl)-2-(trimethylsilylmethyl)prop-2-en-1-ol (17). An oil; IR (neat) 3390, 1726, 1452, and 852 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.07 (9H, s, $SiMe_3$), 1.73–2.48 (9H, m), 2.75–2.84 (1H, m), 4.20 (2H, s, CH_2OH), 5.73 (1H, br, C=C*H*C$_{ring}$), 5.78 (1H, br s, C*H*=CCH_2OH), and 7.18–7.34 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=−0.56 (3C), 19.84, 29.88, 30.02, 33.79, 39.72, 69.34, 124.69, 125.53, 125.98, 126.84 (2C), 128.34 (2C), 135.01, 137.28, and 146.95; MS *m*/*z* 300 (M^+, 2%), 271 (1), 210 (13), 195 (10), 181 (10), 167 (10), 155 (9), 117 (30), 106 (42), 91 (74), and 73 (100); HRMS [Found: *m*/*z* 300.1927 (M^+). Calcd for $C_{19}H_{28}OSi$: 300.1910].

3.6. Cyclization reaction

In a 10 cm^3 round bottomed flask, a solution of **8** (27.4 mg, 0.094 mmol) in dry CH_2Cl_2 (3 cm^3, freshly distilled from CaH_2) was prepared, and to this solution was added successively pyridine (0.055 cm^3) and methanesulfonic anhydride (70.8 mg, 0.40 mmol) at 0 °C with stirring. $CaCl_2$ drying tube was attached, and the stirring was continued for 10 min. Water was added, and the product was

extracted with Et_2O followed by drying and evaporation. The resultant residue was chromatographed on florisil (1 g) using pentane as eluent to afford **15** (15.1 mg, 85%).

Similarly, **9** (6.7 mg, 0.022 mmol) afforded **16** (2.5 mg, 53%) by treatment with methanesulfonic chloride (0.007 cm^3) instead of methanesulfonic anhydride in pyridine (0.015 cm^3) and CH_2Cl_2 (3 cm^3).

3.6.1. 3-*t*-Butyl-8-methylbicyclo[4.3.0]nona-1(6),7-diene (15). An oil; IR (neat) 2924, 1645, 1468, 1365, 1265, and 741 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=0.90$ (9H, s, *t*-Bu), 1.17–1.40 (2H, m), 1.85–2.34 (5H, m), 2.01 (3H, s, Me), 2.70 (1H, dd, $J=3.5$, 22 Hz), 2.79 (1H, br d, $J=22$ Hz), and 5.90 (1H, br s); ^{13}C NMR ($CDCl_3$) $\delta=24.6$, 25.5, 26.8, 27.4 (3C), 29.7, 32.4, 45.3, 46.9, 128.9, 137.0, 138.0, and 141.9; MS *m*/*z* 190 (M^+, 21%), 175 (3), 133 (34), 106 (100), 91 (84), and 41 (44); HRMS [Found: *m*/*z* 190.1691 (M^+). Calcd for $C_{14}H_{22}$: 190.1722].

3.6.2. 8-Methyl-3-phenylbicyclo[4.3.0]nona-1(6),7-dien (16). An oil; IR (neat) 2925, 1452, 1377, 750, and 698 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta=1.77$–2.06 (2H, m), 2.04 (3H, s, Me), 2.35–2.60 (4H, m), 2.77 (1H, br d, $J=22.7$ Hz, C*H*H in cyclopentadiene), 2.84 (1H, br d, $J=22.7$ Hz, CH*H* in cyclopentadiene), 2.84–2.92 (1H, m), 5.95 (1H, s, CH=C), and 7.18–7.34 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) $\delta=16.18$, 24.86, 30.47, 33.63, 41.27, 46.64, 125.94, 126.95 (2C), 128.32 (2C), 128.84, 136.12, 137.98, 142.20, and 147.31; MS *m*/*z* 210 (M^+, 22%), 106 (100), and 91 (90); HRMS [Found: *m*/*z* 210.1375 (M^+). Calcd for $C_{16}H_{18}$: 210.1409].

3.7. Treatment of 17 and 20 with Ms_2O or MsCl

Compound **20** was treated with Ms_2O, and **17** was treated with MsCl following the cyclization of the corresponding (*E*)-isomers. Compound **17** afforded only a complex mixture, while **20** (32.0 mg, 0.09 mmol) afforded **21** (17.1 mg, 77%) after florisil column chromatography using pentane as eluent.

3.7.1. 6-(2-Methylprop-2-enylidene)-3-phenylcyclohex-1-ene (19). This compound could not be isolated in the pure form. The following data were assigned from a complex mixture of hydrocarbon products. ^1H NMR ($CDCl_3$) $\delta=1.92$ (3H, s, Me), 3.54 (1H, br, CHPh), 4.89 (1H, s, C=C*H*H), 5.02 (1H, s, C=CH*H*), 5.80 (1H, s, CH_2=C–C*H*=C), 5.86 (1H, dd, $J=2.5$, 9.4 Hz, C*H*=CH), 6.24 (1H, dd, $J=1.3$, 9.4 Hz, CH=C*H*), and 7.19–7.34 (5H, m, Ph); MS *m*/*z* 210 (M^+, 18%), 195 (9), 167 (14), 106 (100), and 91 (76).

3.7.2. 4-*t*-Butyl-1-(3-methylbuta-1,3-dienyl)cyclohex-1-ene (21). An oil; IR (neat) 2956, 1620, 1468, 1363, and 958 cm^{-1}; ^1H NMR ($C_6D_6=7.15$) $\delta=0.80$ (9H, s, *t*-Bu), 1.02–1.20 (2H, m), 1.68–2.07 (4H, m), 1.86 (3H, s, Me), 2.27–2.35 (1H, m), 4.99 (1H, br s), 5.08 (1H, br s), 5.72–5.79 (1H, m), 6.38 (1H, d, $J=16.0$ Hz), and 6.41 (1H, d, $J=16.0$ Hz); ^{13}C NMR ($C_6D_6=128.0$) $\delta=18.8$, 24.1, 26.2, 27.2 (3C), 27.9, 32.1, 44.4, 115.8, 130.6, 132.6, 135.9, and 142.7 (one carbon was not identified because of overlapping with the solvent signal); MS *m*/*z* 204 (M^+, 13%), 189 (2), 147 (11), 133 (14), 119 (17), 105 (88), 91 (44), 57 (100), and 41 (93); HRMS [Found: *m*/*z* 204.1870 (M^+). Calcd for $C_{15}H_{24}$: 204.1878].

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