The Synthesis and Chemistry of 1,3-Bridged Polycyclic Cyclopropenes: 8-Oxatricyclo[3.2.1.$0^{2,4}$]octa-2,6-dienes

Gon-Ann Lee* (李國安), Chih-Yi Chang (張志毅), Chih-Hwa Cherng (成知華), Chi-Sheng Chen (陳啓盛) and Mei Liu (劉　梅)
Department of Chemistry, Fu Jen Catholic University, Hsinchuang, Taipei 24205, Taiwan, R.O.C.

Three 1,3-bridged polycyclic cyclopropenes, *exo*-8-oxatricyclo[3.2.1.$0^{2,4}$]octa-2,6-diene (**10**), *endo*-8-oxatricyclo[3.2.1.$0^{2,4}$]octa-2,6-diene (**11**), and *exo*-6,7-benzo-1,5-diphenyl-8-oxatricyclo[3.2.1.$0^{2,4}$]octa-2,6-diene (**12**), have been synthesized by elimination of 2-chloro-3-trimethylsilyl-8-oxatricyclo[3.2.1.$0^{2,4}$]-oct-6-enes, **17**, **18** and **30**, which were generated from 1-chloro-3-trimethylsilylcyclopropene with furan and diphenylisobenzofuran. We have demonstrated a facile route to synthesize the highly strained 1,3-fused polycyclic cyclopropenes, **10**, **11**, and **12**. The stereochemistry of the Diels-Alder reactions of cyclopropene **16** with furan and DPIBF are different. Cyclopropene **16** was treated with furan to form *exo-exo* and *endo-exo* adducts (5:2) and treated with DPIBF to generate an *exo-exo* adduct. Compounds **10**, **11** and **12** undergo isomerization reactions to form benzaldehyde and phenyl 4-phenyl-[1]naphthyl ketone to release strain energies *via* diradical mechanisms.

Keywords: 1,3-Bridged tricyclic cyclopropenes; *exo*-8-Oxatricyclo[3.2.1.$0^{2,4}$]octa-2,6-diene; *endo*-8-Oxatricyclo[3.2.1.$0^{2,4}$]octa-2,6-diene; *exo*-6,7-Benzo-1,5-diphenyl-8-oxatricyclo[3.2.1.$0^{2,4}$]octa-2,6-diene; Highly strained; Diels-Alder reactions; Isomerization; Diradical mechanisms.

INTRODUCTION

Although the existence of cyclopropenes has been known for over a century, and the first authenticated synthesis of cyclopropene was reported by Dem'yanoy and Doyarenko in 1922,[1] the cyclopropenes continue to fascinate both theoretical and experimental chemists because of their unique structure, high degree of ring strain, and difficult synthesis.[2] Cyclopropenes undergo many unusual processes such as ene dimerization to give 3-cyclopropylcyclopropenes, ring opening reaction to form vinyl carbene, and [2 + 2] cycloaddition to generate tricyclo[3.1.0.$0^{2,4}$]hexanes in order to release strain energy.[3] Both 1,2- and 1,3-fused bicyclic cyclopropenes, which are more energetic than cyclopropene itself, have been well studied.[3,4] Pioneering work in highly strained cyclopropenes with various polycyclic frameworks done by Szeimies has led to some important studies of dehydroquadricyclane (**1**),[5] tetracyclo[4.1.0.$0^{2,4}$.$0^{3,5}$]hept-3-ene (**2**),[6] tricyclo[3.1.0.$0^{2,6}$]hex-1(6)-ene (**3**),[6] and tricyclo[4.1.0.$0^{2,7}$]-hept-1(7)-ene (**4**).[7] There are five 1,2-fused tricyclics with a cyclopropene fused to a bicyclic ring skeleton, tricyclo[3.2.1.$0^{2,4}$]oct-2(4)-ene (**5**),[8] tricyclo[3.2.1.$0^{2,4}$]octa-2(4),6-diene (**6**),[9] tricyclo[3.2.2.$0^{2,4}$]non-2(4)-ene (**7**),[10] tricyclo[3.2.2.$0^{2,4}$]nona-2(4),6-diene (**8**),[11] and tricyclo[3.3.2.$0^{2,4}$]-dec-2(4)-ene (**9**),[12] which have been synthesized and trapped. Müller has reported that only reduction of the bromine substituent to the hydrogen occurred and the presumed intermediate organo-Li derivative did not undergo β-elimination reaction when 6,7-benzo-2-bromo-4-chloro-1,5-diphenyl-8-oxatricyclo[3.2.1.$0^{2,4}$]oct-6-ene was reacted with BuLi.[13] 1,3-Fused cyclopropene is more stable than 1,2-fused cyclopropene.[14] To the best of our knowledge, this type of 1,3-fused tricyclic cyclopropene has not been reported. We report here easier routes to the synthesis of 1,3-fused tricyclic cyclopropenes, *exo*-8-oxatricyclo[3.2.1.$0^{2,4}$]octa-2,6-diene (**10**), *endo*-8-oxatricyclo[3.2.1.$0^{2,4}$]octa-2,6-diene (**11**), and *exo*-6,7-benzo-1,5-diphenyl-8-oxatricyclo[3.2.1.$0^{2,4}$]octa-2,6-diene (**12**) (Fig. 1).

RESULTS AND DISCUSSION

We have reported that 1-bromo-2,2-dichloro-1-trimethylsilylcyclopropane is a very useful precursor to synthesize

* Corresponding author. Tel: +886-2-29031111-3563; fax: +886-2-2902-3209; email: chem1010@mails.fju.edu.tw

1,2-fused tricyclics with a cyclopropene fused to a bicyclic ring skeleton *via* elimination, Diels-Alder, and elimination reactions.[11] In order to synthesize this type of 1,3-fused tricyclic cyclopropenes, we generated 1-bromo-2,2-dichloro-3-trimethylsilylcyclopropane (**13**) as a starting material.[15] Compound **13** (*trans*:*cis* = 6:1) was prepared by dichlorocarbene addition to β-bromovinyltrimethylsilane (*trans*:*cis* = 12:1). Cyclopropane **13** was treated with methyllithium at -40 °C and the mixture was stirred for one hour before 5.0 equiv. of cyclopentadiene was added. The structure of the Diels-Alder adduct **14** was formed from cyclopentadiene and 1-choro-3-(2-chloro-3-trimethylsilylcyclopropyl)-2-trimethylsilylcyclopropene (**15**).[15] When 1-chloro-3-trimethylsilylcyclopropene (**16**) was generated by treatment of cyclopropane **13** with methyllithium at -40 °C, cyclopropene **16** will undergo ene dimerization to form **15** before reacting with cyclopentadiene. In order to trap **16**, we used furan as solvent and trapping reagent when cyclopropene **16** was generated at room temperature. Theoretically, there are four possible isomers in this Diels-Alder reaction, *exo-endo* (*exo*-addition from the view of the cyclopropene and *endo*-addition from the view of the trimethylsilyl group), *exo-exo*, *endo-endo*, and *endo-exo* adducts (Fig. 2).

There are only two isomers, **17** and **18**, that were generated (yields = 79%, **17**:**18** = 5:2) in this reaction. An X-ray analysis of the Diels-Alder adduct **19** of **17** with diphenylisobenzofuran (DPIBF) was carried out to confirm the stereochemistry of compound **17** (Scheme I).

Because the trimethylsilylmethylene group and oxygen are in a *syn*-conformation and trimethylsilyl group and oxygen are in an *anti*-conformation in compound **17**, compound **17** was formed from the *exo-exo* cycloaddition. According to the steric effects, the transition states of *exo-endo* and *endo-endo* are unstable and these two adducts can't be formed. Compound **18** should be formed from the *endo-exo* cycloaddition of cyclopropene **16** and furan.

When both of the 1,3-fused tricyclic cyclopropenes, **10** and **11**, were synthesized by treatment of compounds **17** and **18** with tetrabutylammonium fluoride in either solution or gas phase (vacuum gas-solid reaction, VGSR)[16] and trapped with cyclopentadiene, the sole product, benzaldehyde, was isolated (Scheme II). The isomerizations of compounds **10** and **11** are faster than the Diels-Alder reactions with cyclopentadiene.

According to the literature, cyclopropenes can undergo diradical[2,11] and cyclopropene-vinyl carbene[17] rearrangement

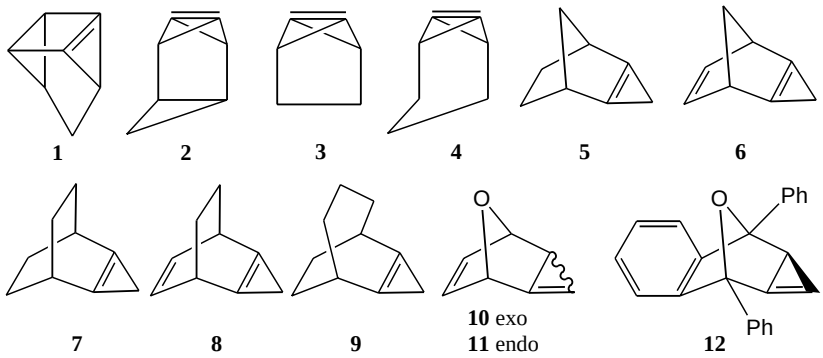


Fig. 1. The structures of polycyclic compounds.

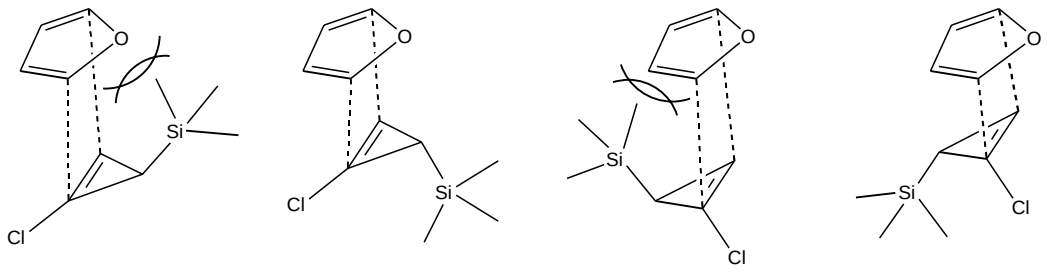
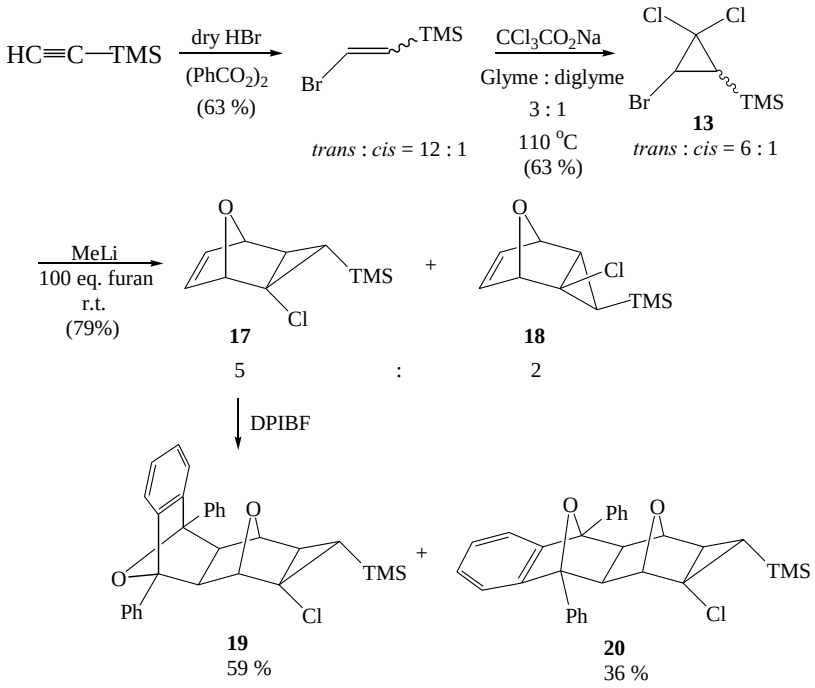
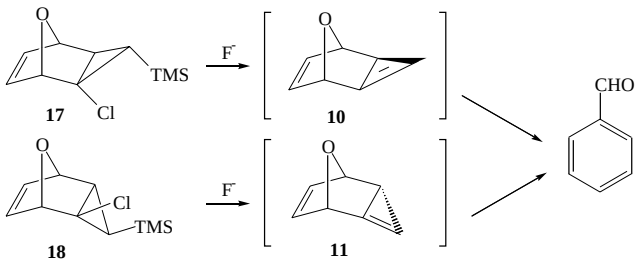


Fig. 2. The transition states of the Diels-Alder reactions of compound **16** and furan.

Scheme I



Scheme II



to release the strain energy. There are three possible mechanisms in these rearrangements – the more stable vinyl carbene (path a), the less stable vinyl carbene (path b), and the diradical mechanisms (path c) (Fig. 3). In the more stable vinyl carbene mechanisms (path a), both 1,3-fused tricyclopropenes, *exo*-8-oxatricyclo[3.2.1.0^{2,4}]octa-2,6-diene (**10**) and *endo*-8-oxatricyclo[3.2.1.0^{2,4}]octa-2,6-diene (**11**), will undergo rearrangement to give vinyl carbene **21** followed by C1-C7 bond insertion to form *anti*-Bredt compound **22** which can be rearranged to yield benzaldehyde. In the less stable vinyl carbene mechanisms (path b), compounds **10** and **11** rearranged to vinyl carbene **23**, which underwent intermolecular reaction to generate zwitterion **24** followed by furan ring opening rearrangement to give **25**. Benzaldehyde can be formed by breaking the C-O bonds of **25**. In the diradical mechanisms (path c), compounds **10** and **11** underwent electrocyclic opening of tetrahydrofuran radical **27**, formed from **26** to give a new 1,3-diradical **28** which was transformed to benzaldehyde by opening the cyclopropane ring. Furthermore, theoretical calculations show that the heat of formation of compound **22** (98.4 kcal/mol) is higher than that of compound **29** (80.5 kcal/mol),[18] formed by C-H bond insertion of vinyl carbene **21**, which will isomerize to generate tropone. Therefore, we propose that these transformations should not proceed *via* the more stable vinyl carbene mechanisms (path a).

The difference of less stable vinyl carbene mechanism and diradical mechanism is the source of the carbon atom of carbonyl group. In order to understand the source of the carbon atom of the carbonyl group of benzaldehyde, we synthesized *exo*-6,7-benzo-1,5-diphenyl-8-oxatricyclo[3.2.1.0^{2,4}]-octa-2,6-diene (**12**). When cyclopropene **16** was synthesized and trapped with DPIBF, only *exo-exo* adduct, 6,7-benzo-2-chloro-3-trimethylsilyl-1,5-diphenyl-8-oxatricyclo[3.2.1.0^{2,4}]-oct-6-ene (**30**), was formed and its structure was determined by single-crystal X-ray analysis. Phenyl 4-phenyl-[1]naphthyl ketone (**31**)[19] was the sole adduct when compound **31** was treated with tetrabutylammonium fluoride at refluxing THF (Scheme III). As a result, we propose that these reactions proceed *via* diradical mechanisms.

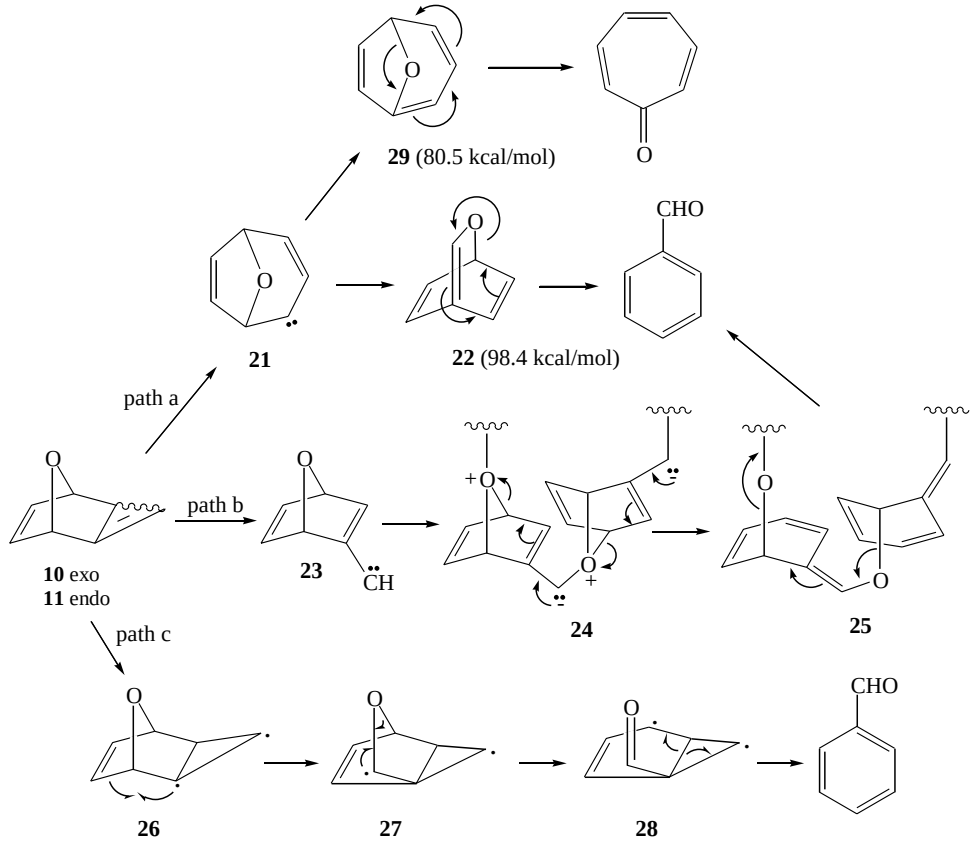
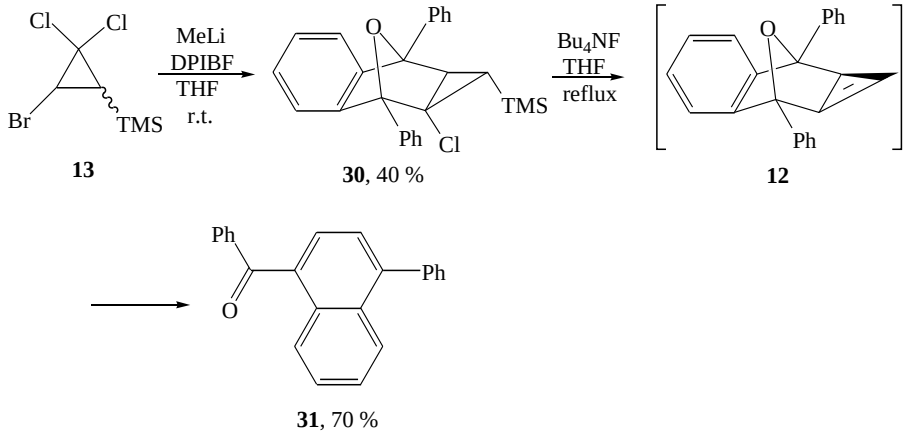


Fig. 3. Transformations of compounds **10** and **11** to benzaldehyde.

Scheme III



CONCLUSIONS

We have demonstrated a facile route to synthesize the highly strained 1,3-fused polycyclic cyclopropenes, **10**, **11**, and **12**. The stereochemistry of the Diels-Alder reactions of cyclopropene **16** with furan and DPIBF are different. Cyclopropene **16** was treated with furan formed *exo-exo* and *endo-exo* adducts (5:2) and treated with DPIBF generated *exo-exo* adduct. Both compounds **10** and **11** undergo isomerizations to form benzaldehyde and compound **12** undergoes rearrangement to give **31** via diradical mechanisms.

EXPERIMENTAL SECTION

Melting points were determined and uncorrected. Proton and carbon-13 NMR spectra were measured in $CDCl_3$ with $CHCl_3$ as the internal standard. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane. Coupling constants are expressed in hertz. X-ray data were recorded on a Siemens R3m/V diffractometer for compound **19** and a Nonius CAD 4 diffractometer for compound **30**.

Vacuum gas-solid reaction apparatus

A modification of the apparatus previously reported was used.[16] The apparatus was prepared by charging a column (30 × 3.5 cm with a 19/22 ground-glass joint at the bottom) with the adsorbed tetrabutylammonium fluoride. The glass helices were supported on a glass-wool plug (1 cm) at the bottom of the column. A series of two or three traps was used to collect and/or fractionate the products from the top of the column. The flask charged starting material was attached to the bottom of the column.

1-Bromo-2,2-dichloro-3-trimethylsilylcyclopropane (13)

A suspension of (2-bromovinyl)trimethylsilane (66.00 g, 0.25 mol) and sodium trichloroacetate (100.00 g, 0.54 mol) in 23 mL of dry glyme:diglyme (3:1) was stirred at 110 °C until CO_2 evolution ceased. The dark slurry was cooled and diluted with pentane. After being stirred 30 min, the mixture was filtered, and the solid was washed with pentane. The solution was concentrated by distillation. The residual was then subjected to the same reaction four more times. After the fifth filtration, the solution was diluted with additional pentane and was washed with water. The organic layer was washed with water and brine and then dried over anhydrous magnesium sulfate. Filtration and vacuum distillation gave 41.27 g (63%) of 1-bromo-2,2-dichloro-3-trimethylsilylcyclopropane (**13**) (bp 48-52 °C/0.4 mmHg, *trans*:*cis* = 6:1). IR (neat): 3044, 1956, 1900, 1416, 844 cm^{-1}; *trans*-**13**: ^{1}H NMR ($CDCl_3$) δ 3.42 (d, 1H, *J* = 8.6 Hz), 1.01 (d, 1H, *J* = 8.6 Hz), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 63.25 (C), 33.04 (CH), 32.37 (CH), -1.47 (CH_3); *cis*-**13**: ^{1}H NMR ($CDCl_3$) δ 3.84 (d, 1H, *J* = 11.1 Hz), 1.29 (d, 1H, *J* = 11.1 Hz), 0.25 (s, 9H).

Diels-Alder reaction of 1-choro-3-(2-chloro-3-trimethylsilylcyclopropyl)-2-trimethylsilylcyclopropene (15) and cyclopentadiene[15]

Methyllithium (1.5 M in ether, 160.0 mL, 0.24 mol) is added dropwise from a syringe to a stirred solution of 1-bromo-2,2-dichloro-3-trimethylsilylcyclopropane (**13**) (52.40 g, 0.20 mol) in 80.0 mL of dry tetrahydrofuran at -78 °C. The mixture was stirred at -40 °C for 1 h, then cyclopentadiene (100 mL, 1.25 mol) was added and allowed to warm to room temperature and stirred 12 h. Add about 150 mL of ether and pour the mixture into a 1-L beaker with 200 g of crushed ice. Separate the organic layer and wash it with water and brine, and then dry over anhydrous magnesium sulfate. Filtration and then concentrated and chromatographed (hexanes) to give white solid **14** (30.5 g, 85%). Compound **14**: mp 78-79 °C; IR (neat): 3067, 2978, 2944, 2900, 1650, 1566, 1244, 839 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.98-6.02 (m, 1H), 5.61-5.64 (m, 1H), 3.08 (dd, 1H, *J* = 8.3, 2.8 Hz), 2.94-2.97 (m, 1H), 2.89-2.94 (m, 1H), 1.99 (dt, 1H, *J* = 7.2, 1.6 Hz), 1.62-1.66 (m, 1H), 1.37 (ddd, 1H, *J* = 9.4, 8.3, 2.8 Hz), 0.37 (d, 1H, *J* = 9.4 Hz), 0.21 (s, 9H), 0.16 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 132.91 (CH), 132.80 (CH), 62.08 (C), 59.85 (CH_2), 54.72 (CH), 40.26 (CH), 24.60 (CH), 19.10 (C), 15.43 (CH), 0.32 (CH_3), -0.18 (CH_3); MS *m/z* (%): 358 (M^+, 0.15); HRMS calcd. for $C_{17}H_{28}Cl_2Si_2$ *m/z* 358.1107, found 358.1108.

2-Chloro-3-trimethylsilyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (17) and (18)

n-Butyllithium (1.6 M in hexane, 75.0 mL, 0.12 mol) is added dropwise from a syringe to a stirred solution of 1-bromo-2,2-dichloro-3-trimethylsilylcyclopropane (**13**) (26.20 g, 0.10 mol) in furan (727.0 mL, 10.00 mol). Stirring is continued for 2 h. Remove most of furan by distillation and cool the mixture to room temperature. Add about 250 mL of ether and pour the mixture into a 1-L beaker with 200 g of crushed ice. Separate the organic layer and wash it with water and brine, and then dry over anhydrous magnesium sulfate. Filtration and vacuum distillation gave 14.15 g (79%) of 2-chloro-3-trimethylsilyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (**17**) and (**18**) (bp 49 °C/0.7 mmHg, *exo*:*endo* = 5:2). Flash chromatography (5% EA in hexanes) yielded colorless oil **17** and **18**. Compound **17**: IR (neat): 3005, 2956, 2899, 1558, 1408, 1250, 1030, 843, 683 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.66 (s, 2H), 4.76 (s, 1H), 4.60 (s, 1H), 1.63 (d, 1H, *J* = 5.9 Hz), 1.38 (d, 1H, *J* = 5.9 Hz), 0.10 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 138.85 (CH), 138.37 (CH), 81.05 (CH), 79.06 (CH), 57.12 (C), 31.57 (CH), 26.42 (CH), -1.24 (CH_3); MS *m/z* (%): 179 ($(M\text{-}Cl)^+$, 20); HRMS calcd. for $C_{10}H_{15}OSi$ *m/z* 179.0892, found 179.0893. Compound **18**: IR (neat): 3013, 2957, 2899, 1408, 1200, 1072, 1019, 842 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.37 (dd, 1H, *J* = 5.7, 1.8 Hz), 6.08 (dd, 1H, *J* = 5.7, 1.6 Hz), 5.10 (dt, 1H, *J* = 4.3, 1.6 Hz), 4.89 (t, 1H, *J* = 1.8 Hz), 2.07 (dd, 1H, *J* = 5.8, 4.3 Hz), 0.95 (d, 1H, *J* = 5.8 Hz), 0.07 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 133.15 (CH), 132.94 (CH), 88.88 (CH), 81.40

(CH), 56.33 (C), 36.85 (CH), 28.35 (CH), -1.19 (CH_3); MS *m/z* (%): 179 ($(M-Cl)^+$, 25); HRMS calcd. for $C_{10}H_{15}OSi$ *m/z* 179.0892, found 179.0886.

Diels-Alder reaction of 2-chloro-3-trimethylsilyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (17) and DPIBF

Compound **17** (4.30 g, 20.00 mmol) and diphenylisobenzofuran (5.94 g, 22.00 mmol) were dissolved in 20 mL of dry tetrahydrofuran. The mixture was refluxed for 6 h and then concentrated and chromatographed (hexane:CH_2Cl_2 = 5:1) to give colorless solid **19** (5.70 g, 59%, R_f = 0.15) and **20** (3.45 g, 36%, R_f = 0.26). Compound **19**: mp 166-168 °C; IR (neat): 3056, 3034, 2956, 2924, 2853, 1604, 1498, 1448, 1365, 1335, 1250, 991, 839, 762, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.73-7.67 (m, 4H), 7.54-7.43 (m, 6H), 7.20-7.17 (m, 2H), 6.95-6.87 (m, 2H), 4.07 (d, 1H, *J* = 8.3 Hz), 4.05 (s, 1H), 3.99 (s, 1H), 3.33 (d, 1H, *J* = 8.3 Hz), 1.31 (d, 1H, *J* = 6.0 Hz), 0.80 (d, 1H, *J* = 6.0 Hz), 0.08 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 147.04 (C), 146.59 (C), 138.80 (C), 138.56 (C), 128.60 (CH), 128.57 (CH), 128.31 (CH), 128.15 (CH), 127.16 (CH), 127.05 (CH), 126.99 (CH), 126.36 (CH), 119.51 (CH), 119.23 (CH), 89.15 (C), 88.88 (C), 78.66 (CH), 76.44 (CH), 57.30 (CH), 54.63 (CH), 52.17 (C), 29.72 (CH), 11.61 (CH), -1.11 (CH_3); MS *m/z* (%): 484 (M^+, 6); HRMS calcd. for $C_{30}H_{29}O_2ClSi$ *m/z* 484.1625, found 484.1623. Compound **20**: mp 292-293 °C; IR (neat): 3056, 3022, 2989, 2956, 2889, 1602, 1498, 1454, 1347, 1306, 1247, 1030, 993, 864, 839, 746, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.76-7.42 (m, 4H), 7.57-7.51 (m, 4H), 7.44-7.40 (m, 2H), 7.16-7.08 (m, 4H), 4.14 (s, 1H), 4.00 (s, 1H), 3.50 (d, 1H, *J* = 6.5 Hz), 2.86 (d, 1H, *J* = 6.5 Hz), 1.19 (d, 1H, *J* = 5.8 Hz), 0.63 (d, 1H, *J* = 5.8 Hz), 0.42 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 149.35 (C), 148.87 (C), 137.06 (C), 136.90 (C), 128.72 (CH), 127.66 (CH), 126.85 (CH), 126.76 (CH), 126.24 (CH), 126.06 (CH), 118.71 (CH), 118.55 (CH), 89.83 (C), 89.68 (C), 79.77 (CH), 77.52 (CH), 57.08 (CH), 54.91 (CH), 51.53 (C), 28.49 (CH), 9.11 (CH), -1.06 (CH_3); MS *m/z* (%): 484 (M^+, 2); HRMS calcd. for $C_{30}H_{29}O_2ClSi$ *m/z* 484.1625, found 484.1621.

Reaction of 2-chloro-3-trimethylsilyl-8-oxatricyclo-[3.2.1.0^{2,4}]oct-6-ene (17) with tetrabutylammonium fluoride by VGSR

2-Chloro-3-trimethylsilyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (**17**) (4.30 g, 20.00 mmol) was passed through the column containing the solid tetrabutylammonium fluoride at room temperature. After the product had been collected onto the walls of a cold trap at -196 °C, the mixture was warmed up to room temperature. The reaction mixture was fractionated to give benzaldehyde (1.99 g, 94%).

Reaction of 2-chloro-3-trimethylsilyl-8-oxatricyclo-[3.2.1.0^{2,4}]oct-6-ene (18) with tetrabutylammonium fluoride by VGSR

2-Chloro-3-trimethylsilyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (**18**) (4.30 g, 20.00 mmol) was passed through the column containing the solid tetrabutylammonium fluoride at room temperature. After the product had been collected onto the walls of a cold trap at -196 °C, the mixture was warmed up to room temperature. The reaction mixture was fractionated to give benzaldehyde (1.95 g, 92%).

6,7-Benzo-2-chloro-3-trimethylsilyl-1,5-diphenyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (30)

1-Bromo-2,2-dichloro-3-trimethylsilylcyclopropane (4.40 g, 16.80 mmol) and diphenylisobenzofuran (5.00 g, 18.50 mmol) were dissolved in 15 mL of dry tetrahydrofuran. Methyllithium (1.5 M in ether, 17.00 mL) was added dropwise. The mixture was stirred at room temperature for 4 h. Cool the mixture to room temperature and then remove the tetrahydrofuran under reduced pressure and the residue was chromatographed (hexanes:CH_2Cl_2 = 5:1) to yield white powder **30** (4.42 g, 95%, R_f = 0.28). Compound **30**: mp 148-151 °C; IR (neat): 3070, 2958, 1608, 1450, 1242, 1190, 1024, 979, 930, 836, 748, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.80-7.77 (m, 2H), 7.61-7.58 (m, 2H), 7.49-7.42 (m, 6H), 7.28-7.24 (m, 3H), 7.10-7.11 (m, 1H), 2.10 (d, 1H, *J* = 6.2 Hz), 1.95 (d, 1H, *J* = 6.2 Hz), 0.24 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 149.87 (C), 148.14 (C), 135.59 (C), 133.52 (C), 129.45 (CH), 129.12 (CH), 128.90 (CH), 128.57 (CH), 128.07 (CH), 126.90 (CH), 126.35 (CH), 122.87 (CH), 119.93 (CH), 91.60 (C), 88.89 (C), 57.76 (C), 36.12 (CH), 24.61 (CH), -1.03 (CH_3). Anal. Calcd. for $C_{26}H_{25}OClSi$, C, 74.88; H, 6.04. Found: C, 74.86; H, 5.90. MS *m/z* (%): 628 (M+, 0.15); HRMS calcd. for $C_{26}H_{25}OClSi$ *m/z* 416.1363, found 416.1354.

Phenyl-(4-phenyl-[1]naphthyl)ketone (31)

6,7-Benzo-2-chloro-3-trimethylsilyl-1,5-diphenyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-ene (**30**) (0.5 g, 1.2 mmol) and *n*-Bu_4NF (1.0 M in THF, 0.35 mL, 1.32 mmol) were dissolved in 5 mL of dry tetrahydrofuran and refluxed for 24 h. Cool the mixture to room temperature and wash it with water and brine. The residue was chromatographed (10% EA/Hexanes) to yield white powder **31** (0.26 g, 70%, R_f = 0.23). Compound **31**: ^1H NMR ($CDCl_3$) δ 8.20-8.18 (m, 1H), 8.00-7.94 (m, 3H), 7.64-7.45 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 198.06 (C), 143.58 (C), 140.26 (C), 138.45 (C), 135.91 (C), 133.31 (CH), 132.12

(C), 131.48 (C), 130.52 (CH), 130.01 (CH), 128.54 (CH), 128.46 (CH), 127.78 (CH), 127.31 (CH), 127.11 (CH), 126.65 (CH), 126.57 (CH), 126.06 (CH), 125.45 (CH).

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Supporting Information Available

Crystal structures for compounds **19** and **30**, the ORTEP drawings of compound **19** (Fig. S1) and **30** (Fig. S2), and ^{1}H, ^{13}C, and DEPT NMR spectra for compounds **17**, **18**, **19**, **20**, **30**, and **31** (31 pages).

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