1,2-Bridged Tricyclic Cyclopropenes: Tricyclo[3.2.1.$0^{2,4}$]octa-2(4),6-diene and Tricyclo[3.2.1.$0^{2,4}$]oct-2(4)-ene

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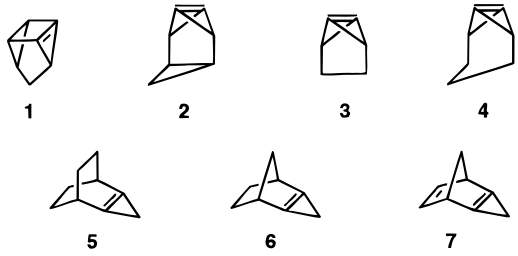
Two 1,2-bridged tricyclic cyclopropenes, tricyclo[3.2.1.$0^{2,4}$]oct-2(4)-ene (**6**) and tricyclo[3.2.1.$0^{2,4}$]octa-2(4),6-diene (**7**), have been synthesized by elimination of 2-bromo-4-chlorotricyclo[3.2.1.$0^{2,4}$]octane (**17**) and 2-bromo-4-chlorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**8**), respectively. Both **6** and **7** were trapped with diphenylisobenzofuran to form two isomers: exo-addition of cyclopropenes and exo-addition of bicyclo[2.2.1]heptenes (exo−exo adducts) and endo-addition of cyclopropenes and exo-addition of bicyclo[2.2.1]heptenes (endo−exo adducts). The stereoselectivity of the Diels−Alder reactions of **6** and **7** with DPIBF is different. The exo−exo/endo−exo ratios of **6** and **7** with DPIBF are 2/1 and 1/2, respectively. Both exo−exo adducts **12** and **18** are stable at refluxing chloroform temperature either with or without DPIBF, but endo−exo adducts **15** and **22** are unstable at room temperature and either isomerize to styrenes **13** and **19** or react with oxygen in the absence of catalyst to generate epoxides **14** and **20**. Both styrenes **13** and **19** can be photooxidized by oxygen to give epoxides **14** and **20**.

Introduction

Cyclopropene has attracted the attention of both the theoretical and the experimental chemists because of its special place as the simplest small ring cycloalkene.[1] Cyclopropene contains 27.7 kcal/mol of olefinic strain energy and 55.2 kcal/mol of strain energy;[2] therefore, it is of great interest and challenge to explore the synthesis and chemistry of cyclopropenes. Although highly strained bicyclic cyclopropenes have been studied very thoroughly,[3] the synthesis of polycyclic 1,2-bridged cyclopropenes is rare and their chemistry little understood. Pioneering work in highly strained cyclopropenes with various polycyclic frameworks done by Szeimies has led to some important studies of dehydroquadricyclane (**1**),[4] tetracyclo[4.1.0.$0^{2,4}$.$0^{3,5}$]hept-3-ene (**2**),[5] 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**).[6] Recently, tricyclic 1,2-bridged cyclopropene, tricyclo-[3.2.2.$0^{2,4}$]non-2(4)-ene (**5**), was also synthesized and trapped with 1,3-diphenylisobenzofuran (DPIBF) by Chenier,[7] but the stereochemistry of this Diels−Alder adduct was not clarified. The lower analog, tricyclo[3.2.1.$0^{2,4}$]oct-2(4)-ene (**6**), was also claimed as an intermediate by Chenier and co-workers; however, further trapping experiments with diene (DPIBF) were unable to give the pure compound for complete characterization.[8] Müehlebach and Neuenschwander also claimed to trap tricyclo-[3.2.1.$0^{2,4}$]octa-2(4),6-diene (**7**) as an intermediate with diene (DPIBF), but they only have NMR evidence for the structures of these compounds.[9]

Since cyclopropenes are reactive, the Diels−Alder reactions of cyclopropenes with dienes are well known to prove their existence.[1c,10] These reactions usually give rise to some particular types of stereoisomers attributable to the competing steric and endo effects of cyclopropenes. However, data on definition of the stereochemistry of these reactions are rare, and a rationale for it is scarcely discussed in the literature.[11] In an attempt to elucidate this issue, we have prepared highly strained 1,2-bridged tricyclic cyclopropenes, tricyclo[3.2.1.$0^{2,4}$]oct-2(4)-ene (**6**) and tricyclo[3.2.1.$0^{2,4}$]octa-2(4),6-diene (**7**), and have studied the stereochemistry of the Diels−Alder reactions of these compounds with DPIBF, the results of which are a major part of this report. Some additional chemical properties of these adducts also are reported, in which a novel epoxidation by oxygen is involved, and a photooxidation of styrenes by oxygen to generate epoxides without any catalyst is described as well.



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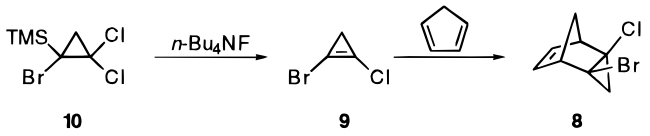
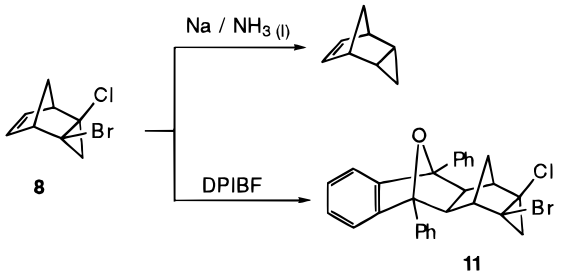
Scheme 1



Results and Discussion

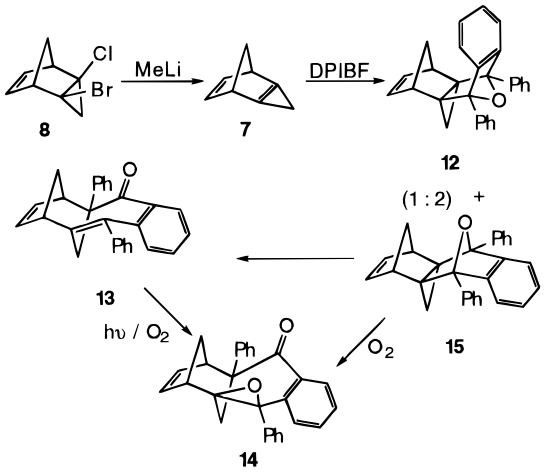
The synthesis of the starting material 2-bromo-4-chlorotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**8**) is illustrated in Scheme 1. Compound **8** is synthesized by reaction of cyclopentadiene with 1-bromo-2-chlorocyclopropene (**9**), which was generated by the fluoride-induced elimination of 1-bromo-2,2-dichloro-1-(trimethylsilyl)cyclopropane (**10**)[10a,12] in CH_2Cl_2. Only one isomer was obtained in this Diels−Alder reaction, and the stereochemistry of the product was proven by reduction of compound **8** using sodium in liquid ammonia yielding *endo*-tricyclo[3.2.1.$0^{2,4}$]-oct-6-ene[13] as the sole reaction product. An X-ray analysis of the Diels−Alder adduct **11** of **8** and DPIBF was carried out to reconfirm the stereochemistry of compound **8**. Because the C−C bond of cyclopropene is intermediate in character between σ and π, the stereoselectivity of this Diels−Alder reaction follows the endo rule.[14]

Elimination of **8** with methyllithium in ether solution yielded tricyclo[3.2.1.$0^{2,4}$]octa- 2(4),6-diene (**7**), which was trapped with DPIBF. In principle, four isomers will be formed in this Diels−Alder reaction.

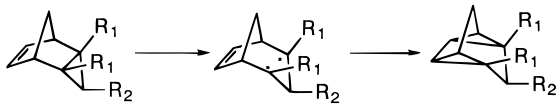


When compound **7** was synthesized and trapped by DPIBF, the adduct was purified readily by flash chromatography. According to the ^{1}H-NMR spectrum (6.18 and 6.02 ppm present olefinic protons and the ratio of adducts was 1:2), there were only two isomers formed. The mixture was allowed to stand at room temperature for several days. Only one of these two isomers (6.02 ppm) decomposed; three compounds were isolated, and their structures were shown by single-crystal X-ray analysis. One of the three compounds was formed directly from **7** and DPIBF, and the stereochemistry of this compound showed that the Diels−Alder reaction occurs via exo-addition from views of both cyclopropene and bicyclo[2.2.1]hepta-2,5-diene (exo−exo adduct **12**) (yield = 31%). Because the methylene groups of the other two compounds, styrene **13** and expoxide **14** (yields = 15% and 45%), are in an anti-conformation, these two compounds should be generated from either exo−exo adduct **12** or endo−exo (endo-addition from the view of the cyclopropene and exo-addition from the view of the bicyclo[2.2.1]hepta-2,5-diene) adduct **15**. In order to define the origin of compounds **13** and **14**, compound **12** was subjected to the reaction conditions but underwent no change. Compound **12** does not react with oxygen or rearrange in refluxing chloroform either with or without DPIBF. As a result, we conclude that compounds **13** and **14** are formed from the Diels−Alder endo−exo adduct **15** (Scheme 2).

Scheme 2



Scheme 3



The isomerizations of tricyclo[3.2.1.$0^{2,4}$]oct-6-enes to tetracyclo[3.3.0.$0^{2,7}$.$0^{4,6}$]octanes are well known, and the intermediates of these reactions are biradicals (Scheme 3).[14] House reported that 2-phenylbicyclo[3.3.1]non-1-en-3-one containing a strained double bond reacted with oxygen to form trans diol, which was formed from epoxide.[15]

On the basis of this mechanism, we propose that the isomerization of endo−exo adduct **15** to styrene **13** is via biradical **16**, which was formed from the ring opening of **15**. The mechanism of this isomerization is shown in Scheme 4. The reaction of compound **15** with oxygen to form epoxide **14** was also via the biradical **16** (Scheme 4, X = CH). If the reaction of **7** with DPIBF is conducted under nitrogen conditions, epoxide **14** is not obtained by NMR spectrum analysis. To prove that the intermediate for formation of styrene **13** and epoxide **14** is the same biradical **16**, irradiation of styrene **13** in the presence of oxygen resulted in formation of epoxide **14** in 94% isolated yield.

To study effects of the double bond at C6 and C7 in compound **7**, we synthesized compound **6**. The immediate precursor of **6**, 2-bromo-4-chlorotricyclo[3.2.1.$0^{2,4}$]octane (**17**), was prepared by hydrogenation of **8** with rhodium on carbon in methanol. Dehalogenation of **17** with methyllithium in ether solution yielded tricyclo[3.2.1.$0^{2,4}$]-oct-2(4)-ene (**6**), which was trapped with DPIBF (Scheme 5). The result is similar to that of compound **7** with

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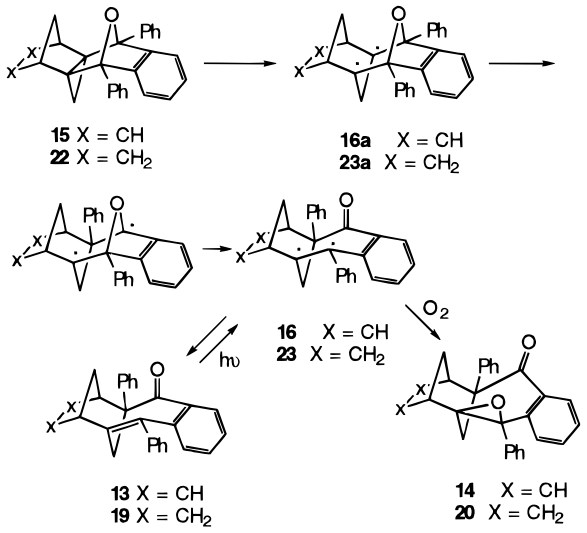
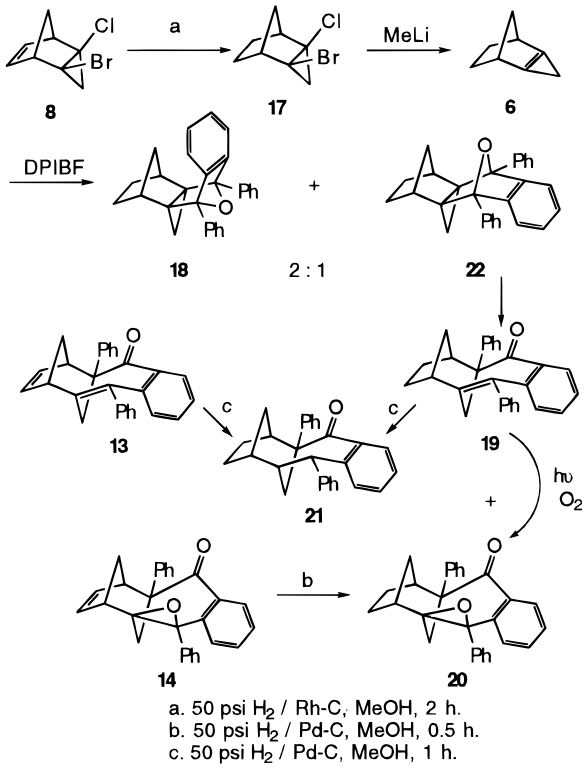
Scheme 4



Scheme 5



a. 50 psi H_2 / Rh-C, MeOH, 2 h.
b. 50 psi H_2 / Pd-C, MeOH, 0.5 h.
c. 50 psi H_2 / Pd-C, MeOH, 1 h.

DPIBF. The mixture was purified readily by flash chromatography. Three compounds, **18**, **19**, and **20**, were isolated (yields = 63, 16, and 15%), and the structure of **18** was shown by single-crystal X-ray analysis. Compound **18** was formed directly from **6** and DPIBF. The stereochemistry of **18** was similar to **12** and showed the Diels−Alder reaction proceeds via exo-addition from both views of cyclopropene and bicyclo[2.2.1]hept-2-ene (exo−exo adduct). The chemical properties of compound **18** were like **12**, and **18** was also stable and did not isomerize or react with oxygen in refluxing chloroform either with or without DPIBF. To determine the stereochemistry of **19** and **20**, we conducted the following reactions: Hydrogenation of either **13** or **19** with palladium on carbon in methanol generated the same compound **21**. Hydrogenation of epoxide **14** with palladium on carbon for 0.5 h formed epoxide **20**. Examination of these results indicates that the frames of the structures of **19** and **20** are similar to those of **13** and **14**, respectively.

Consequently, compounds **19** and **20** are formed from another Diels−Alder adduct **22**. The stereochemistry of **22** was similar to **15** and showed that the Diels−Alder reaction proceeds via endo-addition from the view of cyclopropene and exo-addition from the view of the bicyclo[2.2.1]hept-2-ene (endo−exo adduct). Surprisingly, the ratio of adducts **18** and **22** is 2:1 on the basis of NMR spectral analysis. As with the transformation of adduct **15**, the mechanism of isomerization and epoxidation of adduct **22** to give styrene **19** and epoxide **20** is via biradical **23**, which was formed from ring opening of **22**. The mechanism of this isomerization is shown in Scheme 4 (X = CH_2). When the reaction of **6** with DPIBF was conducted under nitrogen, epoxide **20** was not formed by NMR spectral analysis. To ascertain whether the intermediate to formation of styrene **19** and epoxide **20** is the same biradical **23**, photooxidation of styrene **19** in the presence of oxygen without any catalyst produced epoxide **20** in 90% isolated yield.

The theoretical calculations of the total energies of **18** and **22** are 226.8 and 232.3 kcal/mol, respectively. These results may explain why compounds **12** and **18** are stable in air even under refluxing chloroform, but **15** and **22** are unstable at room temperature. Note that compounds **15** and **22** have similar chemical properties and they undergo ring-opening reactions yielding biradicals **16** and **23**, which rearrange to **13** and **19** or react with oxygen to form epoxides **14** and **20**.

The stereoselectivity of Diels−Alder reactions of cyclopropenes with furans was seldom studied. Banwell and co-workers reported that the reaction of the 1,3-bridged cyclopropenes with furan produced endo- (minor) and exo- (major) adducts,[16] and Halton and co-workers also reported that the cyclopropenes reacted with furan and DPIBF-generated endo (minor) and exo (major) adducts.[17] In these cases, the Diels−Alder reactions favor exo-addition. It is noted, in this study, that the stereoselectivity of the Diels−Alder reactions of **6** and **7** with DPIBF is markedly different. The exo/endo (from the view of cyclopropene) ratios of **6** and **7** with DPIBF are 2/1 and 1/2, respectively. To understand this discrepancy, we carried out the single crystal X-ray analysis of **12** and **18**. The results show that the angle of $C_2-C_1-C_8$ of **12** and **18** is 101.3° and 102.3°, respectively. It is suggested that the reason for this difference is the electron-electron repulsion effect between π-electrons of C6−C7 and cyclopropane ring σ-electrons (with partial π character) of **12**.[18] We believe that the electron-electron repulsion effect between **7** and **6** is greater than that between **12** and **18**. As a result, the C8 methylene group of **7** is closer to the cyclopropene ring than that of **6**. These findings lead us to conclude that the steric effect of the benzene ring is greater than that of the oxygen atom in DPIBF due to the different ratios of adducts obtained from **6** and **7**.

In summary, the chemistry of **6** and **7** is shown in Chart 1. The syntheses of tricyclic 1,2-bridged cyclpropenes **6** and **7** are simple. Both of the Diels−Alder reactions of **6** and **7** with DPIBF form two isomers. While the former favors exo−exo addition, the latter prefers

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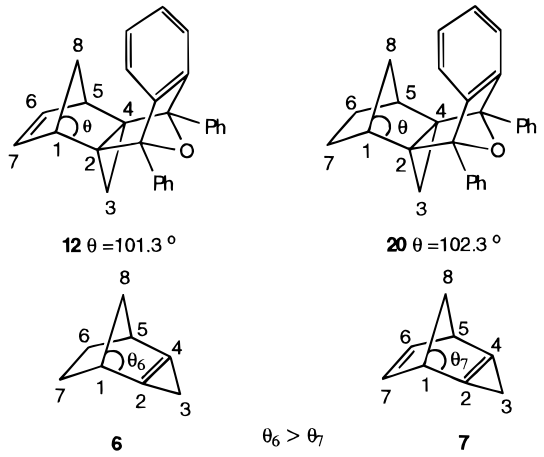
(17) Dent, B. R.; Halton, B.; Smith, A. M. F. *Aust. J. Chem.* **1986**, *39*, 1621.
(18) Ermer, O. *Tetrahedron* **1974**, *30*, 3103.

Chart 1



endo−exo addition. Both exo−exo adducts **12** and **18** are stable, but both endo−exo adducts **15** and **22** are unstable, and they either isomerize to **13** and **19** or react with oxygen without any catalyst to generate epoxides **14** and **20**.

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 Nonius CAD 4 diffractometer for compounds **12**, **13**, and **14** and a Siemens R3m/V diffractometer for compounds **11** and **18**.[19] Calculations were performed using DISCOVER Molecular Simulation Program, Version 2.95, input file for DISCOVER generated by INSIGHT. Silica gel (70−230 mesh) for column chromatography and silica gel (230 mesh) for flash chromatography are from E. Merck. Solvents are of reagent grade.

1-Bromo-2,2-dichloro-1-(trimethylsilyl)cyclopropane (10). A modification of the procedure previously reported was used.[10] A suspension of 1-bromo-1-(trimethyl)silylethene (6.0 g, 34.2 mmol) and sodium trichloroacetate (22.2 g, 0.12 mol) in 5 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 **10** (45−48 °C, 0.1 Torr, 48%). Compound **10**: ^{1}H NMR ($CDCl_3$) δ 1.94 (d, 1H, J = 8.5 Hz), 1.75 (d, 1H, J = 8.5 Hz), 0.28 (s, 9H).

2-Bromo-4-chlorotricyclo[3.2.1.0^{2,4}]oct-6-ene (8). Compound **10** (12 g, 40.5 mmol) was added at −78 °C to 10 mL of cyclopentadiene, and a solution of tetrabutylammonium fluoride (15.72 g, 60.0 mmol) in 30 mL of CH_2Cl_2 was added dropwise. The mixture was stirred at −78 °C for 0.5 h, −40 °C for 1 h, and room temperature for 12 h. Water was added, and the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The organic layer was dried, concentrated, and chromatographed (hexane) to give **8** (1.32 g, 82.3%, mp 141.0−142.0 °C). Compound **8**: IR (neat, cm^{-1}) 2961, 2924, 1637, 1262, 1098, 1022, 803, 615; ^{1}H NMR ($CDCl_3$) δ 6.12−6.05 (m, 2H), 3.23 (bs, 1H), 3.11 (bs, 1H), 2.50 (d, 1H, J = 7.5 Hz), 2.02 (d, 1H, J = 7.5 Hz), 1.87 (d, 1H, J = 7.5 Hz), 1.64 (d, 1H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 135.56 (CH), 135.30 (CH), 60.34 (CH_2), 55.50 (CH), 54.09 (CH), 51.14 (C), 41.78 (C), 38.70 (CH_2); MS m/z 220 (M^+ + 2, 0.32), 218 (M^+, 0.27), 183 (15), 139 (66), 103 (100); HRMS calcd for C_8H_8BrCl m/z 217.9498, found 217.9500.

***endo*-Tricyclo[3.2.1.0^{2,4}]octane.** Sodium (2.5 g, 109 mmol), 50 mL of ether, and 100 mL of ammonia were placed into a three-neck 250 mL flask that was fitted with an equilibrating addition funnel, a 50 mL flask containing 5 g of ammonium chloride connected by a rubber tube, a nitrogen inlet, and a magnetic stirrer. The mixture was cooled to −78 °C for 0.5 h, and then the addition funnel was charged with **8** (1.40 g, 6.40 mmol) in 30 mL of ether. Compound **8** was added dropwise. After the addition was completed, the mixture was refluxed for 4 h. Solid ammonium chloride was added until the blue color was discharged. Pentane (100 mL) was added, and the ammonia was allowed to evaporate. The organic solution was dried, concentrated, and chromatographed (pentane) to give *endo*-tricyclo[3.2.1.0^{2,4}]octane (0.66 g, 95%).

Trapping 2-Bromo-4-chlorotricyclo[3.2.1.0^{2,4}]oct-6-ene (8) with Diphenylisobenzofuran. Compound **8** (1.04 g, 4.75 mmol) and diphenylisobenzofuran (1.35 g, 5.0 mmol) were dissolved in 25 mL of dry THF. The mixture was refluxed for 0.5 h and then concentrated and chromatographed (hexane) to give **11** (2.18 g, 93.4%, mp 197.0−198.0 °C). Compound **11**: IR (neat, cm^{-1}) 3066, 2935, 1638, 1617, 1455, 1305, 769, 751, 741, 689, 685; ^{1}H NMR ($CDCl_3$) δ 7.69−7.65 (m, 4H), 7.58−7.51 (m, 4H), 7.47−7.40 (m, 2H), 7.17−7.09 (m, 4H), 2.63 (d, 1H, J = 9.5 Hz), 2.55 (bs, 1H), 2.47 (bs, 1H), 2.38−2.30 (m, 3H), 1.94 (d, 1H, J = 8.9 Hz), 1.67 (d, 1H, J = 8.9 Hz); ^{13}C NMR ($CDCl_3$) δ 148.87 (C), 136.54 (C), 128.73 (CH), 127.73 (CH), 126.86 (CH), 125.82 (CH), 118.47 (CH), 89.70 (C), 89.67 (C), 56.31 (C), 53.11 (CH), 53.03 (CH), 50.45 (CH), 49.10 (CH), 47.28 (C), 44.50 (CH_2), 38.10 (CH_2); MS m/z 490 (M^+ + 2, 0.55), 488 (M^+, 0.43), 455 (26), 453 (26), 409 (79), 283 (71), 270 (100), 239 (95), 165 (94), 105 (99); HRMS calcd for $C_{28}H_{22}BrClO$ m/z 488.0543, found 488.0540. Anal. Calcd for $C_{28}H_{22}BrClO$: C, 68.66; H, 4.53, found C, 68.50; H, 4.51.

Trapping Tricyclo[3.2.1.0^{2,4}]octa-2(4),6-diene (7) with Diphenylisobenzofuran. To a solution of compound **8** (4.48 g, 20.5 mmol) and diphenylisobenzofuran (8.10 g, 30 mmol) in 25 mL of dry THF at room temperature was added methyllithium (25 mL, 1.5 M) in ether over 10 min. The mixture was stirred for another 2 h. The mixture was readily purified by flash chromatography ($CHCl_3$), and the solution was allowed to stand at room temperature for 5 days. The solution was concentrated and chromatographed (hexanes: CH_2Cl_2 = 1:1) to give **12** (2.38 g, 31%), **13** (1.16 g, 15%), and **14** (3.60 g, 45%). Compound **12**: mp 193.5−194.5 °C; IR (neat, cm^{-1}) 3047, 2949, 2925, 1605, 1453, 1299, 755, 697; ^{1}H NMR ($CDCl_3$) δ 7.74−7.71 (m, 4H), 7.48−7.40 (m, 6H), 7.21−7.18 (m, 2H), 7.04−7.01 (m, 2H), 6.19 (d, 2H, J = 1.7 Hz), 2.86 (bs, 2H), 2.49 (dd, 1H, J = 2.7, 5.6 Hz), 2.01 (d, 1H, J = 5.6 Hz), 1.19 (d, 1H, J = 8.8 Hz), −0.13 (d, 1H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 151.01 (C), 138.34 (CH), 137.44 (C), 128.51 (CH), 128.48 (CH), 128.36 (CH), 126.90 (CH), 120.77 (CH), 91.33 (C), 59.96 (CH_2), 43.59 (CH), 39.47 (C), 33.01 (CH_2); MS m/z 374 (M^+, 74), 375 (M^+ + 1, 23), 307 (92), 285 (100); HRMS calcd for $C_{28}H_{22}O$ m/z 374.1671, found 374.1672. Compound **13**: mp 183.5−184.5 °C; IR (neat, cm^{-1}) 3065, 2980, 1670, 1650, 740, 730, 700, 695; ^{1}H NMR ($CDCl_3$) δ 7.49−7.13 (m, 13H), 6.98 (d, 1H, J = 7.7 Hz), 6.27 (dd, 1H, J = 2.8, 5.6 Hz), 6.11 (dd, 1H, J = 2.6, 5.6 Hz), 3.65−3.61 (m, 3H), 3.00 (d, 1H, J = 12 Hz), 2.08−2.01 (m, 1H), 1.88 (d, 1H, J = 10 Hz); ^{13}C NMR ($CDCl_3$) δ 211.65 (C), 143.62 (C), 143.29 (C), 141.24 (C), 140.96 (C), 140.23(C), 137.08 (CH), 136.89 (C), 136.14 (CH), 130.93 (CH), 130.10 (CH), 130.03 (CH), 128.58 (2 × CH), 128.36 (CH), 127.89 (CH), 127.28 (CH), 127.12 (CH), 126.53 (CH), 67.27 (C), 51.30 (CH_2), 51.01 (CH), 47.36 (CH), 37.62 (CH_2); MS m/z 374 (M^+, 100), 375 (M^+ + 1, 30), 308 (9), 155 (230); HRMS calcd for $C_{28}H_{22}O$ m/z 374.1671, found 374.1673. Compound **14**: mp 234.0−235.0 °C; IR (neat, cm^{-1}) 3100, 2945, 1685, 1580; ^{1}H NMR ($CDCl_3$) δ 7.47−7.16 (m, 14H), 6.30 (dd, 1H, J = 2.9, 5.7 Hz), 6.01 (dd, 1H, J = 2.8, 5.7 Hz), 3.73 (bs, 1H), 2.84 (d, 1H, J = 13 Hz), 2.40 (bs, 1H), 2.12 (d, 1H, J = 13 Hz), 1.81 (t, 2H, J =3.5 Hz); ^{13}C NMR ($CDCl_3$) δ 211.64 (C), 141.30 (C), 140.23

(19) The author has deposited atomic coordinates for **11**, **12**, **16**, **17**, and **20** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(C), 138.74 (C), 137.26 (C), 136.07 (CH), 135.98 (CH), 131.93 (CH), 129.94 (CH), 129.10 (CH), 128.68 (CH), 128.46 (CH), 128.14 (CH), 127.95 (CH), 127.73 (CH), 127.29 (CH), 126.53 (CH), 64.42 (C), 66.62 (C), 56.92 (C), 48.63 (CH), 44.03 (CH_2), 42.23 (CH), 38.46 (CH_2); MS *m/z* 390 (M^+, 14), 296 (47), 258 (37), 194 (100), 165 (45); HRMS calcd for $C_{28}H_{22}O_2$ *m/z* 390.1620, found 390.1625.

Epoxidation of Compound 13. A solution of **13** (503 mg, 1.34 mmol) in 10 mL of $CDCl_3$ was purged with oxygen and irradiated with a UVP BLAKRAY Longwave Ultraviolet Lamp Model B 100 AP. After 24 h of irradiation, the reaction mixture was concentrated, and residue was purified by flash chromatography (dichloromethane:hexanes = 1:1) to give **14** (492 mg, 94%).

2-Bromo-4-chlorotricyclo[3.2.1.0^{2,4}]octane (17). A solution of **8** (5.31 g, 24.2 mmol) in 20 mL of methanol was reduced over 5% Rh/C at 50 psi for 2 h. After filtration, the solvent was removed in vacuo and the residue was purified by column chromatography (hexane) to give **17** (5.25 g, 98%). Compound **17**: mp 50.5−51.0 °C; IR (neat, cm^{-1}) 2963, 2930, 1260, 1109, 1089, 1026, 813, 577; ^{1}H NMR ($CDCl_3$) δ 2.73 (bs, 1H), 2.64 (bs, 1H), 2.07 (d, 1H, J = 8.0), 2.40−2.35 (m, 1H), 1.70 (d, 1H, J = 8.0), 1.53−1.45 (m, 2H), 1.36−1.32 (m, 1H), 1.26−1.20 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 55.71 (C), 49.68 (CH), 48.26 (CH), 48.09 (CH_2), 46.50 (C), 38.48 (CH_2), 26.06 (CH_2), 25.96 (CH_2); MS *m/z* 222 (M^+ + 2, 0.14), 220 (M^+, 0.10), 185 (24), 157 (49), 141 (77), 113 (100), 105 (99); HRMS calcd for $C_8H_{10}BrCl$ *m/z* 219.9654, found 219.9648.

Trapping Tricyclo[3.2.1.0^{2,4}]oct-2(4)-ene (6) with Diphenylisobenzofuran. To a solution of compound **17** (2.52 g, 11.4 mmol) and diphenylisobenzofuran (4.05 g, 15 mmol) in 25 mL of dry THF at room temperature was added methyllithium (20 mL, 1.5 M) in ether over 10 min. The mixture was stirred for another 2 h. The mixture was purified by readily by flash chromatography ($CHCl_3$), and the solution was allowed to stand at room temperature for 5 days. The solution was concentrated and chromatographed (hexanes: CH_2Cl_2 = 1:1) to give **18** (2.70 g, 63%), **19** (0.68 g, 16%), and **20** (0.67 g, 15%). Compound **18**: mp 193.5−194.5 °C; IR (neat, cm^{-1}) 2959, 2939, 2880, 1684, 1447, 1294, 993, 981, 767, 747, 699; ^{1}H NMR ($CDCl_3$) δ 7.74−7.71 (m, 4H), 7.47−7.40 (m, 6H), 7.20−7.17 (m, 2H), 7.01−6.98 (m, 2H), 2.45−2.39 (m, 3H), 1.79 (d, 1H, J = 3.1 Hz), 1.48−1.38 (m, 4H), 0.80 (d, 1H, J = 10.3 Hz), −0.23 (d, 1H, J = 10.3 Hz); ^{13}C NMR ($CDCl_3$) δ 150.73 (C), 137.38 (C), 128.72 (CH), 128.46 (CH), 128.34 (CH), 126.79 (CH), 120.61 (CH), 91.56 (C), 51.12 (CH_2), 43.62 (C), 37.79 (CH), 32.00 (CH_2), 29.76 (CH_2); MS *m/z* 376 (M^+, 100), 330 (60), 271 (62); HRMS calcd for $C_{28}H_{24}O$ *m/z* 376.1827, found 376.1822. Compound **19**: mp 217.0−218.0 °C; IR (neat, cm^{-1}) 3050, 2980, 2850, 1682, 1603, 780, 749, 699; ^{1}H NMR ($CDCl_3$) δ 7.52−7.48 (m, 2H), 7.42−7.05 (m, 10H), 7.04−7.02 (m, 1H), 6.95 (d, 1H, J = 7.5 Hz), 3.58 (d, 1H, J = 12.3 Hz), 3.40−3.37 (m, 1H), 3.30−3.26 (m, 1H), 2.72 (d, 1H, J = 12.3 Hz), 1.97−1.50 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 211.31 (C), 145.41 (C), 142.91 (C), 141.80 (C), 140.98 (C), 140.26 (C), 133.17 (C), 130.87 (CH), 130.09 (CH), 129.81 (CH), 128.45 (CH), 128.25 (CH), 127.86 (CH), 127.70 (CH), 127.18 (CH), 127.07 (CH), 69.44 (C), 46.16 (CH), 44.78 (CH_2), 42.25 (CH), 35.04 (CH_2), 27.77 (CH_2), 27.53 (CH_2); MS *m/z* 378 (M^+, 7), 194 (93), 183 (100), 165 (54), 155 (71); HRMS calcd for $C_{28}H_{24}O$ *m/z* 376.1827, found 376.1821. Compound **20**: mp 230.0−231.0 °C; IR (neat, cm^{-1}) 3060, 2954, 2883, 1680, 781, 749, 701; ^{1}H NMR ($CDCl_3$) δ 7.45−7.20 (m, 13H), 7.05−7.02 (m, 1H), 3.32−3.30 (m, 1H), 2.60 (d, 1H, J = 13.4 Hz), 2.16−1.62 (m, 6H), 1.42−1.33 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 211.68 (C), 140.07 (C), 139.84 (C), 138.75 (C), 137.72 (C), 131.92 (CH), 129.59 (CH), 128.93 (CH), 128.59 (CH), 127.99 (CH), 127.89 (CH), 127.53 (CH), 127.28 (CH), 127.16 (CH), 72.60 (C), 65.72 (C), 60.58 (C), 43.82 (CH), 37.55 (CH), 37.31 (CH_2), 36.18 (CH_2), 27.02 (CH_2), 26.81 (CH_2); MS *m/z* 392 (M^+, 58), 378 (29), 270 (55), 194 (100), 165 (57); HRMS calcd for $C_{28}H_{24}O_2$ *m/z* 392.1776, found 392.1778.

Hydrogenation of Compound 13. A solution of **13** (1.01 g, 2.7 mmol) in 20 mL of methanol was reduced over 5% Pd/C at 50 psi for 1 h. After filtration, the solvent was removed in vacuo, and the residue was purified by column chromatography (hexane) to give **21** (0.98 g, 97%). Compound **21**: mp 185.0−186.0 °C; IR (neat, cm^{-1}) 3055, 3015, 2940, 2872, 1660, 1285, 1203, 755, 605; ^{1}H NMR ($CDCl_3$) δ 7.57−7.54 (m, 1H), 7.40−7.13 (m, 13H), 5.17 (d, 1H, J = 10.4 Hz), 3.43−3.41 (m, 1H), 2.75−2.68 (m, 2H), 2.24−2.17 (m, 1H), 1.80−1.61 (m, 5H), 1.47−1.40 (m, 1H), 1.26−1.22 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 211.79 (C), 144.64 (C), 144.21 (C), 142.07 (C), 139.10 (C), 133.74 (CH), 131.84 (CH), 131.19 (CH), 129.62 (CH), 128.42 (CH), 128.05 (CH), 126.77 (CH), 126.66 (CH), 126.50 (CH), 125.96 (CH), 58.53 (C), 55.87 (CH), 42.84 (CH), 42.05 (CH), 36.79 (CH), 33.40 (CH_2), 31.36 (CH_2), 30.47 (CH_2), 25.90 (CH_2); MS *m/z* 378 (M^+, 7), 194 (93), 183 (100), 165 (54), 155 (71); HRMS calcd for $C_{28}H_{24}O$ *m/z* 378.1984, found 378.1987.

Hydrogenation of Compound 19. A solution of **19** (0.84 g, 2.2 mmol) in 20 mL of methanol was reduced over 5% Pd/C at 50 psi for 1 h. After filtration, the solvent was removed in vacuo, and the residue was purified by column chromatography (hexane) to give **21** (0.81 g, 96%).

Hydrogenation of Compound 14. A solution of **14** (0.98 g, 2.5 mmol) in 20 mL of methanol was reduced over 5% Pd/C at 50 psi for 0.5 h. After filtration, the solvent was removed in vacuo, and the residue was purified by column chromatography (hexane) to give **20** (0.91 g, 92%).

Epoxidation of Compound 19. A solution of **19** (515 mg, 1.37 mmol) in 10 mL of $CDCl_3$ was purged with oxygen and irradiated with a UVP BLAKRAY Longwave Ultraviolet Lamp Model B 100 AP. After 24 h of irradiation, the reaction mixture was concentrated, and residue was purified by flash chromatography (dichloromethane:hexanes = 1:1) to give **20** (483 mg, 90%).

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Supporting Information Available: Crystal structures for **11**, **12**, **13**, **14**, and **18**, and ^{1}H and ^{13}C NMR spectra for compounds **8**, **11**, **12**, **13**, **14**, **17**, **18**, **19**, **20**, and **21** (35 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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