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The Synthesis of Highly Strained Buttaflanes with Aromatic Rings

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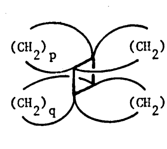
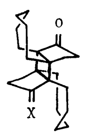
Dibenzo[4.4.2.2]buttaflanes, *syn*-13,14:15,16-dibenzopentacyclo$[6.4.2.2^{2,7}.0^{1,8}.0^{2,7}]$hexadeca-13,15-diene, and *syn*-13,14:15,16-dibenzohexacyclo$[6.4.2.2^{2,7}.0^{1,8}.0^{2,7}.0^{3,12}]$hexadeca-13,15-diene, were synthesized by the intramolecular photocycloaddition of the dibenzo[*a*,*e*]cyclooctene derivatives, *syn*-13,14:15,16-dibenzotricyclo$[6.4.2.2^{2,7}]$hexadeca-1,7,13,15-tetraene and *syn*-13,14:15,16-dibenzotetracyclo$[6.4.2.2^{2,7}.0^{3,12}]$hexadeca-1,7,13,15-tetraene, which had themselves been derived by the catalytic hydrogenation of the biphenylene photodimer, *syn*-13,14:15,16-dibenzotricyclo$[6.4.2.2^{2,7}]$hexadeca-1,3,5,7,9,11,13,15-octaene, and the pentacyclic compound, *syn*-13,14:15,16-dibenzopentacyclo$[6.4.2.2^{2,7}.0^{3,12}.0^{4,11}]$hexadeca-1,5,7,9,13,15-hexaene, respectively.

The synthesis of strained compounds showing unusual chemical and physical properties has been of considerable interest.1) As a part of our studies of the synthesis of a novel polycarbocyclic ring system, we ourselves have previously reported the synthesis of buttaflane (**1**),2) wherein two propellane units share a cyclobutane ring.3) The present [6.3.6.3]buttaflane (**1a**) had its long bonds in the planar cyclobutane ring,4) and, concerning anomalous chemical behavior, a remarkably large rate constant was observed in the chromium trioxide oxidation of **1b**.5) These noteworthy aspects are considered to be due to the nonbonded interaction of hydrogens between alicyclic rings facing each other. Therefore, when aromatic rings facing each other are incorporated into a buttaflane framework, it is very interesting to see if this buttaflane exhibits some *π*-*π* interaction,6) as do cyclophanes7) or janusenes,8) in association with the closeness of the two facing benzene rings. However, what was, to the best of our knowledge, the first attempt to synthesize buttaflane with aromatic rings facing each other was unsuccessful.9) That is, the direct or sensitized photolysis of 9,9′,10,10′-tetradehydrobi(9,10-anthrylene) (**18**) provided no evidence for the formation of tetrabenzo[2.2.2.2]buttaflane. In this connection, we wish now to report the synthesis of new highly strained buttaflanes with aromatic rings facing each other, and the related compounds.



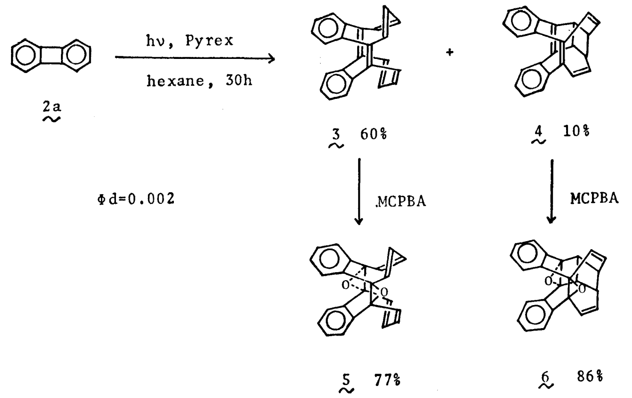
[m.n.p.q]Buttaflane



1 a: X=O
b: X=H,OH

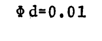
[6.3.6.3]Buttaflane

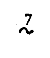
In this successful approach to the synthesis of buttaflanes, we make use of the ready photodimerization of biphenylene (**2a**). On the irradiation of biphenylene (**2a**)10) in hexane through a Pyrex filter for 30 h, a *syn*-photodimer (**3**), with the dibenzo[*a*,*e*]cyclooctene structure, was obtained in a 60% yield, along with the pentacyclic compound (**4**, 10%). In this photoreaction, no *anti*-photodimer was detected at all. This *syn*-photodimer (**3**) might be formed from the excimer of biphenylene (**2a**), though the emission of the excimer fluorescence could not be observed. The quantum yield for the disappearance of biphenylene (**2a**) was 0.002.



In 1968, Goldman *et al.* reported erroneously that the biphenylene photodimer was buttaflane (**7**) and also that the octahydrogenated biphenylene photodimer was buttaflane (**19**).11) Afterward, as we were conducting our investigation, they corrected the structure of the octahydro dimer to correspond to ours (**9**) as a result of X-ray study,12) and Nishida and Furusaki *et al.* reported independently, also as a result of X-ray analysis, that the biphenylene photodimer had the same structure as ours (**3**).13) Significantly, in their photoreactions of biphenylene (**2a**), these two groups did not mention at all the formation of the pentacyclic compound (**4**), the intramolecular photocycloadduct of two peripheral double bonds of the biphenylene photodimer (**3**). In order to confirm the structures of **3** and **4**, epoxidation was examined. The epoxidation of **3** and **4** with *m*-chloroperbenzoic acid took place preferentially at two bridgehead double bonds to give the diepoxides, **5** and **6**, respectively.

Conceivably, the shortest way to the synthesis of buttaflanes is the intramolecular photocycloaddition of the respective two bridgehead double bonds of **3** and **4**. Unfortunately, the direct irradiation of **3** gave no buttaflane (**7**), but only biphenylene (**2a**) and the pentacyclic compound (**4**). The quantum yield for the disappearance of **3** was 0.01. A quenching experiment using 1,3-pentadiene and a sensitizing ex-





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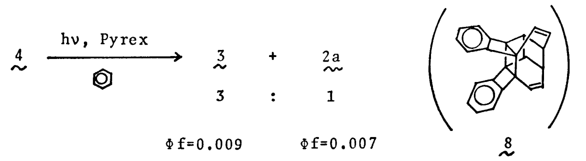
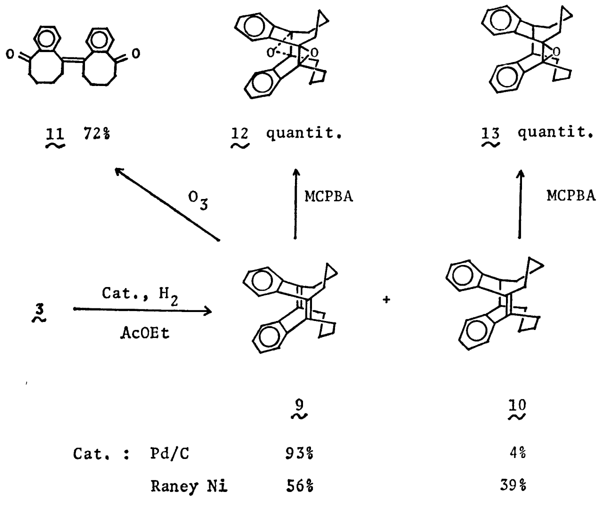
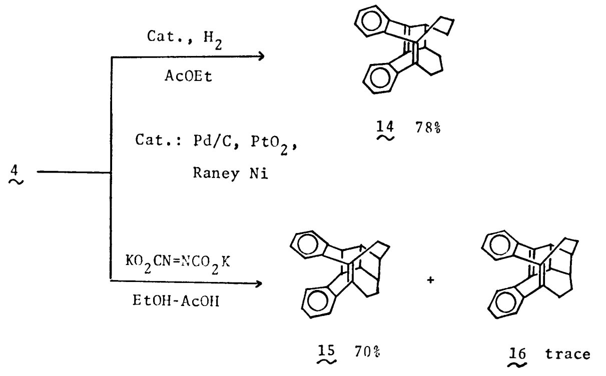
periment using acetone showed no effect on the formation of **4** and **2a**, indicating that this photoreaction proceeded *via* the singlet or unquenchable triplet state.

In the similar irradiation of **4**, cycloreversion took place to give **3** and **2a**, without any formation of buttaflane (**8**). The quantum yields for formation of **3** and **2a** were 0.009 and 0.007 respectively. These results obviously show that **2a**, **3**, and **4** are in a photostationary state. When **2a** was irradiated for 150 h, the ratio of **2a**, **3**, and **4** was 5:1:3. Moreover, the thermal cycloreversion of **4** to **3** also occurred above 180 °C.

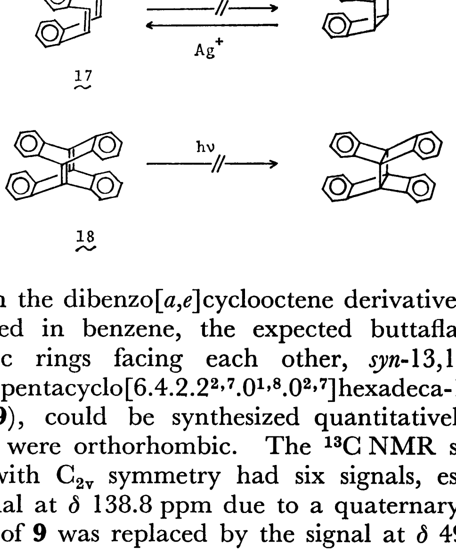


In the attempt at the one-step synthesis of buttaflanes (**7**) and (**8**) from **3** and **4**, some unfavorable reactions took place exclusively, as has been described above. Therefore, the selective hydrogenation of each peripheral double bond of **3** and **4** was attempted for the purpose of the photochemical synthesis of buttaflanes *via* **3** and **4**. The catalytic hydrogenation of **3** with Pd/C in ethyl acetate gave the desired octahydrogenated compound (**9**) retaining two bridgehead double bonds, along with a small amount of the decahydrogenated compound (**10**). In contrast, when Raney Ni was used as a catalyst, the decahydrogenated compound (**10**) was formed predominantly. The structure of dibutano-bridged dibenzo[*a*,*e*]cyclooctene (**9**) was confirmed by ozonolysis to give the diketone (**11**).[14] The epoxidation of **9** and **10** gave the corresponding diepoxide (**12**) and monoepoxide (**13**) quantitatively. On the other hand, the pentacyclic compound (**4**) was hydrogenated with Pd/C, Raney Ni, or PtO_2 to give the tetracyclic compound (**14**), accompanied by the reductive cleavage of one bond of the cyclobutane ring. In the case of the diimide reduction of **4** using potassium azodicarboxylate, the hexahydrogenated compound (**15**) was obtained in a 70% yield, together with a trace of a tetrahydrogenated compound (**16**) retaining two bridgehead double bonds.

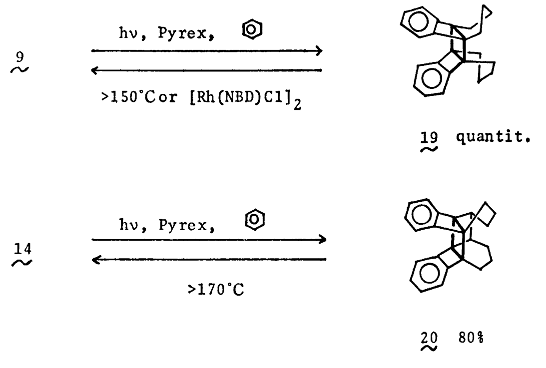




The photochemical behavior of dibenzo[*a*,*e*]cyclooctene derivatives (**9**) and (**14**), in which the central cyclooctatetraene ring takes a tub form and the two bridgehead double bonds are forced by their geometry to interact with each other, is of considerable interest in comparison with that of the fairly planar dibenzo[*a*,*e*]cyclooctene (**17**)[15] or similar tub-form compounds such as 9,9′,10,10′-tetradehydrobi(9,10-anthrylene) (**18**).[9]



When the dibenzo[*a*,*e*]cyclooctene derivative (**9**) was irradiated in benzene, the expected buttaflane with aromatic rings facing each other, *syn*-13,14:15,16-dibenzopentacyclo[6.4.2.$2^{2,7}$.$0^{1,8}$.$0^{2,7}$]hexadeca-13,15-diene (**19**), could be synthesized quantitatively. The crystals were orthorhombic. The ^{13}C NMR spectrum of **19** with C_{2v} symmetry had six signals, especially, the signal at δ 138.8 ppm due to a quaternary olefinic carbon of **9** was replaced by the signal at δ 49.3 ppm, based on the newly formed cyclobutane ring carbon. Similarly, the more highly strained cage buttaflane, *syn*-13,14:15,16-dibenzohexacyclo[6.4.2.$2^{2,7}$.$0^{1,8}$.$0^{2,7}$.$0^{3,12}$]hexadeca-13,15-diene (**20**), was synthesized in an



80% yield by the intramolecular photocycloaddition of **14**.

While it has been reported that the intramolecular [2+2]photocycloaddition of dibenzo[*a*,*e*]cyclooctene (**17**)[15] did not occur, the similar photocycloaddition of **9** and **14** to **19** and **20** took place excellently. This is probably because the two tetramethylene bridges between two bridgehead double bonds in **9** or **14** enforce the relatively small double-bond separations, as well as their parallel orientations,[13,16] which are preferable for photocycloaddition. On the other hand, the failure of the [2+2]photocycloaddition of the similar tub-form compound (**18**) may be attributed to the remarkable instability of the [2.2.2.2]buttaflane moiety of the supposed adduct.[17]

As expected, the tricyclo[4.2.0.0^{2,5}]octa-3,7-diene moiety in buttaflane (**19**) can be opened to **9** quantitatively by reaction with a catalytic amount of [Rh(NBD)Cl]$_2$(NBD=norbornadiene) or above 150 °C.[18] Similarly, the thermal cleavage of cage buttaflane (**20**) occurred to afford **14** almost quantitatively above 170 °C.

Attributable to the transannular π-π interaction, the aromatic ring protons of **19** and **20** in ^{1}H NMR appeared to show a somewhat high-field shift, and the electronic spectra of these compounds showed bathochromic and hyperchromic shifts. It is interesting that these interactions of **19**, **20**, and the cage compound (**21**)[19] successively decrease with an increase in the rigidity of the structure, as is shown by their UV spectra. An X-ray study of buttaflanes (**19**) and (**20**) will now be undertaken.

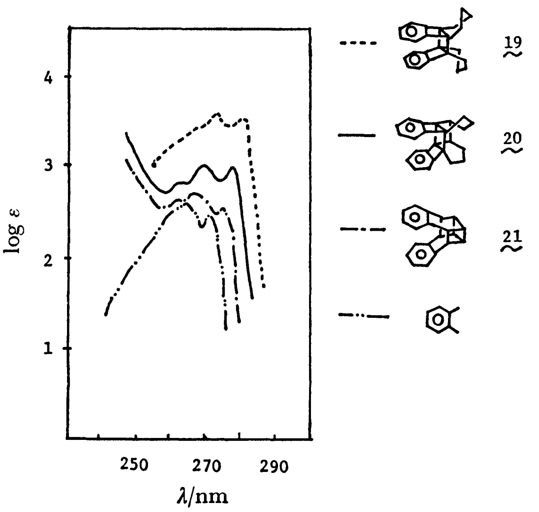


Fig. 1. UV spectra (in CH$_3$CN).

Experimental

The melting points are uncorrected. The infrared spectra were recorded on a JASCO IR-G spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were obtained on JEOL JNM-PS-100 and JEOL JNM-FX60S spectrometers respectively, using CDCl$_3$ as the solvent and Me$_4$Si as the internal standard. The mass spectra were determined with a Hitachi RMU-6E spectrometer. The UV spectra were recorded on a Hitachi 356 spectrometer. Analytical GLC was carried out on a Hitachi 163 gas chromatograph, while preparative GLC separation was undertaken on a Varian Aerograph 90-P gas chromatograph.

Materials. The biphenylene (**2a**) was prepared according to the method of Friedman.[20] The 2-acetyl- (**2b**),[21] 2-methoxy- (**2c**),[22] and 2-cyanobiphenylenes (**2d**)[21] were prepared by a modification of the method of McOmie.

Photoreaction of Biphenylene (2a). A hexane solution of **2a** (0.04 mol dm^{-3}) was irradiated through a Pyrex filter at room temperature for 30 h using 500-W high-pressure mercury lamp. After the solvent had evaporated, the residue was chromatographed on silica gel with petroleum ether to elute biphenylene (**2a**), the pentacyclic compound (**4**, 10%), and the biphenylene photodimer (**3**, 60%), in this order (conv. 43%). When benzene, ether, or acetonitrile was used as the solvent, the yields of the biphenylene photodimer (**3**, 50—60%) and the pentacyclic compound (**4**, 8—15%) were somewhat similar to that of hexane (conv. 30—40%). Further irradiation gave rise to an increase in the formation of **4** and the decrease in that of **3**. After 150 h, the ratio of **2a**, **3**, and **4** was 5:1:3. In addition, when compounds **3** and **4** were allowed to stand for a long time on exposure to air, the diene moieties of **3** and **4** were easily oxidized. **3**; mp 247—252 °C decomp; Mass (*m*/*e*) 304 (M$^+$); UV (CH$_3$CN) λ 310 nm (ε, 1555); ^{1}H NMR (CDCl$_3$) δ 5.54—5.76 (m, 4H), 6.19—6.41 (m, 4H), 7.03 (s, 8H); ^{13}C NMR (CDCl$_3$) δ 124.0 (d), 125.0 (d), 127.1 (d), 134.6 (d), 140.4 (s), 141.2 (s); Found: C, 94.57; H, 5.27%. Calcd for C$_{24}$H$_{16}$: C, 94.70; H, 5.30%. **4**; mp 178—179 °C; Mass (*m*/*e*) 304 (M$^+$); UV (CH$_3$CN) λ 276 nm (ε, 1094), 267 (1600); ^{1}H NMR (CDCl$_3$) δ 3.32—3.52 (m, 2H), 3.68—3.80 (m, 2H), 5.20—5.54 (m, 2H), 6.45 (d, 2H), 6.92—7.20 (m, 8H); ^{13}C NMR (CDCl$_3$) δ 38.7 (d), 45.7 (d), 124.1 (d), 126.5 (d), 126.6 (d), 126.9 (d) 127.6 (d), 137.5 (s), 137.7 (s), 138.5 (d), 146.4 (s), 151.8 (s); Found: C, 94.83; H, 5.20%. Calcd for C$_{24}$H$_{16}$: C, 94.70; H, 5.30%.

Photoreaction of 2-Acetyl-(2b) or 2-Methoxybiphenylene (2c). A hexane solution (4.2×10^{-3} mol dm^{-3}) of 2-acetyl-(**2b**) or 2-methoxybiphenylene (**2c**) was irradiated under conditions similar to those used for biphenylene (**2a**). After the removal of the solvent, the residue was chromatographed to recover unreacted 2-acetyl- or 2-methoxybiphenylene almost quantitatively.

Photoreaction of 2-Cyanobiphenylene (2d). A hexane solution of 2-cyanobiphenylene (**2d**) (3.5×10^{-3} mol dm^{-3}) was irradiated for 50 h. After the removal of the solvent, the residue was chromatographed to give the photodimer (**3d**, 24%) and some polymeric compounds (conv. 35%). This photodimer (**3d**) was labile and readily reacted with atmospheric oxygen to give a new substance in a deuteriochloroform solution. This compound was found to have four oxygens, but the structure had not yet been determined. **3d**; mp 215—220 °C decomp; IR 2200 cm^{-1}; Mass (*m*/*e*) 354 (M$^+$); UV (CH$_3$CN) no maximum, but the end absorption is at 390 nm; ^{1}H NMR (CDCl$_3$) δ 5.64—5.84 (m, 4H), 6.22—6.56 (m, 4H), 7.02—7.45 (m, 6H); ^{13}C NMR (CDCl$_3$) δ 146.8, 147.6 (quaternary olefinic carbon).

Photoreaction of Biphenylene Dimer (3). A degassed benzene solution of the biphenylene dimer (**3**) (1.5×10^{-3} mol dm^{-3}) was irradiated in a sealed Pyrex tube at room temperature for 5 h. After the removal of the benzene, the residue was chromatographed on silica gel. Elution with petroleum ether afforded biphenylene (**2a**, 11%) and the pentacyclic compound (**4**, 88%) (conv. 91%).

Photoreaction of Pentacyclic Compound (4). The irradiation of a degassed benzene solution of **4** (1.5×10^{-3} mol dm^{-3}) in a sealed Pyrex tube for 3 h gave no buttaflane (**8**), but biphenylene (**2a**, 23%) and the biphenylene photodimer

(**3**, 69%) (conv. 36%).

*Epoxidation of **3**.* To a dichloromethane solution (50 ml) of **3** (1 mmol) was added *m*-chloroperbenzoic acid (2.2 mmol) in dichloromethane (30 ml). The mixture was stirred at 20 °C for 48 h. The excess peracid was then destroyed by the addition of 10% sodium sulfite. The reaction mixture was washed with a 5% sodium hydrogencarbonate solution to extract the *m*-chlorobenzoic acid, followed by washing with water and finally with a saturated sodium chloride solution. The organic layer was dried and stripped of the solvent. The residue was chromatographed on silica gel with petroleum ether/ether (10/1) to give the diepoxide (**5**) in a 77% yield. **5**; mp 255—257 °C decomp; Mass (*m*/*e*) 336 (M^+); UV (CH_3CN) λ 275 nm (ε, 2447), 248 (4404); ^1H NMR ($CDCl_3$) δ 5.80 (s, 8H), 7.06—7.25 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 68.3 (s), 124.4 (d), 125.0 (d), 128.3 (d), 134.1 (d), 134.3 (s); Found: C, 85.60; H, 4.56%. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79%.

*Epoxidation of **4**.* The procedure described above was carried out to give the diepoxide (**6**) in an 86% yield. **6**; mp 234—236 °C decomp; Mass (*m*/*e*) 336 (M^+); UV (CH_3CN) λ 269 nm (ε, 315), 263 (396), 257 (360); ^1H NMR ($CDCl_3$) δ 3.36—3.52 (m, 2H), 3.76—3.96 (m, 2H), 5.24—5.42 (m, 2H), 6.32 (d, 2H), 7.04—7.44 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 39.7 (d), 47.9 (d), 67.7 (s), 69.4 (s), 124.9 (d), 125.2 (d), 127.8 (d), 128.8 (d), 129.0 (d), 131.2 (d), 135.4 (s), 138.4 (s); Found: C, 85.62; H, 4.62%. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79%.

*Catalytic Reduction of **3**.* A suspension of **3** (2 mmol) and Pd/C in ethyl acetate (30 ml) was reduced at room temperature during 3 d. After the removal of the catalyst and the solvent, the residue was chromatographed on silica gel. Elution with petroleum ether gave the octahydrogenated compound (**9**, 93%) and the decahydrogenated compound (**10**, 4%). In contrast, when Raney Ni (W7) was used as the catalyst, **10** was obtained in a 39% yield, along with **9** in a 56% yield. **9**; mp 182.5—183.5 °C; Mass (*m*/*e*) 312 (M^+); UV (CH_3CN) λ 276 nm (ε, 788), 268 (1089); ^1H NMR ($CDCl_3$) δ 1.30—1.92 (m, 8H), 1.95—2.41 (m, 4H), 2.55—2.87 (m, 4H), 6.68—6.95 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 28.4 (t), 33.3 (t), 124.5 (d), 126.2 (d), 138.8 (s), 145.0 (s); Found: C, 92.10; H, 7.88%. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74%. **10**; mp 182—183 °C; Mass(*m*/*e*) 314 (M^+); ^1H NMR ($CDCl_3$) δ 1.0—2.28 (m, 10H), 2.28—2.65 (m, 4H), 2.70—3.20 (m, 2H), 3.51—3.76 (m, 2H), 6.62—7.05 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 25.6 (t), 26.6 (t), 32.2 (t), 32.6 (t), 48.7 (d), 125.8 (d), 126.1 (d), 126.2 (d), 126.5 (d), 129.4 (s), 137.4 (s), 144.4 (s); Found: C, 91.57; H, 8.15%. Calcd for $C_{24}H_{26}$: C, 91.67; H, 8.33%.

*Epoxidation of **9**.* The procedure described above was carried out to give the diepoxide (**12**) quantitatively. **12**; mp 219—222 °C decomp; Mass (*m*/*e*) 344 (M^+); UV (CH_3CN) λ 276 nm (ε, 147), 266 (178), 263 (184); ^1H NMR ($CDCl_3$) δ 1.20—2.43 (m, 16H), 6.96—7.20 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 24.1 (t), 35.4 (t), 69.6 (s), 125.5 (d), 127.7 (d), 138.2 (s); Found: C, 83.38; H, 6.97%. Calcd for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02%.

*Epoxidation of **10**.* A dichloromethane solution of *m*-chloroperbenzoic acid (1.2 mmol) was added to a dichloromethane solution of **10** (1 mmol). A monoepoxide (**13**) was thus obtained quantitatively. **13**; mp 180—181 °C; Mass (*m*/*e*) 330 (M^+); UV (CH_3CN) λ 274 nm (ε, 493), 266 (578), 261 (548); ^1H NMR ($CDCl_3$) δ 1.21—2.64 (m, 16H), 3.33—3.62 (m, 2H), 6.63—7.16 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 22.9 (t), 25.6 (t), 32.0 (t), 32.3 (t), 49.6 (d), 72.6 (s), 126.0 (d), 126.3 (d), 127.0 (d), 129.7 (d), 140.5 (s), 141.5 (s); Found: C, 86.90; H, 7.93%. Calcd for $C_{24}H_{26}O$: C, 87.23; H, 7.93%.

*Ozonolysis of **9**.* Ozone was passed through a solution of **9** (1 mmol) in ethyl acetate (30 ml) for 30 min at −78 °C. The ozonide residue was then reduced with Pd/C at room temperature for 24 h. After the subsequent removal of the catalyst and solvent, the residue was chromatographed on silica gel with petroleum ether/ether (7/3) to give the diketone (**11**) in a 72% yield. **11**; mp 171—172 °C; Mass (*m*/*e*) 344 (M^+); ^1H NMR ($CDCl_3$) δ 1.52—2.08 (m, 8H), 2.80 (t, 4H), 3.30 (t, 4H), 6.52—6.68 (m, 2H), 6.95—7.25 (m, 4H), 7.82—8.05 (m, 2H); Found: C, 83.69; H, 6.99%. Calcd for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02%.

*Catalytic Reduction of **4**.* Using Pd/C, Raney-Ni (W7), or PtO_2 as a catalyst, the tetracyclic compound (**14**) was obtained in a 78, 76, or 73% yield respectively. **14**; mp 162—166 °C decomp; Mass (*m*/*e*) 310 (M^+); UV (CH_3CN) λ 273 nm (ε, 679), 266 (931); ^1H NMR ($CDCl_3$) δ 1.85—2.47 (m, 6H), 2.55—3.15 (m, 6H), 3.63—3.78 (m, 2H), 6.75—7.10 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 33.1 (t), 34.6 (t), 39.5 (t), 48.3 (d), 126.1 (d), 126.2 (d), 127.9 (d), 130.0 (d), 138.1 (s), 139.2 (s), 143.3 (s), 144.9 (s); Found: C, 92.73; H, 7.10%. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14%.

*Diimide Reduction of **4**.* A solution of **4** (0.35 mmol) in 30 ml of dry methanol containing potassium azodicarboxylate (4.7 mmol) was treated, drop by drop, under nitrogen at −78 °C with glacial acetic acid (1 ml). After the completion of the addition, the mixture was stirred for 2 h at −78 °C and for 24 h at room temperature. The mixture was then diluted with water and extracted with dichloromethane. The combined organic layers were washed with a 10% aqueous sodium hydrogencarbonate solution and water prior to drying and concentration. The subsequent chromatography of the residue on silica gel with petroleum ether afforded **15** in a 70% yield. **15**; mp 137—140 °C decomp; Mass (*m*/*e*) 310 (M^+); UV (CH_3CN) λ 275 nm (ε, 1010), 248 (3480); ^1H NMR ($CDCl_3$) δ 1.50—1.89 (m, 4H), 1.90—2.21 (m, 4H), 3.38—3.62 (m, 2H), 3.64—3.95 (m, 2H), 4.20—4.42 (m, 2H), 6.92—7.16 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 24.0 (t), 24.5 (t), 41.8 (d), 44.5 (d), 52.2 (d), 126.2 (d), 126.2 (d), 126.9 (d), 131.8 (d), 138.9 (s), 142.3 (s), 147.4 (s); Found: C, 92.75; H, 7.12%. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14%.

*Synthesis of Buttaflane (**19**).* A 90-ml degassed benzene solution of **9** (1 mmol) in a sealed Pyrex tube was irradiated at room temperature for 100 h using a 500-W high-pressure mercury lamp. After the removal of the solvent, the GLC of the residue revealed only one peak with the same retention time as that of **9** because the buttaflane (**19**) was cycloreversed thermally, but ^{13}C NMR showed a new signal at δ 49 ppm based on a cyclobutane ring carbon of buttaflane (**19**). A mixture of buttaflane (**19**) and unreacted **9** was chromatographed on silica gel or silver nitrate-impregnated silica gel, but the two components could not be completely separated. Therefore, the mixture in ethyl acetate was ozonized for 15 min at −78 °C. The workup was analogous to that of the ozonolysis of **9**. Elution with petroleum ether gave buttaflane (**19**, 66%), and elution with petroleum ether/ether (7/3) gave the diketone (**11**, 25%) as the ozonization product of the unreacted **9**. **19**; mp 179—183 °C decomp; Mass (*m*/*e*) 312 (M^+); UV (CH_3CN) λ 278 nm (ε, 3203), 271 (3503), 265 (2588); ^1H NMR ($CDCl_3$) δ 1.35—1.64 (m, 8H), 1.96—2.25 (m, 8H), 6.44—6.76 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 22.2 (t), 25.0 (t), 49.3 (s), 121.2 (d), 126.5 (d), 150.1 (s); Found: C, 92.10; H, 7.69%. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74%.

*Synthesis of Cage Buttaflane (**20**).* A 30-ml degassed benzene solution of **14** (0.5 mmol) in a sealed Pyrex tube was irradiated for 50 h. After the removal of the solvent, the residue was chromatographed on silica gel. The subsequent elution of petroleum ether gave cage buttaflane (**20**) in an 80% yield. **20**; mp 204—208 °C decomp; Mass (*m*/*e*) 310 (M^+); UV (CH_3CN) λ 276 nm (ε, 1040), 268 (1095), 261 (889); ^1H NMR ($CDCl_3$) δ 1.24 (d, 2H), 1.84—3.40 (m, 10H), 3.44—3.56 (m, 2H), 6.52—6.96 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 24.9 (t), 25.5 (t), 30.5 (t), 41.6 (s), 42.4 (d), 50.8 (s), 124.8 (d), 124.9 (d), 126.3 (d), 126.9 (d), 140.3 (s), 144.2 (s); Found: C, 92.72; H, 7.15%. Calcd for $C_{24}H_{22}$: C, 92.86; H, 7.14%.

*Thermal Reaction of **4**.*　The heating of a sealed Pyrex tube containing 10 mg of **4** at 180 °C for 20 min gave **3** quantitatively. In the case of 100 °C or 150 °C, no cycloreversion of **4** to **3** occurred.

*Thermal Reaction of Buttaflane (**19**).*　The heating of a sealed Pyrex tube containing 10 mg of **19** at 150 °C for 30 min gave **9** quantitatively.

*Thermal Reaction of Cage Buttaflane (**20**).*　The heating of a sealed Pyrex tube containing 10 mg of **20** at 170 °C for 2 h gave **14** almost quantitatively.

*Catalytic Reaction of Buttaflane (**19**) with* $[Rh(NBD)Cl]_2$. A catalytic amount of $[Rh(NBD)Cl]_2$ and **19** (20 mg) in 5 ml of $CDCl_3$ was allowed to stand at room temperature in a sealed Pyrex tube for 5 d. ^{13}C NMR showed clearly that the cycloreversion of **19** to **9** occurred quantitatively.

Quenching with 1,3-Pentadiene.　Five samples were prepared each containing 10 ml of a degassed benzene solution of **3** (0.1 mmol). Four samples also contained 1,3-pentadiene (0.05, 0.10, 0.50, or 1.00 mol dm^{-3}). All the sealed samples were irradiated for 2 h. 1,3-Pentadiene exhibited no quenching effect on the formation of **4** and **2a** in any case.

Quantum Yield Measurement.　The quantum yields were measured by the method using potassium ferrioxalate as the actinometer.[23)]

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