$(CH_3)_2$), 2.26 (s, 3 H, CH_3S), 3.67 (s, 3 H, 4-CH_3O), 3.79, 3.85 (2 s, 6 H, $CO_2\mathit{C}H_3$), 5.46, 5.55 (2 d, 2 H, *J* = 1.6 Hz, H-6, H-8); ^{13}C NMR ($CDCl_3$) δ 16.3 (CH_3S), 30.0 (7-$(CH_3)_2$), 40.4 (C-7), 52.9, 53.0 ($CO_2\mathit{C}H_3$), 63.5 (4-CH_3O), 123.1 (C-4a), 126.5 (C-3), 127.8 (C-2), 128.7 (C-5), 129.3 (C-8a), 132.5, 134.5 (C-6, C-8), 134.3 (C-4), 161.7, 166.2 ($\mathit{C}O_2CH_3$); MS [CI-NH_3] 386 (100, M^+ + 18), 369 (50, M^+ + 1); UV (EtOH) 458 (650), 358 (700), 269 (4300), end absorption at 200 (8000).

Dimethyl 5,6,7,8-tetrahydro-7,7-dimethyl-4,5-dioxobenzo[*b*]thiopyran-2,3-dicarboxylate (10) was obtained as pale yellow needles, mp 149–151 °C, after recrystallization from toluene–heptane: ^1H NMR ($CDCl_3$) δ 1.08 (s, 6 H, 7-$(CH_3)_2$), 2.47 (s, 2 H, H-6), 2.77 (s, 2 H, H-8), 3.87, 3.90 (2 s, 6 H, CO_2CH_3); ^{13}C NMR ($CDCl_3$) δ 27.8 (7-$(CH_3)_2$), 34.0 (C-7), 45.3 (C-6), 53.1 (C-8), 53.4, 54.3 (CO_2CH_3), 129.7 (C-3), 134.7 (C-4a), 141.9 (C-2), 161.0 (C-8a), 163.8, 164.6 ($\mathit{C}O_2CH_3$), 174.8 (C-4), 191.1 (C-5); MS [70 eV] 324 (26, M^+), 309 (37), 277 (49), 268 (42), 208 (64), 82 (20), 77 (42), 69 (25), 66 (75), 59 (100), 55 (38), 41 (45), 39 (60); high-resolution MS (M^+) found 324.0660, calcd for $C_{15}H_{16}O_6S$ 324.0668; UV (EtOH) 338 sh (3100), 326 sh (5200), 302 (9700), 295 sh (9300), 252 sh (7700), 223 (13 700).

Hydrolysis of 11a. First, 0.2 N HCl (5 mL) was added to a boiling solution of **11a** (0.0144 g) in methanol (20 mL). After being refluxed for 20 min the mixture was cooled, $NaHCO_3$ (0.1 g) was added, and after being stirred the mixture was filtered and worked up as described above. Column chromatography of the methylene chloride extract gave unreacted **11a** (0.0056 g) and **8** (0.0053 g, nearly quantitative yield based on reacted material), identified by its ^1H NMR spectrum.

All solvents were carefully dried and distilled before use, and the reactions were performed under argon or nitrogen atmosphere.

NMR spectra were recorded with a Varian Model XL-300 NMR spectrometer. Resonances of protonated carbons were assigned by use of the DEPT pulse sequence and in some cases by 2D ^1H–^{13}C chemical shift correlation,[19] and those of quaternary carbons by use of coupled spectra and by predicted chemical shifts.[20]

The temperature-dependent ^1H NMR spectra of **11a** and **11c** were recorded in toluene-d_8 solution in the temperature range 50–85 °C, and the rate constants were evaluated by complete bandshape analysis.[21] The major source of error is the temperature regulation, which was found by calibration with a standardized sample of ethylene glycol to be precise to within ±2 °C. This corresponds to error limits of ±0.1 kcal/mol in the free energies of activation.

Mass spectra were recorded with a Finnigan Model 4021 and a JEOL Model SX-102 (for high resolution) mass spectrometer, ultraviolet–visible spectra with a Cary Model 2290 spectrometer, and the CD spectrum with a JASCO Model J-500A spectropolarimeter. The elemental analyses are precise within ±0.4%.

The enantiomer resolution of **7b** was performed with the equipment described by Isaksson and Roschester[22] with ethanol as the mobile phase. The eluted fractions were used directly to record the CD spectra, and their concentrations were monitored by UV spectroscopy after suitable dilution.

Acknowledgment. We are grateful to the Swedish Natural Science Research Council and to the Knut and Alice Wallenberg Foundation for financial support.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of 1-benzyl-3-isopropyl-2-(4,4-dimethyl-2,6-dioxocyclohexylidene)imidazolidine, 1,3-dibenzyl-2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hexahydropyrimidine, **3b**, **3e**, **4a–c**, **5a**, **5b**, **7a**, **7b**, **8–10**, **11a–d**, **11d$_2$**, **12a**, **12c**, **12d**; assigned chemical shifts (^1H and ^{13}C) (Tables I–IV and Scheme IV), and UV spectra (Table V) (67 pages). Ordering information is given on any current masthead page.

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Novel Photoreactions of Benzhydrylidenequadricyclane and Quadricyclanone: A New Route to Trimethylenemethane and Oxyallyl Derivatives

Takashi Hirano, Tsutomu Kumagai, and Tsutomu Miyashi*

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

Kimio Akiyama* and Yusaku Ikegami

Chemical Research Institute of Nonaqueous Solution, Tohoku University, Sendai 980, Japan

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The irradiation of 3-benzhydrylidenequadricyclane (**1**) generated a trimethylenemethane (TMM) derivative, 3-benzhydrylidenebicyclo[3.2.0]hept-6-ene-2,4-diyl (**3**), which dimerized and could be chemically captured by molecular oxygen and acrylonitrile, but not by furan, methanol, or ethyl vinyl ether. The triplet nature of **3** was confirmed by EPR, emission, and absorption spectra. By contrast, the irradiation of quadricyclanone (**2**) generated the singlet oxyallyl (OA), 3-oxobicyclo[3.2.0]hept-6-ene-2,4-diyl (**4**), which could be captured by furan, methanol, and ethyl vinyl ether, but not by molecular oxygen or acrylonitrile, indicating the zwitterionic and electron-accepting nature of **4**.

Trimethylenemethane (TMM) and its hetero analogue oxyallyl (OA) are intriguing 1,3-diradical species which have been widely discussed not only experimentally[1,2] but also theoretically.[3,4] Among a variety of precursor for

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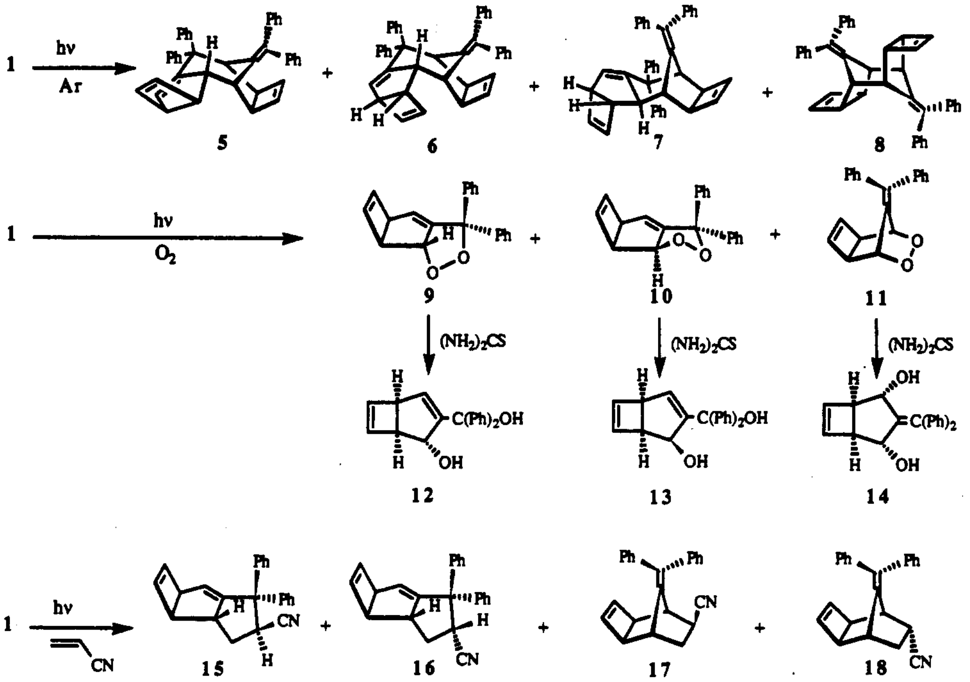
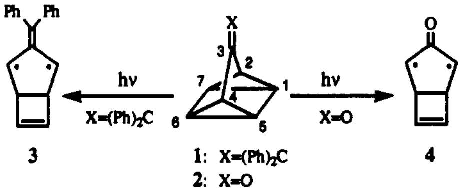
Scheme I



TMMs, diazenes[5,6] and strained hydrocarbons such as 5-alkylidenebicyclo[2.1.0]pentanes[7] and bicyclo[3.1.0]hex-1-enes[8,9] are most successful precursors to give chemically and spectroscopically capturable cyclic TMMs. Although the replacement of a methylene group of TMM by oxygen produces OA, similar diazene-photolysis methodology is not always successful. For instance, photolysis of tetramethylpyrazolinone was reported to involve competitive nitrogen and carbon monooxide extrusion reactions.[10] Thus, OAs are generated mostly from cyclopropanones and cross-conjugated dienones as well as allene oxides,[2] and it is not easy to generate stable cyclic TMM and OA in the same molecular framework. If possible, we can directly compare chemical and physical properties of TMM with those of OA in the same molecular environment, minimizing different molecular perturbation. We found a novel photochemical reaction of the quadricyclane system[11] which is convenient for this purpose. Photolyses of 3-benzhydrylidenequadricyclane (1) and quadricyclanone (2) involve a simultaneous C_1–C_2 and C_4–C_5 bond cleavage,[12] giving rise to the triplet TMM (3) and the singlet OA (4), respectively. Herein we report contrastive chemical and physical properties of 3 and 4 generated in the same molecular framework.



Results and Discussion

3-Benzhydrylidenequadricyclane (1) was prepared by the reaction of quadricyclanone (2) and diphenylmethyllithium followed by dehydration. Irradiation of 1 with 300-nm light in *n*-hexane under argon gave a mixture of four dimers (5–8) in 21, 15, 13, and 3% yields, respectively. Similar irradiations in benzene or acetonitrile gave nearly the same mixtures of dimers. The benzophenone-sensitized irradiation (350-nm light) of 1 gave the same result as that of the direct irradiation, giving a mixture of 5–8 in 17, 10, 8, and 4% yields, respectively. Each dimer exhibited its molecular ion peak at m/z 512, and the stereochemical assignment was unequivocally established by

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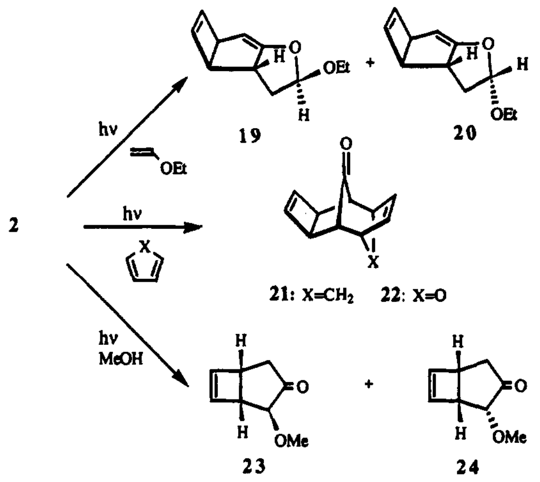
(10) Gleiter, R.; Veszprémi, T.; Quast, H. *Chem. Ber.* **1989**, *122*, 985.

(11) For instance, the previously known photochemical reactions of methylenequadricyclane and quadricyclanone derivatives are photochemical decarbonylation of substituted quadricyclanone (Prinzbach, H. *Pure Appl. Chem.* **1968**, *16*, 17) and photochemical isomerization of 3-(dicyanomethylene)quadricyclane to 8,8-dicyanoheptafulvene (Babsch, H.; Fritz, H.; Prinzbach, H. *Tetrahedron Lett.* **1975**, 4677).

(12) This bond fission was postulated for the isomerization of quadricyclane to cycloheptatriene by photolysis of 185-nm. See: Srinivasan, R.; Baum, T.; Epling, G. *J. Chem. Soc., Chem. Commun.* **1982**, 437. The simultaneous C_1–C_2 and C_4–C_5 bond fission has been investigated in thermal reactions of 3-heteroquadricyclanes. See: Prinzbach, H.; Bingmann, H.; Markert, J.; Fischer, G.; Knothe, L.; Eberbach, W.; Brokatzky-Geiger, J. *Chem. Ber.* **1986**, *119*, 589. Prinzbach, H.; Bingmann, H.; Fritz, H.; Markert, J.; Knothe, L.; Eberbach, W.; Brokatzky-Geiger, J.; Sekutowski, J. C.; Krüger, C. *Ibid.* **1986**, *119*, 616.

Scheme II



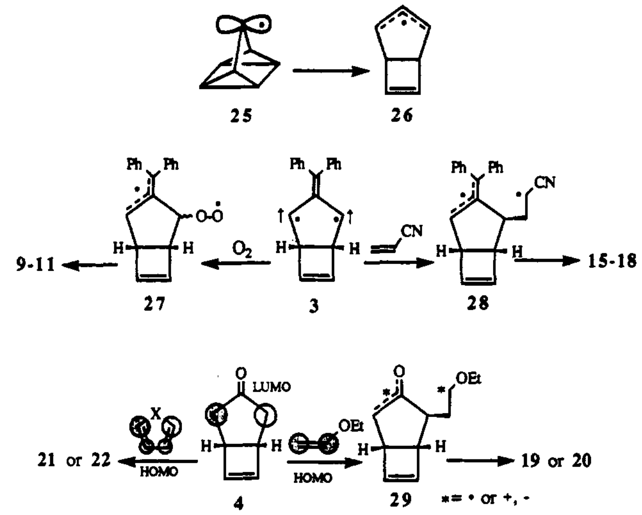
NOE and C,H-COLOC NMR spectra.

When 1 was irradiated in *n*-hexane under oxygen, however, dimerization was completely suppressed and instead the fused endoperoxides 9 and 10 and the bridged one (11) were formed in 66, 7, and 4% yields, respectively. Product 9 could be isolated, but minor products 10 and 11 were unstable and were characterized as diols 13 and 14. The irradiation of 1 in furan, ethyl vinyl ether, or methanol did not give any adduct besides dimers 5–8. By contrast, the irradiation in acrylonitrile gave the fused 1,2-cycloadducts 15 (32%) and 16 (21%) along with the bridged isomers 17 (11%) and 18 (10%). The composition of acrylonitrile adducts was independent upon the concentration of acrylonitrile in the range of 0.05–5 M in acetonitrile. Nearly the same mixture of acrylonitrile adducts was formed under benzophenone sensitization.

The irradiation of quadricyclanone (2) in *n*-pentane with 300-nm light either under nitrogen or under oxygen did not give any isolable product. Similarly, the irradiation of 2 in acrylonitrile did not provide any fruitful result, but the irradiation in electron-rich ethyl vinyl ether resulted in the regiospecific formation of fused 1,2-cycloadducts 19 and 20 in 15 and 33% yields, respectively. The regio- and stereospecific 1,4-cycloadditions with cyclopentadiene and furan also occurred to give 21 and 22, respectively, in 37 and 50% yields. The formation of methanol adducts 23 and 24 is a characteristic reaction which could not be observed in the photoreaction of 1.

The observed photoproducts from 1 and 2 are characteristic of TMMs and OAs, indicating the generation of TMM 3 and OA 4, respectively. Because quadricyclane itself can be viewed as a formal intramolecular bridged 1,2-cycloadduct of cyclopentane-1,3-diyl and cyclobutene,[13,14] photoexcitation of 1 and 2 apparently induced a simultaneous C_1–C_2 and C_4–C_5 bond cleavage. This process resembles the rearrangement of 3-quadricyclyl radical 25 to bicyclo[3.2.0]heptadienyl radical 26[15,16] but is unprecedented in photochemical reactions of quadricyclane derivatives. The good overlap of spin at the C_3 of excited 1 and 2 with the cyclopropane Walsh orbital might induce a simultaneous ring cleavage. In support of this assumption is spectroscopic evidence derived from the photoelectron spectroscopy for 3-methylenequadricyclane which indicates significant interaction between the exo methylene double bond and the cyclopropane σ-orbital in the ground state.[17]

Scheme III



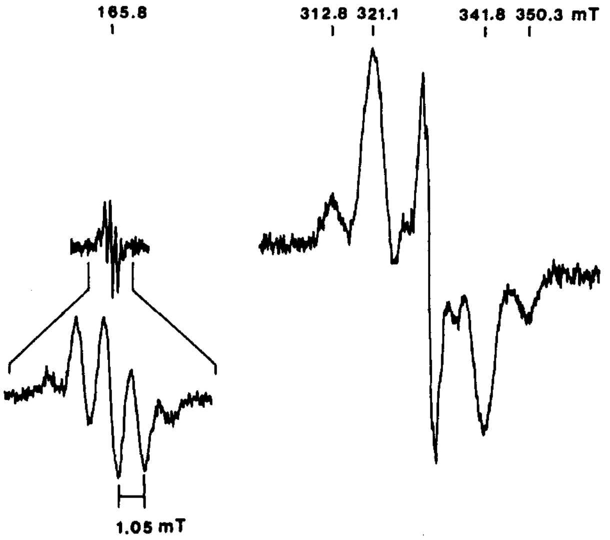


Figure 1. EPR spectrum of 3 generated by the photolysis of 1 in a methylcyclohexane matrix at 77 K. Scale expanded (×4) signal of $\Delta M_s = 2$ transition is also presented. The peak positions shown are in mT.

Oxygenation[18-20] leading to 9, 10, and 11 as well as the nonregiospecific addition of acrylonitrile[1a,b,21] strongly support the triplet nature of 3, and the concentration-independent formation of acrylonitrile adducts makes it likely that the reactive intermediate is only one species, the triplet 3. Since also the direct and benzophenone-sensitized photoreactions of 1 gave the same results in dimerization and acrylonitrile addition, it is likely that the triplet 3 is derived from the triplet 1, though the rapid intersystem crossing of the singlet 3 to the triplet 3 cannot

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be completely ruled out. Thus, the nonregiospecific 1,2-cycloaddition with acrylonitrile[1a,b,21] occurs from the triplet **3** through **28** in a stepwise manner as shown in Scheme III and oxygen may react nonregiospecifically with **3** in the same manner.

In support of the structure and the spin multiplicity of the intermediate (**3**) is spectroscopic evidence from EPR, emission, and absorption spectra. Upon irradiation of **1** in a methylcyclohexane (MCH) matrix at 77 K, we observed a characteristic EPR spectrum as shown in Figure 1 which persisted with undiminished intensity for at least 30 min after light irradiation. The zero-field splitting (ZFS) parameters estimated from the spectrum with $|D| = 0.0174$ and $|E| = 0.0006$ cm^{-1}. These values are nearly identical with those of 2-benzhydrylidenecyclopentane-1,3-diyl, i.e., $|D| = 0.0180$ and $|E| = 0.0013$ cm^{-1}.[22] In the present system, the splitting due to hyperfine interaction was also observed in the signal at $|\Delta M_s| = 2$ transition as shown in Figure 1. The spectrum was analyzed by four equivalent protons irrespective of broader signal ($\Delta H_{pp} = 0.2$ mT). Hfs constants obtained by the computer simulation were 1.05 mT, the value being close to those of the parent TMM in magnitude.[23,24] Considering the structure of **3**, hfs constants should be assigned to the protons at the 1-, 2-, 4-, and 5-positions. Similar results were also obtained in other matrices such as benzene and 2-methyltetrahydrofuran.

As the triplet EPR signal persisted at 77 K, the absorption and luminescence spectra of **3** were easily recorded by conventional spectrometers. Upon irradiation of **1** with near-UV light in MCH, the absorption due to **3** appeared with peaks at 308, 315, 329 nm and an isosbestic point at 285 nm. A weak absorption was also observed in the visible region. By excitation at 329 nm, the vibrationally structured fluorescence was observed with maxima at 488 and 517 nm. The fluorescence excitation spectrum completely coincided with the absorption spectrum. The decay of luminescence both at 488 and 517 nm fitted a double exponential decay, the two components having lifetimes of 3.03 and 96.3 ns. The spectroscopic behavior of the present system resembles the diphenyl-substituted TMM derivative reported previously except for the decay rate.[25]

By analogy with *m*-xylylene,[26] the nonexponential decay measured for the present TMM **3** could be consistent with emission from independent T_1 sublevels at a rate faster than the rate of equilibration by spin lattice relaxation. The mixing of singlet and triplet sublevels will destroy the equality of the three transition moments between the sublevels of T_0 and T_1 state, leading to bi- and triexponential radiative decay from T_1 sublevels. A spin orbit vibronic mechanism has also been pointed out to interpret the nonexponential decay of $T_1 \rightarrow T_0$ fluorescence.[26] The T_1 sublevels can decay with different rates as a result of intersystem crossing induced by spin orbit coupling. The radiationless decay competing with the radiative transition could be responsible for the selective depopulation of one or two triplet sublevels among three.

On the basis of the above results, the intermediate **3** was definitely established for photochemical reactions of **1**. The ground-state triplet of **3** was suggested not only by the persistence of the EPR signal at 77 K but also by the nonexponential decay of the luminescence. Nonexponential decay is often seen for the $S_1 \rightarrow S_0$ transition, but in the present case the $T_1 \rightarrow T_0$ transition is responsible because the fluorescence intensity increases as the EPR signal intensity increases. Direct information will be obtained through the analysis of the temperature dependence of the EPR signal intensity.

The generation of **4** can be presumed from observed photoreactions of **2**, which resemble those of previously known OAs.[27-30] No EPR signal during irradiation of **2** in a MCH matrix at 77 K and the addition of methanol[28] to **4** consist with **4** being a singlet ground state with a zwitterionic nature. This is supported by the recent ab initio calculation for cyclic OA, 2-oxocyclopentane-1,3-diyl.[4c] In addition, the facts that **4** reacts with ethyl vinyl ether rather than acrylonitrile but the reactivity[1a,b,21,31,32] of **3** to these olefins reverses accord with a theoretical prediction[4c] that OAs act more as electron acceptors than TMMs. The regio- and stereospecific 1,4-cycloaddition of **4** with cyclopentadiene and furan can be explained by the concerted LUMO (**4**)–HOMO (diene) interaction.[4c,29] Since the LUMO of **4** cannot concertedly interact with the HOMO of ethyl vinyl ether, a stepwise mechanism through **29** would most likely explain the formation of a mixture of **19** and **20** as shown in Scheme III,[4c,30] though no bridged 1,2-cycloadduct was identified.

In conclusion, novel photochemical reactions of quadricyclane derivatives provided a convenient new route to the triplet TMM and the singlet OA, both of which have the same molecular framework. This method can be further applicable for the generation of a variety of TMMs with electron-withdrawing substituents at the exocyclic position. The experimental verification of a theoretical prediction that electron-withdrawing substituents should increase the splitting of the two degenerate nonbonding MOs of TMM will be soon reported.

Experimental Section

General Methods. All melting and boiling points are uncorrected. Elemental analyses were performed by the Instrumental Analyses Center for Chemistry, Faculty of Science, Tohoku University. Low-temperature absorption spectra were measured at 77 K, immersing a deaerated sample directly in liquid N_2 in an all-quartz dewar. Fluorescence spectra were recorded on a spectrofluorometer in a similar way, and decay of the fluorescence was measured by a time-correlated single photon counting tequnique. Sample solutions for EPR spectra were deaerated by using a vacuum line tequnique and irradiated with excimer laser (308 nm). ^{1}H NMR spectra were recorded at 90, 200, or 600 MHz, and ^{13}C NMR spectra were recorded at 50 or 150 MHz. Reverse-phase high-performance liquid chromatography (HPLC) analyses were carried out by using a Merck Lichrocart Superspher 100 RP-18 column (25 cm × 4 mm). Medium-performance liquid chromatography (MPLC) was carried out by using a 100 cm × 15 mm glass column packed with silica Wolem 32-63 (column A) or YMC gel SIL120A S50 (column B). For low-temperature

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MPLC, a column was immersed in a dewar filled with cold methanol. Preparative thin-layer chromatography was performed on 0.5 mm × 20 cm × 20 cm silica gel (E. Merck 60PF$_{254}$) plates. Column chromatography was carried out on Merck silica gel 60 (230–400 mesh ASTM). For short path chromatography, Merck silica gel 60 (70–230 mesh ASTM) was used. For a neutral alumina column, Merck aluminum oxide 90 active neutral (70–230 mesh ASTM) was used.

Preparation of 3-Benzhydrylidenetetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (1). To a solution of diphenylmethane[33] (10.47 g, 62.2 mmol) in 170 mL of anhydrous ether was added 36 mL of a solution of *n*-butyllithium (56.2 mmol) in ether over 20 min under nitrogen at ambient temperature. After heating to between 26 and 34 °C for 26 h, the dark red solution was cooled to between −75 and −70 °C, and a solution of quadricyclanone[34] (3.01 g, 28.4 mmol) in 15 mL of ether was introduced dropwise during 10 min. After being warmed to room temperature, the reaction mixture was stirred for 1 h and then poured into 60 mL of water and extracted with ether. The combined extract was washed with brine and dried over Na_2SO_4. After removal of solvent in vacuo, the residue was purified by silica gel chromatography (elution with 9% ethyl acetate in *n*-hexane) and recrystallization from *n*-hexane to give 5.95 g (76%) of 3-(diphenylmethyl)tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-3-ol as colorless cubes: mp 95.5–96.5 °C; IR (KBr) 3566, 1597, 1578, 1493, 1450, 1372, 1094 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.63 (d, J = 3.6 Hz, 4 H), 7.4–7.1 (m, 6 H), 4.22 (s, 1 H), 1.85 (s, 1 H), 1.77 (m, 2 H), 1.65 (m, 2 H), 1.26 (m, 2 H); MS (13.5 eV) m/z (relative intensity) 274 (M^+, 1.2), 257 (23), 256 (88), 178 (17), 169 (12), 168 (100), 167 (46), 107 (52).

Anal. Calcd for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.51; H, 6.69.

A solution of 3-(diphenylmethyl)tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-3-ol (6.02 g, 21.9 mmol) in 200 mL of pyridine was cooled in an ice bath, and phosphorus oxychloride (10.0 mL, 109 mmol) was introduced dropwise over 10 min under N_2. After stirring for 150 min, the resulting mixture was poured into 200 mL of ice–water and extracted with ether. The combined extract was washed with 5% HCl, saturated $NaHCO_3$, and brine and dried over Na_2SO_4. The residue obtained after removal of solvent was purified by silica gel chromatography (elution with 9% ethyl acetate in *n*-hexane) and recrystallization from *n*-hexane to give 4.04 g (72%) of 1 as colorless plates: mp 101.5–102.5 °C; IR (KBr) 1654, 1595, 1490, 1442, 813, 772, 748, 702 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40–7.16 (m, 10 H), 1.94 (m, 4 H), 1.82 (m, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.27, 143.64, 131.38, 130.25, 127.81, 126.25, 24.64, 19.32; UV (cyclohexane) λ_{max} = 262 nm (18 300), (CH_3CN) λ_{max} = 260 nm (17 100); MS (25 eV) m/z (relative intensity) 257 (M^+ + 1, 17), 256 (M^+, 99.9), 255 (77), 254 (13), 253 (15), 241 (44), 240 (27), 239 (26), 230 (22), 229 (19), 228 (12), 180 (14), 179 (94), 178 (100), 165 (24).

Anal. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.62; H, 6.50.

Photolysis of 1 under Argon. A solution of 1 (150.1 mg, 0.586 mmol) in 280 mL of *n*-hexane in a quartz vessel was irradiated with four Rayonet ultraviolet lamps (RUL-3000Å) for 20 min under argon at room temperature. The solvent was removed in vacuo to afford 176 mg of a pale yellow oil. By repetitive preparative thin-layer chromatography on silica gel (1:8 benzene/*n*-hexane) and on silica gel containing 10% silver nitrate (10:1 and 3:1 $CHCl_3$/*n*-hexane), dimers **5**, **6**, **7**, and **8** were isolated in 21, 15, 13, and 3% yields, respectively, together with recovered 1 (8%), 6,6-diphenylfulvene (1%), and 7-benzhydrylidenenorbornadiene (2%). R_f values of **5**, **6**, **7**, and **8** were 0.64, 0.64, 0.69, and 0.58 on silica gel (elution four times with 1:8 benzene/*n*-hexane), respectively, and those of **5** and **6** were 0.49 and 0.54 on 10% $AgNO_3$ and silica gel (elution twice with 3:1 $CHCl_3$/*n*-hexane), respectively.

5: mp 273–274 °C (colorless prisms); IR (KBr) 1596, 1490, 1442, 758, 745, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.30–6.80 (m, 20 H), 6.46 (d, J = 2.6 Hz, 1 H), 6.35 (d, J = 2.7 Hz, 1 H), 6.31 (d, J = 2.6 Hz, 1 H), 5.88 (dd, J = 2.7, 0.4 Hz, 1 H), 5.57 (dd, J = 2.7, 1.6 Hz, 1 H), 4.20 (s, 1 H), 3.60 (ddd, J = 3.5, 3.5, 2.7 Hz, 1 H), 3.35 (dd, J = 3.2, 0.4 Hz, 1 H), 3.34 (m, 1 H), 3.06 (dd, J = 3.5, 2.2 Hz, 1 H), 2.88 (d, J = 3.2 Hz, 1 H), 2.34 (d, J = 3.2 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.49, 146.60, 145.07, 144.44, 143.57, 142.49, 141.94, 139.50, 139.08, 137.98, 137.02, 131.47, 130.72, 129.11, 128.59, 128.0 (broad), 127.69, 127.60, 127.53, 126.38, 126.16, 125.25, 124.81, 57.70, 54.97, 50.04, 49.28, 48.87, 48.48, 46.72, 46.11; UV (cyclohexane) λ_{max} = 254 nm (16 200); MS (DEI, 70 eV) m/z (relative intensity) 514 (M^+ + 2, 10), 513 (M^+ + 1, 46), 512 (M^+, 100), 345 (10), 255 (20), 253 (11), 243 (25), 179 (11), 178 (15).

Anal. Calcd for $C_{40}H_{32}$: C, 93.71; H, 6.29. Found: C, 93.54; H, 6.57.

6: mp 251.5–253 °C (colorless prisms); IR (KBr) 1597, 1490, 1442, 756, 740, 698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.25–6.64 (m, 20 H), 6.34 (d, J = 2.7 Hz, 1 H), 6.18 (s, 2 H), 5.91 (d, J = 2.7 Hz, 1 H), 5.76 (dd, J = 2.4, 1.8 Hz, 1 H), 4.06 (s, 1 H), 3.86 (ddd, J = 3.8, 2.4, 2.0 Hz, 1 H), 3.64 (dd, J = 10.3, 3.8 Hz, 1 H), 3.59 (d, J = 3.4 Hz, 1 H), 3.40 (d, J = 3.4 Hz, 1 H), 3.35 (dddd, J = 10.3, 3.1, 2.0, 1.8 Hz, 1 H), 2.65 (d, J = 3.1 Hz, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.56, 145.93, 145.18, 143.71, 142.47, 142.38, 141.41, 139.12, 138.90, 138.61, 137.07, 130.55, 130.24, 129.11, 129.09, 127.96, 127.91, 127.73, 127.59, 127.40, 126.30, 126.14, 125.25, 124.86, 58.21, 54.95, 48.90, 48.27, 47.63, 45.99, 42.70; UV (cyclohexane) λ_{max} = 251 nm (15 600); MS (DEI, 70 eV) m/z (relative intensity) 514 (M^+ + 2, 11), 513 (M^+ + 1, 47), 512 (M^+, 100), 345 (14), 269 (14), 255 (20), 254 (11), 253 (11), 244 (13), 243 (57), 241 (10), 191 (10), 178 (12), 167 (11), 85 (19), 83 (29).

Anal. Calcd for $C_{40}H_{32}$: C, 93.71; H, 6.29. Found: C, 93.69; H, 6.38.

7: mp 264–264.5 °C (colorless prisms); IR (KBr) 1599, 1574, 1554, 1492, 1441, 756, 750, 740, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.46–6.58 (m, 20 H), 6.40 (d, J = 2.6 Hz, 1 H), 6.30 (d, J = 2.6 Hz, 1 H), 6.24 (d, J = 2.7 Hz, 1 H), 5.91 (d, J = 2.7 Hz, 1 H), 4.82 (dd, J = 2.8, 2.1 Hz, 1 H), 3.91 (s, 1 H), 3.85 (br ddd, J = 3, 3, 3 Hz, 1 H), 3.29 (dd, J = 3.5, 2.5 Hz, 1 H), 2.92 (d, J = 3.1 Hz, 1 H), 2.70 (d, J = 3.1 Hz, 1 H), 2.51 (m, 1 H), 2.19 (s, 1 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.01, 149.81, 146.13, 144.25, 144.10, 143.87, 142.84, 140.01, 139.80, 138.83, 138.61, 130.49, 130.34, 130.13, 129.19, 128.19, 127.73, 127.55, 127.03, 126.84, 126.40, 125.76, 125.13, 58.33, 54.99, 54.76, 54.50, 52.37, 49.37, 48.66, 48.25; UV (cyclohexane) λ_{max} = 249 nm (16 700); MS (DEI, 70 eV) m/z (relative intensity) 513 (M^+ + 1, 49), 512 (M^+, 100), 459 (23), 447 (32), 446 (63), 256 (23), 255 (45), 254 (22), 253 (24), 243 (53), 241 (22), 239 (21), 191 (20), 179 (29), 178 (34), 167 (27), 165 (25), 91 (10).

Anal. Calcd for $C_{40}H_{32}$: C, 93.71; H, 6.29. Found: C, 93.67; H, 6.23.

8: mp 285–286 °C (colorless prisms); IR (KBr) 1597, 1490, 1441, 774, 757, 714, 702 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26–7.20 (m, 16 H), 7.17–7.13 (m, 4 H), 5.96 (s, 4 H), 3.34 (s, 4 H), 2.64 (s, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.64, 141.03, 137.21, 136.90, 129.21, 128.03, 126.05, 50.98, 44.07; UV (cyclohexane) λ_{max} = 251 nm (26 600); MS (DEI, 70 eV) m/z (relative intensity) 513 (M^+ + 1, 25), 512 (M^+, 60), 459 (31), 447 (46), 446 (100), 255 (48), 254 (22), 253 (23), 243 (58), 241 (23), 179 (25), 178 (26), 167 (29), 165 (21).

Anal. Calcd for $C_{40}H_{32}$: C, 93.71; H, 6.29. Found: C, 93.68; H, 6.46.

Assignments of the carbon and proton chemical shift of **5**, **6**, and **7** were made by ^{1}H–^{13}C 2D NMR shift correlation experiments (C–H COSY and COLOC[35] spectra) and are shown in Table I. Stereochemical assignments of dimers **5**, **6**, and **7** were obtained by NOESY spectra or NOE difference spectra. NOEs were observed between H_{14} (2.88 ppm) and H_3 (3.06 ppm) and between H_{14} and H_6 (3.60 ppm) for **5**, between H_{14} (3.59 ppm) and H_4 (6.18 ppm) or H_5 (6.18 ppm) for **6**, between H_1 (2.19 ppm) and H_3 (3.29 ppm), between H_1 and H_{13} (5.91 ppm), and between H_{14} (2.70 ppm) and H_2 (2.51 ppm) for **7**.

Photolysis of 1 under Oxygen. A solution of 1 (100.1 mg, 0.390 mmol) in 125 mL of *n*-hexane in a quartz vessel was irradiated with 4 RUL-3000Å lamps for 20 min with oxygen bubbling.

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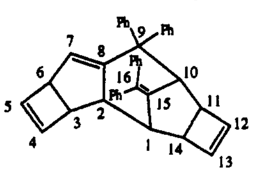
Table I. ^{13}C NMR [150 MHz, Chemical Shift (δ)] and ^{1}H NMR [200 MHz, Chemical Shift (δ)] Data for Dimer 5, 6, and 7 in $CDCl_3$



carbon[a] number	chemical shift (δ) ^{13}C (^{1}H)		
	5	6	7
1	46.11 (2.34)	42.70 (2.65)	48.66 (2.19)
2	48.87 (3.34)	47.63 (3.35)	52.37 (2.51)
3	50.04 (3.06)	48.90 (3.64)	54.50 (3.29)
4	139.08 (6.31)	139.12 (6.18)	140.01 (6.30)
5	144.44 (6.46)	141.41 (6.18)	144.25 (6.40)
6	54.97 (3.60)	54.95 (3.86)	54.76 (3.85)
7	131.47 (5.57)	130.24 (5.76)	130.13 (4.82)
8	147.49 (none)	145.93 (none)	152.01 (none)
9	57.70 (none)	58.21 (none)	58.33 (none)
10	46.72 (4.20)	45.99 (4.06)	49.37 (3.91)
11	49.28 (3.35)	48.27 (3.40)	48.25 (2.92)
12	137.02 (6.35)	137.07 (6.34)	138.61 (6.24)
13	137.98 (5.88)	138.61 (5.91)	138.83 (5.91)
14	48.48 (2.88)	48.90 (3.59)	54.99 (2.70)
15	141.94 (none)	142.38 (none)	143.87 (none)
16	139.50 (none)	138.90 (none)	139.80 (none)

[a] Assignments were made by the analyses of ^{1}H–^{13}C2D NMR shift correlation experiments (C–H COSY and COLOC spectra).

The resulting yellow oil (113 mg) obtained after removal of the solvent in vacuo at 15–20 °C was separated by low temperature MPLC on silica gel (column B) at −67 °C, eluting with 2% ethyl acetate in *n*-hexane, to give 82.6 mg of a mixture of **9** (66%) and **10** (7%) (by NMR) and 4.4 mg of **11** (4%) together with recovered **1** (12%), 6,6-diphenylfulvene (2%), and 7-benzhydrylidenenorbornadiene (1%). The major product **9** was separated from a mixture of **9** and **10** by fractional recrystallization from ether/*n*-hexane at 0 °C. The NMR data of **10** were derived from the spectrum of a mixture of **9** and **10**. Compound **11** was unstable and could not be further purified.

9: mp 108–108.5 °C dec (colorless cubes); IR (KBr) 1600, 1488, 1447, 999, 893, 752, 706, 698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45–7.20 (m, 10 H), 6.56 (br d, *J* = 2.7 Hz, 1 H), 6.17 (ddd, *J* = 2.7, 0.9, 0.5 Hz, 1 H), 5.65 (ddd, *J* = 3.5, 1.6, 0.5 Hz, 1 H), 5.12 (ddd, *J* = 3.9, 1.6, 1.6 Hz, 1 H), 4.24 (dddd, *J* = 3.9, 3.5, 3.4, 0.9 Hz, 1 H), 3.57 (m, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.95, 146.03, 142.28, 140.96, 136.66, 130.55, 128.46 (2 C), 128.19, 128.04 (2 C), 127.53, 127.39 (2 C), 127.26 (2 C), 88.79, 88.67, 62.54, 51.35; UV (cyclohexane) λ_{max} = 252 (673), 259 (671), 265 nm (550); MS (13.5 eV) *m/z* (relative intensity) 289 (M$^+$ + 1, 4), 288 (M$^+$, 25), 259 (21), 256 (50), 220 (30), 183 (11), 182 (100), 181 (18), 106 (22), 105 (96), 78 (15).

Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.38; H, 5.73.

10: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.50–7.15 (m, 10 H), 6.38 (ddd, *J* = 2.7, 0.8, 0.7 Hz, 1 H), 6.12 (ddd, *J* = 2.7, 1.1, 0.9 Hz, 1 H), 5.73 (dd, *J* = 1.6, 1.6 Hz, 1 H), 5.23 (dddd, *J* = 8.2, 1.6, 0.8, 0.8 Hz, 1 H), 4.04 (ddddd, *J* = 2.8, 1.6, 0.9, 0.8, 0.7 Hz, 1 H), 3.71 (ddd, *J* = 8.2, 2.8, 1.1 Hz, 1 H).

11: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.36–7.15 (m, 10 H), 6.15 (br s, 2 H), 4.94 (br s, 2 H), 3.27 (br s, 2 H); MS (13.5 eV) *m/z* (relative intensity) 289 (M$^+$ + 1, 24), 288 (M$^+$, 100), 270 (21), 237 (77), 207 (24).

Reduction of Endoperoxides 9, 10, and 11. To a solution of **9**, **10**, and **11** (226 mg, a 82:11:7 mixture obtained photooxygenation of **1** (200 mg)) in 2 mL of CH_2Cl_2 was added a solution of thiourea (71.0 mg, 0.93 mmol) in 5 mL of methanol at room temperature. After the mixture was stirred for 30 min and the solvent was removed in vacuo, the residue was passed through a short column of silica gel, eluting with 33% ethyl acetate in *n*-hexane. The resulting 218 mg of a yellow oil was further separated by MPLC on silica gel (column A, 17% ethyl acetate in *n*-hexane) to give **12** (153.8 mg, 68%), **13** (16.7 mg, 7%), and **14** (11.5 mg, 5%) together with recovered **1** (7%).

12: mp 112–113 °C (colorless cubes); IR (KBr) 3468, 3345, 1598, 1488, 1447, 1034, 1018, 761, 738, 697 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.44–7.15 (m, 10 H), 6.44 (dd, *J* = 2.6, 0.8 Hz, 1 H), 6.17 (ddd, *J* = 2.6, 1.1, 0.8 Hz, 1 H), 5.56 (dd, *J* = 2.2, 0.8 Hz, 1 H), 4.63 (dddd, *J* = 4.9, 3.0, 1.1, 0.8 Hz, 1 H), 4.38 (s, 1 H (OH)), 3.77 (ddddd, *J* = 3.0, 3.0, 2.2, 0.8, 0.8 Hz, 1 H), 3.28 (ddd, *J* = 3.0, 1.1, 1.1 Hz, 1 H), 2.71 (d, *J* = 4.9 Hz, 1 H (OH)); ^{13}C NMR (50 MHz, CD_2Cl_2) δ 149.17, 146.79, 146.47, 145.54, 138.50, 138.23, 128.43 (2 C), 127.97 (2 C), 127.83, (2 C), 127.53 (2 C), 127.48, 127.35, 80.57, 77.41, 55.79, 53.84; UV (CH_3CN) λ_{max} = 248 (sh, 256), 253 (343), 258 (412), 264 nm (311); MS (13.5 eV) *m/z* (relative intensity) 290 (M$^+$, 0.4), 273 (19), 272 (100), 271 (11), 243 (15), 213 (11), 195 (12), 105 (17).

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.84; H, 6.26.

13: mp 135–136 °C (colorless needles); IR (KBr) 3339, 3276, 1600, 1492, 1449, 1059, 1024, 725, 701 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.50–7.15 (m, 10 H), 6.60 (d, *J* = 2.8 Hz, 1 H), 6.19 (d, *J* = 2.8 Hz, 1 H), 5.50 (br d, *J* = 2.7 Hz, 1 H), 4.87 (br dd, *J* = 9.1, 7.8 Hz, 1 H), 4.75 (s, 1 H (OH)), 3.70 (dd, *J* = 9.1, 3.3 Hz, 1 H), 3.57 (dd, *J* = 3.3, 2.7 Hz, 1 H), 2.16 (br d, *J* = 7.8 Hz, 1 H (OH)); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.07, 147.76, 145.60, 145.13, 135.76, 135.67, 128.02 (2 C), 127.70 (2 C), 127.31 (2 C), 127.15 (2 C), 127.09, 126.98, 79.90, 75.53, 52.09, 49.37; UV (CH_3CN) λ_{max} = 247 (287), 253 (353), 258 (418), 264 nm (312); MS (13.5 eV) *m/z* (relative intensity) 290 (M$^+$, 0.6), 273 (24), 272 (100), 271 (10), 244 (38), 243 (37), 195 (23), 194 (11), 192 (19), 191 (51), 183 (29), 167 (19), 165 (12), 105 (19).

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.51; H, 6.14.

14: mp 136.5–137.5 °C (colorless needles); IR (KBr) 3316, 1599, 1490, 1443, 1030, 1015, 994, 978, 737, 701 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.20–7.40 (m, 10 H), 6.03 (dd, *J* = 0.7, 0.7 Hz, 2 H), 4.49 (d, *J* = 5.9 Hz, 2 H), 3.63 (br s, 2 H), 2.51 (d, *J* = 5.9 Hz, 2 H (OH)); ^{13}C NMR (50 MHz, $CDCl_3$) δ 146.08, 143.13, 141.03 (2 C), 138.80 (2 C), 129.56 (4 C), 128.07 (4 C), 127.48 (2 C), 73.65 (2 C), 54.44 (2 C); UV (CH_3CN) λ_{max} = 226 (15 000), 248 nm (14 200); MS (25 eV) *m/z* (relative intensity) 290 (M$^+$, 11), 272 (13), 244 (14), 243 (32), 237 (13), 228 (14), 222 (10), 208 (16), 207 (100), 206 (30), 178 (13), 167 (24), 165 (30).

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.46; H, 6.06.

Photolysis of 1 in Acrylonitrile. A solution of **1** (200.1 mg, 0.781 mmol) in 120 mL of acrylonitrile in a quartz vessel was irradiated with 4 RUL-3000Å lamps for 1 h under N_2. Removal of acrylonitrile in vacuo afforded 592 mg of yellow residue, which was passed through a short column of silica gel, eluting once with ether and twice with 17% ethyl acetate in *n*-hexane. The resulting orange oil (211 mg) was separated by MPLC on silica gel (column B), eluting with 2% ethyl acetate in *n*-hexane to give **15** (76.5 mg, 32%), **16** (50.7 mg, 21%), **17** (25.4 mg, 11%), and **18** (24.5 mg, 10%) together with recovered **1** (1%), 6,6-diphenylfulvene (2%), and 7-benzhydrylidenenorbornadiene (3%).

15: mp 129.5–130.5 °C (colorless cubes); IR (KBr) 2230, 1594, 1552, 1495, 1487, 1446, 762, 752, 704, 696 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40–7.11 (m, 10 H), 6.43 (ddd, *J* = 2.7, 0.8, 0.8 Hz, 1 H), 6.31 (br d, *J* = 2.7 Hz, 1 H), 5.11 (br dd, *J* = 3.3, 2.5 Hz, 1 H), 4.03 (dd, *J* = 8.8, 4.0 Hz, 1 H), 3.92 (dddd, *J* = 4, 4, 4, 0.8 Hz, 1 H), 3.37 (ddddd, *J* = 10.3, 8.2, 3.8, 3.0, 2.5 Hz, 1 H), 3.21 (br dd, *J* = 3.7, 3.0 Hz, 1 H), 2.37 (ddd, *J* = 12.2, 8.2, 4.0 Hz, 1 H), 1.97 (ddd, *J* = 12.2, 10.3, 8.8 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.88, 145.88, 143.43, 142.76, 139.65, 129.03 (2 C), 128.28 (4 C), 127.33, 127.08 (3 C), 126.55, 121.16, 59.76, 58.81, 51.63, 48.86, 42.91 35.61; UV (cyclohexane) λ_{max} = 255 (390), 260 nm (459); MS (25 eV) *m/z* (relative intensity) 310 (M$^+$ + 1, 24), 309 (M$^+$, 100), 256 (72), 255 (83), 241 (50), 240 (22), 230 (24), 218 (29), 205 (29), 191 (21), 179 (59), 178 (70), 167 (22), 165 (42), 104 (99).

Anal. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.23; H, 6.37; N, 4.49.

16: mp 130–131 °C (colorless cubes); IR (KBr) 2225, 1595, 1554, 1488, 1446, 757, 728, 698 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.45–7.14 (m, 8 H), 7.02–6.91 (m, 2 H), 6.43 (ddd, *J* = 2.7, 0.7, 0.7 Hz, 1 H), 6.21 (br d, *J* = 2.7 Hz, 1 H), 5.18 (br dd, *J* = 3.4, 2.6 Hz, 1 H), 4.07 (dddd, *J* = 4.1, 3.4, 3.4, 0.7 Hz, 1 H), 3.73 (dd, *J* = 11.7, 6.7 Hz, 1 H), 3.28 (br dd, *J* = 3.4, 2.6 Hz, 1 H), 2.84

Table II. Composition of Cycloadducts from Photolysis of 1 in the Presence of Acrylonitrile in Acetonitrile

		yields of cycloadducts, %					
[acrylonitrile], M	conversion of 1, %	total adducts	15	16	17	18	(ratio)
0.05^a	16.8	4.52	1.73	1.31	0.66	0.81	(38:29:15:18)
0.5^a	18.1	12.9	5.1	3.3	2.2	2.3	(40:26:17:18)
5^a	16.8	13.9	5.6	3.4	2.3	2.6	(40:24:17:19)
5^b	14.6	11.2	4.5	2.8	1.9	2.0	(40:25:17:18)

[a] Direct photolysis of 1. [b] Benzophenone sensitization of 1.

(ddddd, *J* = 12.2, 6.7, 4.1, 2.6, 2.6 Hz, 1 H), 2.47 (ddd, *J* = 11.5, 6.7, 6.7 Hz, 1 H), 1.92 (ddd, *J* = 12, 12, 12 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 159.30, 144.91, 144.68, 143.74, 139.14, 128.97 (2 C), 128.84 (2 C), 127.69 (2 C), 127.66 (2 C), 127.60, 127.24, 126.88, 120.50, 59.93, 58.61, 50.30, 49.14, 45.72, 36.39; UV (cyclohexane) λ_{max} = 254 (372), 260 (448), 265 nm (345); MS (25 eV) *m/z* (relative intensity) 310 (M^+ + 1, 20), 309 (M^+, 100), 256 (56), 255 (73), 241 (46), 230 (21), 205 (22), 179 (48), 178 (61), 165 (35), 104 (74).

Anal. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.16; H, 6.23; N, 4.52.

17: mp 96–97 °C (colorless cubes); IR (KBr) 2229, 1598, 1488, 1444, 759, 750, 700 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.35–7.15 (m, 10 H), 6.13 (d, *J* = 2.7 Hz, 1 H), 6.01 (d, *J* = 2.7 Hz, 1 H), 2.90 (s, 1 H), 2.83 (d, *J* = 4.7 Hz, 1 H), 2.71 (d, *J* = 3.2 Hz, 1 H), 2.66 (d, *J* = 3.2 Hz, 1 H), 2.38 (dd, *J* = 9.3, 4.7 Hz, 1 H), 2.06 (ddd, *J* = 12.5, 4.7, 4.7 Hz, 1 H), 1.75 (dd, *J* = 12.5, 9.3 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.85, 141.58, 140.55, 139.28, 138.09, 137.72, 129.47 (2 C), 129.19 (2 C), 128.06 (2 C), 127.94 (2 C), 126.91 (2 C), 122.76, 49.10, 48.72, 43.63, 38.65, 33.64, 28.61; UV (cyclohexane) λ_{max} = 223 (15 300), 242 nm (15 800); MS (25 eV) *m/z* (relative intensity) 310 (M^+ + 1, 19), 309 (M^+, 100), 256 (23), 255 (24), 230 (20), 229 (23), 191 (23), 179 (37), 178 (45), 167 (20), 165 (23).

Anal. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.26; H, 6.00; N, 4.52.

18: mp 104.5–105.5 °C (colorless prisms); IR (KBr) 2226, 1597, 1490, 1440, 770, 764, 752, 720, 704 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.31–7.22 (m, 6 H), 7.11–7.07 (m, 4 H), 6.10 (d, *J* = 2.7 Hz, 1 H), 6.06 (d, *J* = 2.7 Hz, 1 H), 3.32 (d, *J* = 3.2 Hz, 1 H), 2.96 (ddd, *J* = 11.3, 5.0, 4.3 Hz, 1 H), 2.93 (d, *J* = 4.3 Hz, 1 H), 2.85 (d, *J* = 3.2 Hz, 1 H), 2.78 (d, *J* = 4.6 Hz, 1 H), 2.26 (ddd, *J* = 12.3, 11.3, 4.6 Hz, 1 H), 1.56 (dd, *J* = 12.2, 5.0 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 141.92, 141.63 (2 C), 138.63, 137.79, 136.73, 129.25 (4 C), 128.08 (2 C), 127.99 (2 C), 127.07, 126.99, 121.36, 49.52, 45.49, 42.02, 39.00, 32.78, 27.79; UV (cyclohexane) λ_{max} = 224 (16 100), 245 nm (17 300); MS (13.5 eV) *m/z* (relative intensity) 310 (M^+ + 1, 11), 309 (M^+, 100), 308 (10), 256 (21).

Anal. Calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 89.30; H, 6.25; N, 4.31.

Stereochemical assignments of **15** and **16** were made by NOE difference spectra. A NOE was observed between H_2 (2.84 ppm) and H_4 (3.73 ppm) for **16**, but none between H_2 (3.37 ppm) and H_4 (4.03 ppm) for **15**.

Photolysis of 1 in the Presence of 5, 0.5, and 0.05 M Acrylonitile in Acetonitrile. Three acetonitrile (2 mL) solutions of 1 (1.00 × 10^{-3} M) containing 5, 0.5, and 0.05 M of acrylonitrile, respectively, in a quartz tube were degassed by repeating three freeze (−196 °C)–pump (10^{-5}–10^{-6} mmHg)–thaw (0 °C) cycles and then sealed at 10^{-5}–10^{-6} mmHg. Three solutions were irradiated for 10 min in a Rayonet merry-go-round photoreactor (2 Rayonet RPR 3000Å lamps) at room temperature. To three photolyzed solutions was added 100 μL of acetonitrile containing 4.174 × 10^{-3} M triphenylmethane as an internal standard. Three photolyzed solutions were analyzed twice by reverse-phase HPLC (elution with 60% acetonitrile in water at the rate of 0.8 mL/min, UV monitor at 227 nm). Retention times of **1**, **15**, **16**, **17**, **18**, and triphenylmethane were 74, 44, 45, 40, 49, and 52 min, respectively. Conversion of **1** and yields of cycloadducts **15**, **16**, **17**, and **18** were determined by relative peak integrations and individual response factors to triphenylmethane. The results are shown in Table II.

Benzophenone-Sensitized Irradiation of 1 in the Presence of 5 M Acrylonitrile in Acetonitrile. A solution of **1** (1.00 × 10^{-3} M), acrylonitrile (5 M), and benzophenone (3.00 × 10^{-2} M) in 2 mL of acetonitrile was degassed by the procedure described above and irradiated in a Rayonet merry-go-round photoreactor (4 Rayonet RPR-3500Å lamps) at room temperature for 30 min. Conversion of **1** and yields of cycloadducts **15**, **16**, **17**, and **18** were analyzed by the procedure described above, and the results are shown in Table II.

Photolysis of Quadricyclanone (2) in Ethyl Vinyl Ether. A solution of quadricyclanone (**2**, 100.4 mg, 0.946 mmol) in 120 mL of ethyl vinyl ether was placed in a quartz vessel and irradiated with 4 RUL-3000Å lamps for 12 h at 2 °C under N_2. Removal of ethyl vinyl ether gave 168 mg of a yellow oil, which was chromatographed on alumina (neutral Al_2O_3, activity V, 50 g). Elution with *n*-pentane gave a mixture of **19** and **20** (90.5 mg) and elution with 50% ether in *n*-pentane gave 29.7 mg of a yellow oil containing recovered **2**. A mixture of **19** and **20** was rechromatographed on alumina (neutral Al_2O_3, activity IV, 100 g). Elution with *n*-pentane afforded **19** (25.9 mg, 15%) as a colorless oil and **20** (54.2 mg, 33%) as a colorless oil. A yellow oil containing recovered **2** was rechromatographed on silica gel to give 10.4 mg of **2** (10%) by eluting with dichloromethane.

19: bp 53–70 °C (4 mmHg); IR (neat) 1665, 1554, 1189, 1164, 1098, 1081, 755 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.35 (ddd, *J* = 2.7, 1.1, 0.7 Hz, 1 H), 6.24 (br d, *J* = 2.7 Hz, 1 H), 5.43 (d, *J* = 5.3 Hz, 1 H), 4.49 (dddd, *J* = 3.4, 2.7, 0.7, 0.7 Hz, 1 H), 3.94 (br ddd, *J* = 3.9, 3.9, 3.9 Hz, 1 H), 3.80 (dq, *J* = 9.5, 7.0 Hz, 1 H), 3.49 (dq, *J* = 9.5, 7.0 Hz, 1 H), 3.19 (ddddd, *J* = 12.4, 7.1, 4.0, 4.0, 2.7 Hz, 1 H), 3.09 (dddd, *J* = 4.0, 4.0, 1.0, 0.8 Hz, 1 H), 2.03 (ddd, *J* = 11.9, 7.1, 0.7 Hz, 1 H), 1.69 (ddd, *J* = 12.4, 11.9, 5.3 Hz, 1 H), 1.20 (dd, *J* = 7.0, 7.0 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 167.10, 143.13, 139.13, 109.61, 92.03, 63.91, 57.40, 47.78, 43.35, 36.15, 15.01; MS (25 eV) *m/z* (relative intensity) 178 (M^+, 16), 149 (60), 133 (31), 132 (75), 131 (100), 123 (32), 121 (91), 107 (75), 106 (21), 105 (36), 104 (36), 103 (32), 95 (30), 91 (25), 78 (58), 77 (29), 72 (46); HRMS (M^+) calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0992.

20: bp 56–70 °C (2 mmHg); IR (neat) 1664, 1555, 1172, 1140, 1120, 801, 746 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.33 (ddd, *J* = 2.7, 0.9, 0.8 Hz, 1 H), 6.18 (br d, *J* = 2.7 Hz, 1 H), 5.56 (dd, *J* = 7.2, 4.7 Hz, 1 H), 4.53 (br dd, *J* = 3.5, 2.6 Hz, 1 H), 3.93 (1 H), 3.91 (dq, *J* = 9.6, 7.0 Hz, 1 H), 3.60 (dq, *J* = 9.6, 7.0 Hz, 1 H), 3.11 (br dd, *J* = 3.9, 3.9 Hz, 1 H), 2.91 (ddddd, *J* = 12.6, 7.7, 3.9, 3.9, 2.6 Hz, 1 H), 2.31 (dddd, *J* = 12.2, 7.7, 4.7, 0.8 Hz, 1 H), 1.56 (br ddd, *J* = 12.2, 12.2, 7.2 Hz, 1 H), 1.25 (dd, *J* = 7.0, 7.0 Hz, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 164.99, 143.30, 138.58, 111.69, 92.88, 65.77, 56.95, 47.55, 45.50, 36.39, 15.12; MS (25 eV) *m/z* (relative intensity) 178 (M^+, 33), 149 (86), 133 (43), 132 (83), 131 (97), 123 (36), 121 (95), 107 (84), 106 (30), 105 (36), 104 (25), 103 (33), 95 (39), 93 (30), 91 (33), 79 (33), 78 (100), 77 (47), 72 (93); HRMS (M^+) calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0991.

Stereochemistry of adducts **19** and **20** were confirmed by NOE difference spectra. There was a NOE between H_2 (2.91 ppm) and H_4 (5.56 ppm) for **20**, but none between H_2 (3.19 ppm) and H_4 (5.43 ppm) for **19**.

Photolysis of Quadricyclanone (2) in the Presence of Cyclopentadiene. A solution of quadricyclanone (**2**, 200.1 mg, 1.89 mmol) and cyclopentadiene (1.26 g, 19.1 mmol) in 250 mL of *n*-pentane was irradiated with 4 RUL-3000Å lamps for 11 h under N_2. Removal of solvent in vacuo gave 603 mg of a yellow oil, which was chromatographed on silica gel (60 g). Elution with *n*-hexane afforded 198 mg of a complex mixture containing cyclopentadiene dimer and elution with 9% ethyl acetate in *n*-hexane gave **21** (121.8 mg, 37%) and recovered **2** (15%). Cycloadduct **21** was recrystallized from *n*-hexane at 0 °C to give colorless needles.

21: mp 40.5–41.5 °C; IR (KBr) 1739, 735, 720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.23 (s, 2 H), 6.01 (s, 2 H), 3.34 (s, 2 H), 2.80 (dd, *J* = 5.9, 3.6 Hz, 2 H), 2.49 (d, *J* = 11.0 Hz, 1 H), 2.38 (d, *J*

= 5.9 Hz, 2 H), 1.52 (dt, J = 11.0, 3.6 Hz, 1 H); UV (cyclohexane) λ_{max} = 274 (12.0), 283 (13.4), 295 nm (sh, 11); MS (25 eV) m/z (relative intensity) 172 (M^+, 9), 129 (16), 128 (16), 107 (100), 79 (25), 78 (17), 66 (45).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.52; H, 6.83.

The 2D NOESY spectrum for **20** showed a cross peak between H_3 (H_6) (3.34 ppm) and one of the methylene protons at C_{11} (2.49 ppm).

Photolysis of Quadricyclanone (2) in Furan. A solution of quadricyclanone (**2**, 211.2 mg, 1.99 mmol) in 130 mL of furan in quartz vessel was irradiated with 4 RUL-3000Å lamps for 20 h under N_2. Removal of furan in vacuo gave 451 mg of a yellow oil. After passing the material through a short column of silica gel (33% ethyl acetate in n-hexane), a crude photolysate was separated by MPLC on silica gel (column A). Elutions with 9% ethyl acetate in n-hexane and with 17% ethyl acetate in n-hexane afforded **2** (8.9 mg, 4%) and **22** (172.4 mg, 50%) as pale yellow crystals which was recyrstallized from n-hexane to give colorless plates.

22: mp 81–81.5 °C; IR (KBr) 1751, 1130, 1010, 741, 702 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 6.36 (s, 2 H), 6.00 (s, 2 H), 4.80 (d, J = 3.6 Hz, 2 H), 3.55 (s, 2 H), 2.51 (d, J = 3.6 Hz, 2 H); UV (cyclohexane) λ_{max} = 274 (11.4), 283 (12.9), 293 (sh, 11.2), 307 nm (sh, 6.0); MS (25 eV) m/z (relative intensity) 174 (M^+, 3), 146 (69), 145 (100), 131 (31), 117 (76), 115 (31), 91 (35), 81 (31), 78 (55), 68 (69).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.78; H, 5.86.

Photolysis of Quadricyclanone (2) in Methanol. A solution of quadricyclanone (**2**, 303.1 mg, 2.86 mmol) in 700 mL of methanol was irradiated with 4 RUL-3000Å lamps for 6 h under N_2. Removal of methanol in vacuo gave 297 mg of a yellow oil, which was chromatographed on silica gel (50 g). Elution with 14% ether in n-pentane gave 39.4 mg of exo adduct **23** (10%) as a pale yellow oil and 72.4 mg of recovered **2** (24%). Elutions with 14% ether in n-pentane and 33% ether in n-pentane gave 55.3 mg of endo adduct **24** (14%) as a pale yellow oil. **23** and **24** were further purified as a colorless oil by distillation.

23: bp 64–73 °C (35 mmHg); IR (neat) 2816, 1747, 1090, 1068, 784, 740 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 6.16 (d, J = 2.7 Hz, 1 H), 5.98 (br d, J = 2.7 Hz, 1 H), 3.47 (dd, J = 8.5, 3.5 Hz, 1 H), 3.39 (s, 3 H), 3.35 (d, J = 3.5 Hz, 1 H), 3.24 (s, 1 H), 2.66 (dd, J = 17.5, 8.5 Hz, 1 H), 2.19 (d, J = 17.5 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 214.15, 143.03, 135.37, 82.33, 57.65, 49.49, 41.99, 39.40; HRMS (M^+) calcd for $C_8H_{10}O_2$ 138.0681, obsd 138.0675.

24: bp 65–75 °C (22 mmHg); IR (neat) 2816, 1753, 1135, 1110–1098 (br), 776 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 6.17 (br d, J = 2.9 Hz, 1 H), 6.14 (br d, J = 2.9 Hz, 1H), 4.09 (dd, J = 8.3, 2.1 Hz, 1 H), 3.66 (dd, J = 8.3, 3.7 Hz, 1 H), 3.54 (s, 3 H), 3.44 (ddd, J = 8.2, 3.7, 0.9 Hz, 1 H), 2.50 (ddd, J = 17.1, 8.2, 2.1 Hz, 1 H), 2.22 (dd, J = 17.1, 0.9 Hz, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 211.80, 141.13, 136.97, 84.74, 58.32, 43.95, 39.02, 37.78; HRMS (M^+) calcd for $C_8H_{10}O_2$ 138.0681, obsd 138.0677.

Stereoselective Synthesis of Terminal 1,3-Butadienes by the Condensation Reaction of Aldehydes and Ketones with the γ-Trimethylsilyl-Substituted Allylboranes

Kung K. Wang,* Chin Liu, Yu Gui Gu, and Friedrich N. Burnett

Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

Prem D. Sattsangi

Department of Chemistry, The Pennsylvania State University, Fayette Campus, Uniontown, Pennsylvania 15401

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Allylboranes **7–12**, readily prepared from allenylsilanes **1–6** by hydroboration with 9-borabicyclo[3.3.1]nonane, smoothly condense with aldehydes and ketones to afford, after basic or acidic workup to promote the Peterson olefination reaction, a variety of terminal 1,3-butadienes. The dienes derived from aldehydes have high isomeric purity except in the cases with allylborane **12**. Apparently, high diastereoselectivity was obtained during the condensation step with **7–11** to form **14**. In each case, by simply changing the workup conditions to induce syn or anti elimination of hydroxytrimethylsilane, either the Z or the E isomer of the diene was obtained.

The synthetic utility of 1,3-butadienes in the Diels–Alder reaction[1] and the discovery of many biologically active natural products possessing a conjugated diene functionality[2] have prompted the development of a large number of stereoselective synthetic methods for the preparation of these compounds.[3] We recently reported a simple and stereoselective route to 2-[(trimethylsilyl)methyl]-1,3-butadienes using 1,2-bis(trimethylsilyl)-2,3-butadiene (**3**) as the starting material (Scheme I).[3a] The ready availability of a variety of trimethylsilyl-substituted terminal allenes[4] allows the extension of this methodology to the synthesis of many other terminal 1,3-butadienes.[5] We now disclose the full account of the research effort in this area.

Hydroboration of allenes **1–6** with 9-borabicyclo[3.3.1]nonane[6] afforded the corresponding allylboranes **7–12** (Scheme I). Allylboranes **7–11** had predominantly the E geometry (E:Z ≥ 91:9), whereas allylborane **12**

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