totaling 100 min. Concentrated methanolic ammonia (2 h at 25 °C) was used to cleave the dimer from the support and to deprotect the phosphorus.

HPLC Methods. A Beckman high-performance liquid chromatography system equipped with System Gold software, a 126 solvent module, and a 168 diode array detector was used with an Ultrasphere reversed-phase 5 μm spherical 80-Å pore C-18 guard (4.6 × 45 mm) and analytical (4.6 × 250 mm) column. A gradient elution was carried out with an aqueous triethyl ammonium acetate (TEAA, 0.1 M, pH 7) vs CH_3CN with a flow rate of 1 mL/min. The gradient used was as follows: 100% TEAA to 22% CH_3CN over 5 min, 22–30% CH_3CN over 15 min, 30–50% CH_3CN over 25 min, and 50–100% CH_3CN over 15 min.

Synthetic Procedures. Preparation of 3′-[5′-*O*-(4,4′-Dimethoxytrityl)deoxythymidinyl] Methyl [2-[(Dicarbonyl)(η^5-cyclopentadienyl)iron]ethyl]phosphonate (7). Compound **5a** (99 mg, 0.14 mmol), tetrazole (43 mg, 0.61 mmol), methanol (24 μL, 0.56 mmol), and CH_3CN (10 mL) were combined in a 50-mL schlenck tube under an atmosphere of argon. After 30 minutes 1 (90 mg, 0.3 mmol) was added; an IR assay showed complete conversion after an additional hour. IR (ν CO, CH_3CN): 2011 and 1953 cm^{-1}. The solvent was removed in vacuo and coevaporated with acetone (3 × 5 mL). The resulting oil was dissolved in acetone (5 mL) and combined with NaI (300 mg, 2 mmol). This reaction mixture was allowed to stir at ambient temperature for 1 h under an atmosphere of argon, at which time the reaction mixture was diluted with CH_2Cl_2 (10 mL) and extracted with water (4 × 15 mL). The organic layer was dried ($MgSO_4$), filtered, and dried in vacuo. The resulting oil was dissolved in a minimal amount of CH_2Cl_2 and loaded onto an activated (Brockmann III) aluminum oxide (neutral) column (10 g), which was eluted with CH_2Cl_2/NEt_3 (99/1). The yellow fractions were combined and concentrated to yield a thick gold oil which was triturated with hexane to yield 7, a beige powder (77 mg, 67%). IR (ν CO, CH_2Cl_2): 2011 and 1953 cm^{-1}. ^{31}P NMR (δ, acetone-d_6): 32 ppm (d, RP=O). ^1H NMR (δ, acetone-d_6) 7.59 (m, H-6), 7.48–6.92 (m, aromatic), 6.38 (m, H-1′), 4.99 (s, Cp), 4.27 (m, H-3′), 3.91 (m, H-4′), 3.79 (s, OCH_3), 3.65 (d, $POCH_3$), 3.44 (m, H-5′), 2.55 (m, H-2′), 1.83 (m, PCH_2), and 1.46 (m, CH_3 and $FeCH_2$) ppm. MS: low-resolution *m/e* calcd (M + Na^+) 849, obsd 849; high-resolution *m/e* calcd for daughter ion $C_8H_7O_2Fe$ 190.9795, obsd 190.9790; *m/e* calcd for $C_{33}H_{36}O_9N_2PNa$ 658.2056, obsd 658.2061.

In an alternate procedure, compound **5b** (R = CH_2CH_2CN) was used in place of **5a** in order to determine if a β-cyano ethyl group could be selectively removed by concentrated methanolic ammonia (5 mL). The remainder of the work up was identical, yielding a similar product. IR (ν CO, acetone): 2009 and 1953 cm^{-1}. ^{31}P NMR (δ, acetone-d_6): 32 ppm (d, RP=O).

Preparation of 5′-[(3′-*O*-Levulinyl)deoxythymidinyl] 3′-[N^6-Benzoyl-5′-*O*-(4,4′-dimethoxytrityl)deoxyadenosyl] [2-[(Dicarbonyl)(η^5-cyclopentadienyl)iron]ethyl]phosphonate (11). Compound **8a** (100 mg, 0.12 mmol), tetrazole (43 mg, 0.61 mmol), compound **9a** (41 mg, 0.12 mmol), and CH_3CN (10 mL) were combined in a 50-mL schlenk tube under an atmosphere of argon. After 30 min 1 (36 mg, 0.12 mmol) was added to the reaction mixture and stirred under an atmosphere of argon for 1 h. The solvent was removed in vacuo and coevaporated with acetone (3 × 5 mL) and then dissolved in acetone (5 mL). NaI (300 mg, 2 mmol) was added and the solution allowed to stir for 1 h at ambient temperature. The reaction mixture was dissolved in CH_2Cl_2 (10 mL) and washed with water (4 × 15 mL). The organic layer was dried ($MgSO_4$), filtered, and dried in vacuo to yield an amber oil. The oil was triturated with hexane to yield 11 as a beige solid (101 mg, 53%). IR (ν CO, acetone): 2009 and 1953 cm^{-1}. ^{31}P NMR (δ, acetone-d_6): 32 ppm (d, RP=O). ^1H NMR (δ, acetone-d_6): 8.60 (s, H-8 A), 8.30 (s, H-2 A), 7.59 (m, H-6 T), 8.04 (m, aromatic), 7.65–6.85 (m, aromatic), 6.55 (m, H-1′ A), 6.28 (m, H-1′ T), 5.31 (m, H-3′ T), 5.03 (s, Cp), 4.68 (m, H-3′ A), 4.46 (m, H-4′ A), 4.15 (m, H-4′ T), 3.78 (s, OCH_3), 3.59 (m, H-5′ T), 3.48 (m, H-5′ A), 2.81–2.57 (m, H-2″ and H-3″ T), 2.36 (m, H-2′ T), 2.13 (s, H-5″ T), 1.84 (s, CH_3 T), and 1.83–1.66 (m, $FeCH_2$ and PCH_2) ppm (A = deoxyadenosine and T = thymidine). MS: low-resolution *m/e* calcd (M + Na^+) 1270, obsd 1270; high-resolution *m/e* calcd for daughter ion $C_8H_7O_2Fe$ 190.9795, obsd 190.9792; *m/e* calcd for $C_{54}H_{55}O_{14}N_7PNa$ 1079.3442, obsd 1079.3445.

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Supplementary Material Available: ^1H NMR spectra of 7 and 11 and ^{31}P NMR spectrum of 11 (3 pages). This material is contained in many 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.

Inversion of the Ground-State Spin Multiplicity by Electron-Withdrawing Groups in Trimethylenemethane Derivatives Generated Photochemically from Methylenequadricyclane Derivatives

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An inversion of the ground-state spin multiplicity of trimethylenemethane (TMM) by electron-withdrawing groups was investigated by EPR spectroscopy, for a series of TMMs **2b–g** generated photochemically from methylenequadricyclanes **1b–g**. Curie law analyses between 4 and 50 K proved the triplet ground states of the monophenyl derivative **2b** and the monocyano derivatives **2c–d** as well as that of the diphenyl derivative **2a**. The dicarbomethoxy derivative **2e** also exhibited the EPR signal, but the Curie plot was nonlinear and the signal disappeared irreversibly above 10K. The triplet ground state was inverted to the singlet by the carbomethoxy-cyano and dicyano substitutions, and **2f** and **2g** were EPR silent species similar to the singlet oxyallyl (OA) derivative **2h**. The singlet ground state of **2g** was demonstrated by its chemical behaviors which resemble those of **2h**.

We previously reported that photoreactions of benzhydrylidenequadricyclane (**1a**) and quadricyclanone (**1h**) formed the triplet trimethylenemethane (TMM) derivative **2a** and the singlet OA derivative **2h**, respectively.[1] These

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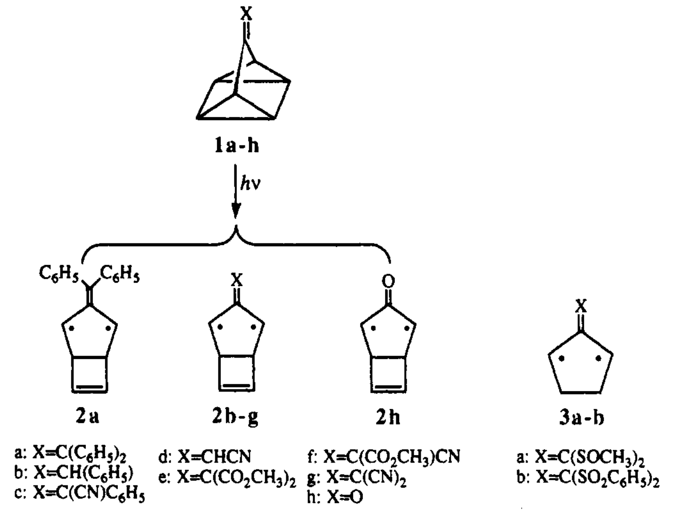
Scheme I



results experimentally verified theoretical predictions that replacement of one terminus of TMM by a heteroatom would result in the splitting of two degenerate nonbonding orbitals (NBMO) of TMM, and the OA's singlet state would be preferred to be the lowest ground state or would become energetically close to the triplet state.[2-4] The splitting of NBMOs of TMM had been also theoretically predicted to be induced by substitution of electron-donating or electron-withdrawing groups at one methylene group of TMM.[5] Experimental verification of this prediction was examined for TMMs of 2-methylenecyclopentane-1,3-diyl series by Berson and co-workers.[2a,e,f,6] For instance, Curie law analysis established the triplet ground state of the methylsulfinyl derivative **3a**, whereas no EPR signal was observed for the phenylsulfonyl derivative **3b**.[2a,e,f] However, it was noted that an inversion of the spin multiplicity due to the phenylsulfonyl substitution was not fully confirmed because of some practical problems.[2a,e,f] In connection with this, our procedure, i.e., the photochemical generation of TMM from the methylenequadricyclane system, is convenient for systematic test of substituent effects on an inversion of the TMM spin multiplicity by electron-withdrawing groups, because electron-withdrawing groups such as the carbomethoxy and cyano groups can be readily introduced to the exocyclic position of the methylenequadricyclane system. In order to investigate substituent effects on an inversion of the TMM ground-state spin multiplicity, a series of symmetrical disubstituted and unsymmetrical mono- and disbustituted methylenequadricyclanes **1b–g** was synthesized from **1h** and subjected to EPR spectroscopy. Spectroscopic results for the photogenerated TMMs **2b–g** and chemical behaviors of **2g** were compared with those[1] for **2a** and **2h**. Herein we report that the carbomethoxy-cyano and dicyano substitutions are strong enough to invert a ground state from the triplet to the singlet in a series of TMMs **2a–g**.

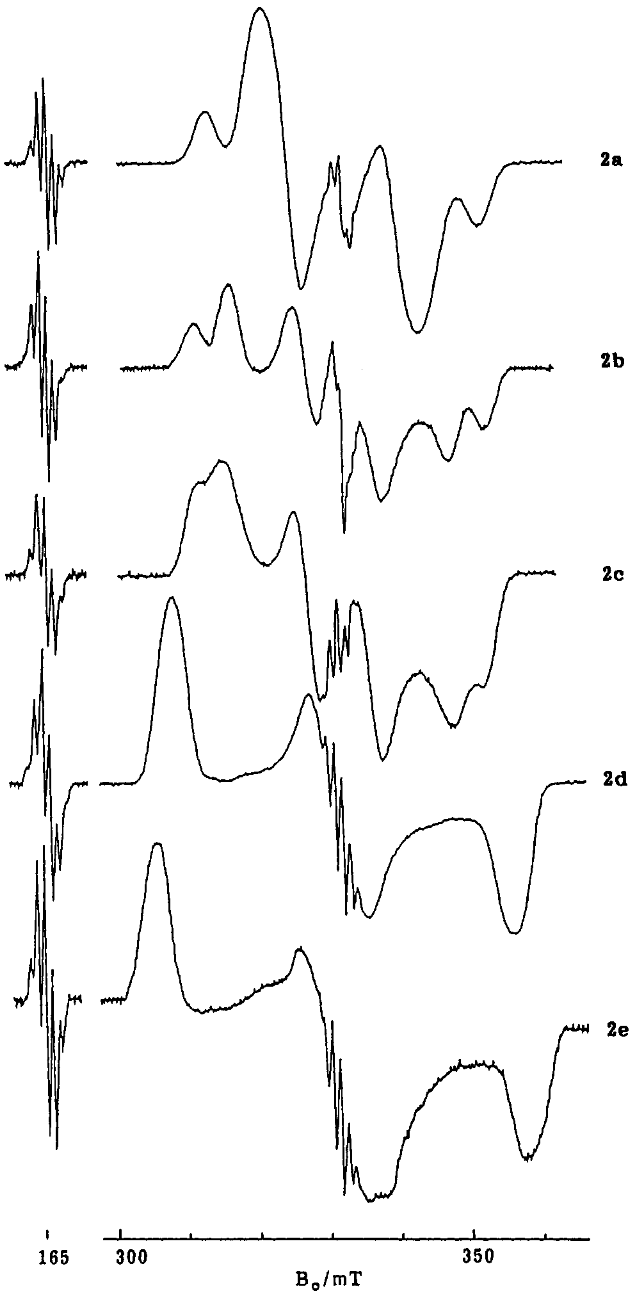


Figure 1. Steady-state EPR spectra of **2a–e** obtained during irradiation of **1a–e** in toluene at 20 K in the presence of benzophenone.

Results and Discussion

EPR Spectroscopy of TMM Derivatives 2b–g. Methylenequadricyclane derivatives **1b**,[7] **1f**,[8] and **1g**[8] were prepared according to the literature, and **1c–e** were prepared by the Knoevenagel condensation or the Wittig reaction from quadricyclanone (**1h**).[9] Upon separate irra-

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Table I. ZFS Parameters and Hfs Constants of 2a–e Obtained during Irradiation of 1a–e in Toluene at 20 K

compd	$\lvert D\rvert$/cm^{-1}	$\lvert E\rvert$/cm^{-1}	a^H/mT
2a	0.0179	<0.0006	1.05 (4H)
2b	0.0191	0.0032	1.05 (5H)
2c	0.0189	0.0040	1.04 (4H)
2d	0.0226	0.0075	1.03 (5H)
2e	0.0251	0.0084	0.98 (4H)

diation of **1b** and **1c** with 308-nm light in a methylcyclohexane, benzene, or toluene matrix at 20 K, a bright yellow color immediately developed and characteristic EPR spectra of randomly oriented triplet TMMs **2b** and **2c** were observed, respectively. Similar to the triplet **2a**, the signal intensities of **2b** and **2c** increased upon irradiation in the presence of benzophenone. Absorption coefficients of **1d** and **1e** at 308 nm were so small that the EPR signal intensities of **2d** and **2e** were markedly weak compared with those of **2a–c** under the direct irradiation conditions, but the benzophenone-sensitized irradiations of **1d** and **1e** exhibited characteristic EPR signals corresponding to **2d** and **2e**, respectively, as shown in Figure 1. Interestingly, no EPR signal was observed for **1f** and **1g** at cryogenic temperature between 4.2 and 50 K under either the direct or benzophenone-sensitized irradiation conditions. The zero-field splitting (ZFS) parameters estimated from the specta of **2b–e** were summarized together with those for **2a** in Table I. Because the $|D|$ value is proportional to $1/r^3$, where r is an average distance of two unpaired electrons, the $|D|$ value should decrease with an increase in spin delocalization.[10] It is thus reasonable that the $|D|$ values for the phenyl-substituted TMMs **2a–c** are much smaller than those for **2d** and **2e**.[11] The $|\Delta M_s| = 2$ line is the most useful to obtain interpretable hyperfine splitting (Hfs) constants in a powder spectrum because the $|\Delta M_s| = 2$ line is only minimally anisotropic for the small $|D|$ value ($|D| < 0.03$ cm^{-1}) in Table I.[10] As the spectra of TMMs **2a–e** in Figure 1 showed substantial hyperfine splittings on the $|\Delta M_s| = 2$ line, a unique set of Hfs constants could be extracted from the spectra. However, rather broader signals due to the observation in a solid solution put small differences in the Hfs constants for each proton into the shade. In all cases the signals were tentatively assigned by a set of equivalent protons. As summarized in Table I, the Hfs constants obtained by computer simulation ranged between 1.05 and 0.98 mT, the values being close to those of the parent TMM[12] and the known cyclic TMM derivatives[13] in magnitude. Although substituent effects on Hfs constants are not clear at this stage, the Hfs constant tends to decrease with an increase in the electron-withdrawing properties of substituents.

The temperature-dependent variation of the $|\Delta M_s| = 2$ transition line intensity provided definite evidence for the triplet ground state of TMMs **2a–d**.[10] The changes were reversible between 4.2 and 50 K and corresponded to strict adherence to the Curie law, IT = constant, where I is the EPR signal intensity and T is absolute temperature. In Figure 2, the Curie plots for **2a** and **2e** were exemplified. In contrast with the Curie plots for **2a–d**, that for **2e** was reversible only between 4.2 and 10 K, and spectroscopic behavior of **2e** was apparently different from those of **2a–d** even in taking into account of effects of saturation which were serious at low temperature. The Curie plot in a narrow temperature range thus inhibited the firm confirmation of the ground-state spin multiplicity of **2e**. However, it would be conceivable that a markedly small energy gap between the equilibrating triplet and singlet states might cause **2e** to behave differently from **2a–d**. In fact, the energy gap obtained by the least-square fitting of the data to the equation[14] proposed by Wasserman was quite small, $E_T - E_s = 0.02$ kJ/mol, suggesting that the singlet state of **2e** is slightly lower than the triplet state or at least very close to the triplet state. Because typical TMM chemistry was observed in the room-temperature photolyses of **1a**, **1g**, and **1h** and the matrix photolyses of **1a–e** formed TMMs **2a–e**, the formations of TMMs **2f** and **2g** can be reasonably assumed in the matrix photolyses of **1f** and **1g**, respectively. Thus, the fact that the matrix photolyses of **1f** and **1g** did not give EPR signal suggests that the lowest ground states of **2f** and **2g** may be singlets and further stabilized by the stronger electron-withdrawing carbomethoxy-cyano and dicyano substitutions. As a MO perturbation theory had suggested, the substitution of one methylene group of TMM with electron-withdrawing groups induces the splitting of the NBMOs of TMM.[5] In the case of the dicyano derivative **2g**, the symmetric component of NBMOs of TMM in which a large coefficient locates at C_8 interacts with the symmetric combination of LUMO to two cyano groups. This interaction consequently induces the splitting of NBMOs. Although a quantitative argument for an inversion of the spin multiplicity is not available in terms of degree of the electron-withdrawing ability of substituents, the observed EPR spectroscopic results for **2a–h** can be well accounted for by the predicted

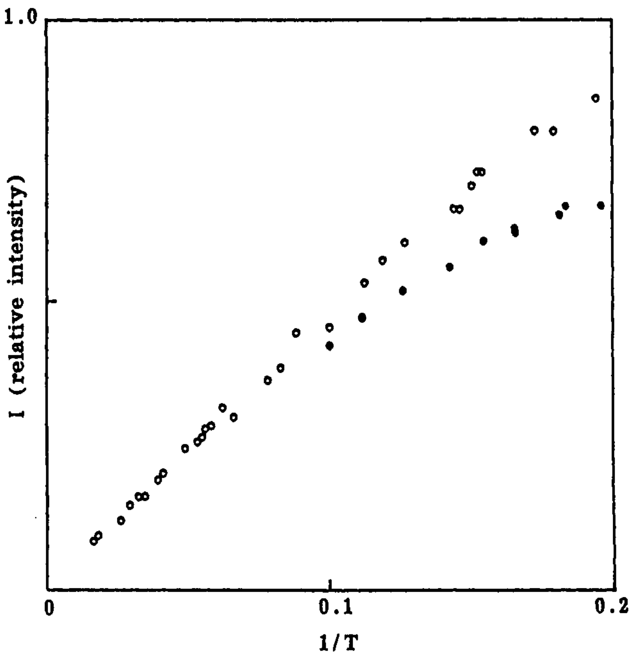

Figure 2. The Curie plots for the signal intensity on $|\Delta M_s| = 2$ transitions of TMMs **2a** (○) and **2e** (●) in toluene.

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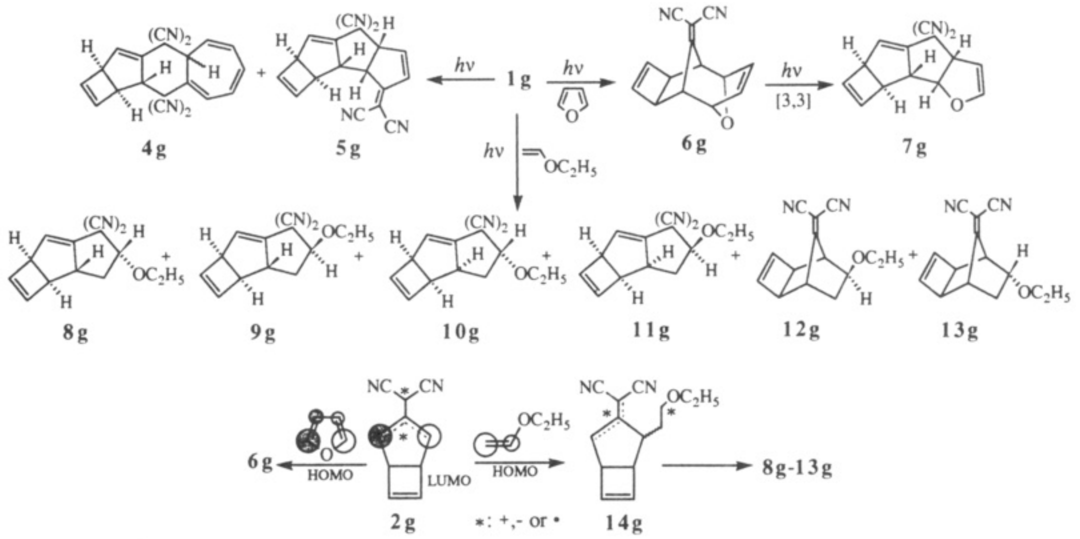
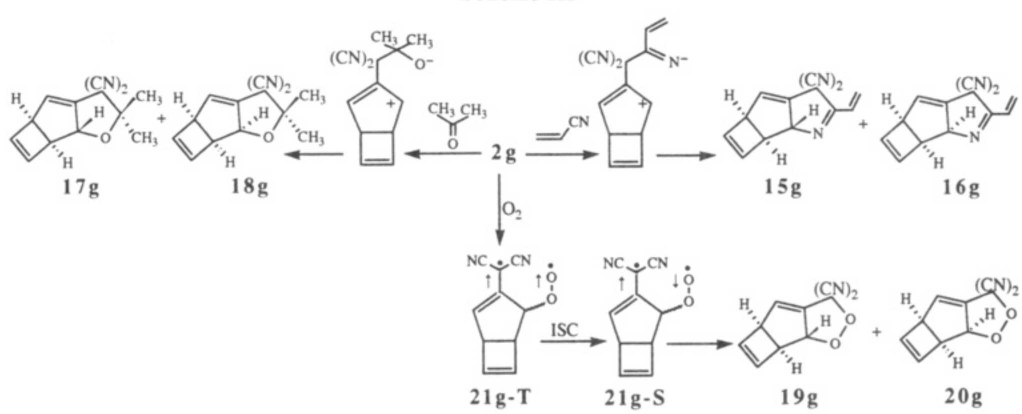
Scheme II



Scheme III



substituent effects on an inversion of the spin multiplicity of TMM.[3-5]

Chemical Capture of the Singlet TMM 2g. As we previously reported,[1] the triplet TMM **2a** generated from **1a** dimerized[15,16] and was captured by molecular oxygen[17,18] and an electron-deficient diylophile such as acrylonitrile, but not by electron-rich olefins such as ethyl vinyl ether and furan.[16,19,20] By contrast, the singlet OA **2h** from **1h** was captured by furan,[21] cyclopentadiene,[21] ethyl vinyl ether,[22] and methanol,[23] but not by acrylonitrile, providing its zwitterionic and electron-accepting properties. In order to gain insight chemically into the lowest gound state of EPR silent species **2f** and **2g**, we applied those reactions to the symmetrically substituted **2g** for experimental conveniences.

Irradiation (245 nm) of **1g** in *n*-hexane under argon gave a complex mixture including **4g** and **5g** in poor yields, but the formation of homodimers of **2g**, a characteristic reaction of the triplet TMM,[15,16] was not observed.[24] However, similar irradiation in furan resulted in the formation of a mixture of **6g** and **7g** in 59% yield, which was also obtained in 80% yield under the benzophenone-sensitized conditions. Because adduct **6g** rearranged to **7g** under irradiation conditions and **6g** was a major product at low conversion, **7g** is the secondary product from **6g**. Both the direct and benzophenone-sensitized irradiations of **1g** in ethyl vinyl ether gave a mixture including the fused adducts **8g–11g** and the bridged adducts **12g** and **13g**. On the other hand, photoreaction of **1g** in acrylonitrile gave adducts **15g** and **16g** in 12 and 2% yields, respectively, under the direct irradiation conditions and in 18 and 6% yields, respectively, under the benzophenone-sensitized conditions. Interestingly, similar cycloaddition occurred to give **17g** and **18g** in 62 and 3% yields, respectively, in photoreaction (300 nm) of **1g** in acetone. Contrary to expectation, both the direct (254 nm) and benzophenone-sensitized irradiations of **1g** in oxygen-saturated *n*-hexane gave peroxides **19g** and **20g** in nearly the same yields.

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[24] The photoisomerization of **1g** to 8,8-dicyanoheptafulvene[8] was concurrent upon irradiation in the presence or absence of trapping agents. Small amounts of 7-(dicyanomethylene)norbornadiene and 4-(dicyanomethylene)bicyclo[3.2.0]hepta-2,6-diene were also formed as described in the Experimental Section.

Among the above experimental results, the failure to give homodimers of **2g** and cycloadditions with furan and ethyl vinyl ether resemble results observed for OA **2h**[1] and thus well represent the electron-accepting nature of **2g**. The regio- and stereospecific 1,4-cycloaddition with furan can be explained by the concerted LUMO (**2g**)–HOMO (furan) interaction.[1,4c,21] As the LUMO of **2g** cannot interact with the HOMO of ethyl vinyl ether in a concerted manner, a stepwise mechanism through **14g** is reasonable to account for the nonregio- and nonstereospecific formation of adducts **8g**–**13g** as shown in Scheme II.[1,4c,22]

It is of interest to note that **2g** undergoes the [3 + 2] cycloaddition not only with the cyano group rather than the double bond of acrylonitrile but also with the carbonyl group of acetone. Although yields of the former reaction were low, those types of cycloadditions were not observed for the triplet **2a** and suggest a different spin state of **2g** from **2a** as well as the zwitterionic nature[25] of **2g**. The initial nucleophilic addition of the electronegative C_8 carbon of **2g** to the cyano and carbonyl groups followed by closure can account for these cycloadditions as shown in Scheme III. Recently, a TMM derivative[26a,b] generated thermally from dialkoxymethylenecyclopropane was reported to be captured by methanol[26b] and carbonyl compounds.[27] Thus the observed [3 + 2] cycloaddition of **2g** with the carbonyl group can be also regarded as one characteristic reaction of a singlet TMM with the zwitterionic nature.

Similarities and differences in chemical behaviors among **2a**, **2g**, and **2h** thus strongly suggest the singlet ground state of **2g**. Under the direct irradiation conditions, the singlet excited state of **1g** directly undergoes a spin-allowed ring cleavage to give the singlet **2g**. On the other hand, under the benzophenone sensitization, the formation of the triplet **2g** from the triplet excited state of **1g** followed by the intersystem crossing to the singlet **2g** is a plausible sensitized photochemical process. Because no EPR signal was observed even at 4.2 K and both the direct and benzophenone-sensitized irradiations gave nearly the same photochemical results, this intersystem crossing must be markedly rapid. Thus, one possible explanation for oxygenation of **2g** is the direct capture of the singlet **2g** by molecular oxygen to give the triplet **21g-T** followed by the intersystem crossing to the singlet **21g-S** which, in turn, cyclizes to **19g** and **20g**. This oxygenation process was suggested to operate in oxygenation of singlet tetramethyleneethane derivatives.[28,29] However, an alternative mechanism, i.e., the capture of the thermally equilibrating triplet **2g**, cannot be completely ruled out,[30] but would be rather unlikely to operate because of a rapid intersystem crossing. Nevertheless, the singlet ground state of **2g** is consistent with the failure to detect EPR signal and chemical behaviors of **2g** which resemble those of **2h**.

By combination of EPR spectroscopic results for **2a**–**h** with chemical results for **2a**, **2g**, and **2h**, it is concluded that the singlet energy level of TMM **2** gets lowered continuously with an increase in the electron-withdrawing nature of substituents. The monocyano substitution was not yet strong enough for an inversion, but the carbomethoxy-cyano and dicyano substitutions were strong enough to invert a ground state from the triplet to the singlet in this series of TMMs. The dicarbomethoxy derivative **2e** bonds between the triplet TMMs **2a**–**d** and singlet TMMs **2f**–**g**. Strong electron-withdrawing substitutions disclosed the electron-accepting and zwitterionic properties of a singlet TMM and the heteroanalogue OA is one extreme species of singlet TMMs with such properties.

Experimental Section

General Methods. Sample solutions for EPR spectra were deaerated by a vacuum line technique and irradiated with an excimer laser (308 nm). Temperatures below 77 K were achieved by a continuous flow cryostat using liquid helium and monitored throughout experiments with another gold-chromel thermocouple. To minimize effects of saturation at low temperature, an incident microwave power to the cavity was maintained at about 10 μW or lower for the I vs $1/T$ plot. All melting and boiling points are uncorrected. Elemental analyses were performed by the Instrumental Analyses Center for Chemistry, Faculty of Science, Tohoku University. ^{1}H NMR spectra were recorded at 90, 200, 400, or 600 MHz, and ^{13}C NMR spectra were recorded at 50 or 150 MHz. Medium-performance liquid chromatography (MPLC) was carried out by using a 100 cm × 15 mm glass column packed with silica Woelm 32-63 or YMC gel SIL120A S50. For low-temperature MPLC, a column was immersed in a dewar filled with cold methanol. 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.

Preparation of 3-(Cyanophenylmethylene)tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (1c). Quadricyclanone (**1h**)[31] (100.5 mg, 0.95 mmol), phenylacetonitrile (113.8 mg, 0.97 mmol), and sodium hydroxide (5.7 mg, 0.014 mmol) were dissolved in 2 mL of ethanol, and the mixture was heated under reflux for 3 h. After being cooled to room temperature, the reaction mixture was poured into water and extracted with ether. The combined extract was washed with water, dried over Na_2SO_4, and concentrated. Silica gel chromatography of the resulting brown residue gave colorless solid, which was recrystallized from ether–*n*-hexane to give 130 mg (67%) of **1c** as colorless needles: mp 110.5–111 °C; IR (KBr) 2203, 1644, 1597, 1489, 1443 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.58–7.50 (m, 2 H), 7.46–7.28 (m, 3 H), 2.24–2.11 (m, 5 H), 1.99 (m, 1 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 170.4, 134.9, 128.7, 128.5, 128.0, 119.5, 103.5, 27.5, 24.5, 22.6, 20.9; UV (cyclohexane) λ_{max} 212 (16 200), 260 nm (18 000), (CH$_3$CN) λ_{max} 212 (15 100), 260–nm (17 200); MS (25 eV) m/z (relative intensity) 205 (M$^+$, 41), 204 (100), 203 (33), 190 (51), 178 (37), 177 (24), 140 (69).

Anal. Calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82. Found: C, 88.07; H, 5.40; N, 6.94.

Preparation of 3-(Cyanomethylene)tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (1d). To a suspension of NaH containing 40% of oil (2.58 g, 64.5 mmol) in 100 mL of dry THF was added dropwise under nitrogen at 0–3 °C a solution of diethyl(cyanomethyl)phosphonate (6.00 g, 33.9 mmol) in 50 mL of dry THF. After the mixture was stirred for 20 min, a solution of **1h** (2.12 g, 20.0 mmol) in 50 mL of dry THF was added dropwise at 0–3 °C for 20 min and then the reaction mixture was poured into 300 mL of water. The combined ether 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

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[25] Similar to irradiation of **1h** in methanol,[1] irradiation of **1g** in methanol afforded the methanol adducts, *exo*- and *endo*-3-(dicyanomethylene)-2-methoxybicyclo[3.2.0]hept-6-enes. The water adducts, *exo*- and *endo*-(dicyanomethylene)bicyclo[3.2.0]hept-6-en-2-ols were also formed when **1g** was irradiated in ether saturated with water. A mechanisms for those reactions will be separately reported by one of authors (T.K.).

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n-hexane and 17% ethyl acetate in *n*-hexane) and recrystallization from *n*-hexane to give 2.47 g (96%) of **1d** as colorless plates: mp 69.5–70.5 °C; IR (KBr) 2203, 1649 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 5.45 (s, 1 H), 2.20–2.10 (m, 4 H), 1.99 (m, 1 H), 1.66 (m, 1 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 176.4, 117.9, 85.9, 26.4, 25.5, 21.6 (2 C), 21.3 (2 C); UV (cyclohexane) λ_{max} 220 nm (18 900), (CH$_3$CN) λ_{max} 224 nm (19 400); MS (25 eV) *m/z* (relative intensity) 129 (M$^+$, 85), 128 (34), 103 (44), 102 (100), 76 (22).

Anal. Calcd for C_9H_7N: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.74; H, 5.45; N, 10.79.

Preparation of 3-[Bis(methoxycarbonyl)methylene]tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (1e). A solution of **1h** (302.5 mg, 2.85 mmol), dimethyl malonate (1.884 g, 14.3 mmol), piperidine (242.5 mg, 2.85 mmol), and acetic acid (169.8 mg, 2.83 mmol) in 5 mL of benzene was heated under reflux for 2 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with ether. The combined extract was washed with water and brine, dried over Na_2SO_4, and concentrated. Silica gel chromatography (elution with 9% ethyl acetate in *n*-hexane) of the resulting brown residue gave a mixture of **1e** and the recovered dimethyl malonate. Removal of dimethyl malonate in vacuo at room temperature gave a colorless solid which was recrystallized from *n*-hexane to give 419 mg (65%) of **1e** with $^1/_3$ mol of H_2O as colorless needles: mp 60.5–61.5 °C; IR (KBr) 2836, 1722, 1651, 1258, 1237 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 3.82 (s, 6 H), 2.32 (br t, *J* = 4.2 Hz, 2 H), 2.15 (br d, *J* = 4.2 Hz, 4 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 173.7, 166.3, 117.7, 52.1, 25.3, 21.9; UV (cyclohexane) λ_{max} 234 nm (14 800), (CH$_3$CN) λ_{max} 238 nm (14 800); MS (25 eV) *m/z* (relative intensity) 220 (M$^+$, 11), 189 (100), 188 (31), 173 (41), 161 (29), 160 (51), 131 (29), 129 (24), 121 (31), 102 (36), 75 (42); HRMS (M$^+$) calcd for $C_{12}H_{12}O_4$ 220.0736, obsd 220.0730.

Anal. Calcd for $(C_{12}H_{12}O_4)_3{\cdot}H_2O$: C, 63.71; H, 5.64. Found: C, 63.65; H, 5.44.

Photolysis of 1g in *n*-Hexane under Nitrogen. A solution of **1g** (100.8 mg, 0.655 mmol) in 270 mL of *n*-hexane in a quartz vessel was irradiated with 2 RUL-2537 Å lamps for 15 min under N$_2$ at room temperature. After removal of solvent in vacuo, the resulting residue (118 mg) was purified by passing through a short silica gel column and then separated by MPLC on silica gel. Elution with 9% ethyl acetate in *n*-hexane afforded 5.2 mg of **4g** (5%), 7-(dicyanomethylene)norbornadiene (3%), 4-(dicyanomethylene)bicyclo[3.2.0]hepta-2,6-diene (5%), and the recovered **1g** (5%). Elution with 17% ethyl acetate in *n*-hexane gave a mixture of **5g** (16%), 8,8-dicyanoheptafulvene (1%), and 5-(dicyanomethylene)tricyclo[4.1.0.0^{2,7}]hept-3-ene (2%) (by NMR), which was formed secondarily from **1g** during separation.[8]

4g: mp 182–183 °C (colorless powder); IR (KBr) 2244, 1642, 1633, 1593 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 6.80 (dd, *J* = 7.6, 0.8 Hz, 1 H), 6.68 (dd, *J* = 2.7, 2.0 Hz, 1 H), 6.43 (dd, *J* = 2.8, 0.7 Hz, 1 H), 6.34 (br ddd, *J* = 10.7, 7.2, 1.4 Hz, 1 H), 6.25 (br dd, *J* = 10.8, 7.2 Hz, 1 H), 6.23 (dd, *J* = 2.8, 1.0 Hz, 1 H), 6.04 (br ddd, *J* = 10.8, 7.6, 1.4 Hz, 1 H), 5.64 (br dd, *J* = 10.7, 7.2 Hz, 1 H), 4.06 (d, *J* = 7.2 Hz, 1 H), 4.01 (dddd, *J* = 3.6, 3.3, 2.7, 0.7 Hz, 1 H), 3.65 (ddd, *J* = 3.3, 2.2, 1.0 Hz, 1 H), 3.27 (ddd, *J* = 3.6, 2.2, 2.0 Hz, 1 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 145.1, 139.6, 137.6, 132.9, 132.3, 130.7, 129.6, 126.3, 124.2, 121.6, 112.3, 112.0, 111.2, 110.8, 55.3, 53.8, 51.9, 48.5, 47.4, 42.7; UV (CH$_3$CN) λ_{max} 210 (13 800, sh), 326–nm (2540); MS (25 eV) *m/z* (relative intensity) 308 (M$^+$, 5), 167 (18), 155 (15), 154 (100), 149 (31), 127 (43). The carbon and proton chemical shifts were assigned by the ^{1}H–^{13}C 2D NMR shift correlation experiments (C–H COSY and COLOC spectra).

Anal. Calcd for $C_{20}H_{12}N_4$: C, 77.91; H, 3.92; N, 18.17. Found: C, 78.07; H, 3.95; N, 18.14.

5g: mp 194–195 °C (colorless plates); IR (KBr) 2244, 2225, 1580 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 6.98 (m, 1 H), 6.94 (m, 1 H), 6.41 (br d, *J* = 2.8 Hz, 1 H), 6.35 (br d, *J* = 2.8 Hz, 1 H), 6.14 (dd, *J* = 2.9, 2.9 Hz, 1 H), 4.29 (ddd, *J* = 4.8, 1.6, 1.6 Hz, 1 H), 3.97 (m, 1 H), 3.94 (dd, *J* = 11.6, 4.8 Hz, 1 H), 3.67 (dddd, *J* = 11.6, 3.9, 2.9, 2.9 Hz, 1 H), 3.33 (br dd, *J* = 2.9, 2.9 Hz, 1 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 178.8, 151.2, 143.1, 139.6, 139.4, 136.8, 132.9, 112.2, 112.1, 111.4, 111.1, 80.2, 62.8, 58.7, 48.3, 48.3, 47.1, 36.7; UV (CH$_3$CN) λ_{max} 212 (4320), 286 nm (18 600); MS (25 eV) *m/z* (relative intensity) 282 (M$^+$, 2), 155 (21), 154 (100), 128 (16), 127 (22).

Anal. Calcd for $C_{18}H_{10}N_4$: C, 76.58; H, 3.57; N, 19.85. Found: C, 76.73; H, 3.59; N, 19.79.

Photolysis of 1g in Furan. A solution of **1g** (100.2 mg, 0.651 mmol) in 120 mL of furan in a quartz vessel was irradiated with 4 RUL-2537 Å lamps for 20 min under N$_2$. After removal of furan in vacuo, the resulting reddish residue (139 mg) was passed through a short column on silica gel and then separated by MPLC on silica gel. Elution with 9% ethyl acetate in *n*-hexane afforded 86.8 mg of a 1:6 mixture of **6g** and **7g** in 59% yield, and 7-(dicyanomethylene)norbornadiene (1%). 4-(Dicyanomethylene)bicyclo[3.2.0]hepta-2,6-diene (5%) and the recovered **1g** (1%) were afforded from elution with 17% ethyl acetate in *n*-hexane. Elution with 25% ethyl acetate in *n*-hexane gave 8,8-dicyanoheptafulvene in 13% yield.

Benzophenone-Sensitized Irradiation of 1g in the Presence of Furan. A solution of **1g** (199.9 mg, 1.30 mmol) and benzophenone (236.2 mg, 1.30 mmol) in 300 mL of benzene containing 0.04 M of furan in a Pyrex vessel was irradiated with a RUL-3500Å lamp for 11 h under N$_2$. After removal of furan in vacuo, the resulting yellow residue was passed through a short column on silica gel and then separated by MPLC on silica gel. Elution with 9% ethyl acetate in *n*-hexane gave 229 mg of a mixture of **6g** and **7g** in 80% yield together with the recovered benzophenone (99%) and 7-(dicyanomethylene)norbornadiene (0.3%). Elution with 33% ethyl acetate in *n*-hexane gave the recovered **1g** (3%), 8,8-dicyanoheptafulvene (4%), 4-(dicyanomethylene)bicyclo[3.2.0]hepta-2,6-diene (3%), and 5-(dicyanomethylene)tricyclo[4.1.0.0^{2,7}]hept-3-ene (6%). Adducts **6g** and **7g** were separated by fractional recrystallization from *n*-hexane.

6g: mp 115–115.5 °C (colorless needles); IR (KBr) 2220, 1621, 1308, 919, 712 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.34 (s, 2 H), 5.99 (s, 2 H), 4.81 (d, *J* = 3.6 Hz, 2 H), 3.63 (s, 2 H), 3.24 (d, *J* = 3.6 Hz, 2 H); ^{13}C NMR (50 MHz, C$_6$D$_6$) δ 186.8, 138.6, 133.5, 111.6, 84.4, 83.6, 50.0, 49.4; UV (cyclohexane) λ_{max} 248 nm (10 700); MS (25 eV) *m/z* (relative intensity) 222 (M$^+$, 14), 154 (100), 128 (21), 127 (39), 68 (66). The stereochemistry was confirmed by the shift reagent experiment using Eu(fod)$_3$.

Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.53; N, 12.60. Found: C, 75.73; H, 4.36; N, 12.60.

7g: mp 83–84.5 °C (colorless leaves); IR (KBr) 2230, 1610, 1149, 1070 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.48 (dd, *J* = 2.6, 1.6 Hz, 1 H), 6.40 (d, *J* = 2.8 Hz, 1 H), 6.27 (d, *J* = 2.8 Hz, 1 H), 6.16 (dd, *J* = 3.0, 3.0 Hz, 1 H), 5.02 (dd, *J* = 3.0, 2.6 Hz, 1 H), 5.01 (dd, *J* = 8.0, 6.0 Hz, 1 H), 4.26 (ddd, *J* = 8.0, 3.0, 1.6 Hz, 1 H), 4.05 (ddd, *J* = 3.2, 3.0, 3.0 Hz, 1 H), 3.58 (dd, *J* = 3.2, 3.2 Hz, 1 H), 3.30 (m, 1 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 151.4, 143.0, 140.5, 139.0, 132.6, 114.0, 112.3, 96.9, 82.6, 62.4, 59.8, 52.0, 47.5, 38.3; UV (cyclohexane) λ_{max} 214 nm (7700); MS (25 eV) *m/z* (relative intensity) 222 (M$^+$, 13), 193 (15), 154 (100), 127 (63), 68 (46).

Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.53; N, 12.60. Found: C, 75.70; H, 4.45; N, 12.68.

Photolysis of 1g in Ethyl Vinyl Ether. A solution of **1g** (201.2 mg, 1.31 mmol) in 270 mL of ethyl vinyl ether in a quartz vessel was irradiated with 2 RUL-2537Å lamps for 25 min at 9 °C under N$_2$. After removal of ethyl vinyl ether in vacuo at 25–30 °C, the reddish residue (268 mg) was passed through a short column on silica gel and then separated by repetitive MPLC on silica gel (elution with 17, 9, 4, and 2% ethyl acetate in *n*-hexane) to give 109.2 mg of **8g** (37%), 13.0 mg of **9g** (4%), 1.1 mg of **10g** (0.4%), 9.7 mg of **11g** (3%), 8.1 mg of **12g** (3%), 2.5 mg of **13g** (1%), together with the recovered **1g** (2%), 8,8-dicyanoheptafulvene (7%), 7-(dicyanomethylene)norbornadiene (3%), 4-(dicyanomethylene)bicyclo[3.2.0]hepta-2,6-diene (3%), and 5-(dicyanomethylene)tricyclo[4.1.0.0^{2,7}]hept-3-ene (3%).

Benzophenone-Sensitized Irradiation of 1g in Ethyl Vinyl Ether. A solution of **1g** (100.4 mg, 0.652 mmol) and benzophenone (118.4 mg, 0.651 mmol) in 100 mL of ethyl vinyl ether in a Pyrex vessel was irradiated with 4 RUL-3500Å lamps for 5 h at 9 °C under N$_2$. After removal of solvent in vacuo at 20 °C, the yellow residue (318 mg) was passed through a short column on silica gel and then separated by repetitive MPLC on silica gel (elution with 12.5 and 4% ethyl acetate in *n*-hexane) to give 91.6 mg of **8g** (62%), 10.7 mg of **9g** (7%), 0.9 mg of **10g** (0.5%), 8.9 mg of **11g** (6%), 9.2 mg of **12g** (6%), and 2.5 mg of **13g** (2%).

8g: mp 57.5–58.5 °C (colorless prisms); IR (KBr) 2238, 1555, 1126 cm^{-1}; MS (25 eV) *m/z* (relative intensity) 226 (M$^+$, 12), 155 (31), 154 (100), 143 (13), 127 (11).

Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.27; H, 6.32; N, 12.68.

9g: colorless oil; IR (neat) 2240, 1561, 1118, 1092 cm^{-1}; MS (25 eV) *m/z* (relative intensity) 226 (M$^+$, 10), 198 (13), 155 (38), 154 (100); HRMS (M$^+$) calcd for $C_{14}H_{14}N_2O$ 226.1106. obsd 226.1104.

10g: colorless oil; MS (EI, 70 eV) *m/z* (relative intensity) 226 (M$^+$, 2), 180 (15), 169 (25), 155 (33), 154 (100), 127 (19), 115 (17); HRMS (M$^+$) calcd for $C_{14}H_{14}N_2O$ 226.1106, obsd 226.1115.

11g: colorless oil; IR (neat) 2237, 1131 cm^{-1}; MS (13.5 eV) *m/z* (relative intensity) 226 (M$^+$, 2) 198 (13), 182 (22), 155 (9), 154 (100), 142 (6); HRMS (M$^+$) calcd for $C_{14}H_{14}N_2O$ 226.1106, obsd 226.1102.

12g: colorless oil; IR (neat) 2227, 1650, 1090 cm^{-1}; MS (25 eV) *m/z* (relative intensity) 226 (M$^+$, 10), 198 (16), 155 (29), 154 (100), 153 (10), 142 (10), 127 (16); HRMS (M$^+$) calcd for $C_{14}H_{14}N_2O$ 226.1106, obsd 226.1106.

13g: mp 73–74 °C (colorless cubes); IR (KBr) 2227, 1650, 1116, 1088 cm^{-1}; MS (25 eV) *m/z* (relative intensity) 226 (M$^+$, 16), 198 (10), 169 (11), 155 (31), 154 (100), 143 (12), 142 (11), 127 (18); HRMS (M$^+$) calcd for $C_{14}H_{14}H_2O$ 226.1106, obsd 226.1107.

The stereochemical assignments of **8g**, **9g**, **10g**, and **11g** were made by their NOE difference spectra. There were NOE between H_2 (2.85 ppm) and H_4 (4.50 ppm) for **8g** and between H_2 (3.08 ppm) and H_4 (4.61 ppm) for **11g**, but none between H_2 (3.25 ppm) and H_4 (4.44 ppm) for **9g** and between H_2 (3.37 ppm) and H_4 (4.22 ppm) for **10g**.

Photolysis of 1g in Acrylonitrile. A solution of **1g** (100.6 mg, 0.653 mmol) in 100 mL of acrylonitrile and 2.0 g of molecular sieve (4A) were placed in a quartz vessel and irradiated with 2 RUL-2537Å lamps for 25 min under N_2. After filtration and removal of solvent in vacuo at 15–20 °C, the resulting orange residue (143 mg) was passed through a short column on silica gel and then separated by MPLC on silica gel. Elution with 17% ethyl acetate in *n*-hexane gave **15g** (12%) and **16g** (2%) as a colorless oil together with the recovered **1g** (5%), 8,8-dicyanoheptafulvene (16%), 7-(dicyanomethylene)norbornadiene (3%), 4-(dicyanomethylene)bicyclo[3.2.0]hepta-2,6-diene (8%), and 5-(dicyanomethylene)tricyclo[4.1.0.0^{2,7}]hept-3-ene (4%).

Benzophenone-Sensitized Irradiation of 1g in Acrylonitrile. A solution of **1g** (100.3 mg, 0.651 mmol) and benzophenone (118.4 mg, 0.650 mmol) in 100 mL of acrylonitrile and 2.0 g of molecular sieve (4A) were placed in a Pyrex vessel and irradiated with 4 RUL-3500Å lamps for 3 h under N_2. After removal of solvent in vacuo at 25 °C, the resulting residue (343 mg) was passed through a short column on silica gel and then separated by repetitive MPLC on silica gel (elution with 17, 12.5, and 5% ethyl acetate in *n*-hexane) to give 24.8 mg of **15g** (18%) and 2.9 mg of **16g** (2%) together with the recovered **1g** (15%), 8,8-dicyanoheptafulvene (8%), 7-(dicyanomethylene)norbornadiene (3%), 4-(dicyanomethylene)bicyclo[3.2.0]hepta-2,6-diene (1%), and *exo*-3-(dicyanomethylene)bicyclo[3.2.0]hept-6-en-2-ol (2%), which was formed by addition of water contaminated in acrylonitrile.[25]

15g: colorless oil; IR (neat) 2237, 1629, 1574, 1414, 986, 942 cm^{-1}; MS (70 eV, EI) *m/z* (relative intensity) 207 (M$^+$, 10), 206 (12), 155 (13), 154 (100), 153 (11), 128 (24), 127 (40), 103 (10); HRMS (M$^+$) calcd for $C_{13}H_9N_3$ 207.0797, obsd 207.0797.

16g: colorless oil; MS (25 eV) *m/z* (relative intensity) 207 (M$^+$, 5), 206 (11), 179 (12), 155 (15), 154 (100), 128 (44), 127, (76); HRMS (M$^+$) calcd for $C_{13}H_9N_3$ 207.0797, obsd 207.0794.

Photolysis of 1g in Acetone. A solution of **1g** (151.6 mg, 0.984 mmol) in 350 mL of acetone in a pyrex vessel was irradiated with 4 RUL-3000Å lamps for 1 h under N_2. After removal of solvent in vacuo, the yellow residue (203 mg) was passed through a short column on silica gel and then separated by repetitive MPLC on silica gel. Elution with 17% ethyl acetate in *n*-hexane gave 135 mg of a mixture of **17g** (62%) and **18g** (3%) (by NMR), and the recovered **1g** (5%) together with *exo*-3-(dicyanomethylene)-2-methoxybicyclo[3.2.0]hept-6-ene (2%) and *exo*-3-(dicyanomethylene)bicyclo[3.2.0]hept-6-en-2-ol (14%) which were formed by additions of methanol and water contaminated in acetone, respectively.[25] The major adduct **17g** was isolated from a mixture of **17g** and **18g** by fractional recrystallization from *n*-hexane at −60 °C. The NMR data of **18g** was deduced from the spectrum of a mixture of **17g** and **18g**.

17g: mp 24.5–25 °C (colorless leaves); IR (neat) 2245, 1559, 1130, 1100, 1013 cm^{-1}; MS (25 eV) *m/z* (relative intensity) 212 (M$^+$, 3), 154 (91), 128 (43), 127 (100), 105 (17), 78 (17), 77 (11), 58 (11); HRMS (M$^+$) calcd for $C_{13}H_{12}N_2O$ 212.0950, obsd 212.0952.

Photolysis of 1g in *n*-Hexane under Oxygen. A solution of **1g** (101.1 mg, 0.656 mmol) in 270 mL of *n*-hexane in a quartz vessel was irradiated with 2 RUL-2537Å lamps for 15 min with oxygen bubbling. The resulting orange residue (171 mg) obtained after removal of solvent in vacuo at 10–14 °C was separated by low-temperature MPLC on silica gel at −62 °C. Elution with 17% ethyl acetate in *n*-hexane gave 54.1 mg of **19g** (45%) and 4.6 mg of a mixture of **20g** (3%) and 7-(dicyanomethylene)norbornadiene (2%) (by NMR). Elution with 33% ethyl acetate in *n*-hexane gave the recovered **1g** (2%), 8,8-dicyanoheptafulvene (ca. 12%), 4-(dicyanomethylene)bicyclo[3.2.0]hepta-2,6-diene (5%), and 5-(dicyanomethylene)tricyclo[4.1.0.0^{2,7}]hept-3-ene (2%).

Benzophenone-Sensitized Irradiation of 1g under Oxygen. A solution of **1g** (250.9 mg, 1.63 mmol) and benzophenone (295.7 mg, 1.63 mmol) in 600 mL of *n*-hexane in a Pyrex vessel was irradiated with 4 RUL-3500Å lamps for 2 h under O_2. The resulting yellow residue (606 mg) obtained after removal of solvent in vacuo was separated by low-temperature MPLC on silica gel at −49 to −57 °C (elution with 17 and 33% ethyl acetate in *n*-hexane) to give **19g** (42%), **20g** (3%), the recovered **1g** (28%), and 8,8-dicyanoheptafulvene (≤3%). The major product **19g** was purified by recrystallization from CH_2Cl_2–*n*-hexane at −78 °C, but the minor **20g** could not be isolated. The NMR data for **20g** was deduced from the spectrum of a mixture containing **20g** exclusively and a small amounts of 7-(dicyanomethylene)norbornadiene.

19g: mp 81.5–82.5 °C dec (colorless needles); IR ($CHCl_3$) 2240, 1677, 1659, 1558 cm^{-1}; MS (13.5 eV) *m/z* (relative intensity) 186 (M$^+$, 0.4), 154 (100); HRMS (M$^+$) calcd for $C_{10}H_6N_2O_2$ 186.0429, obsd 186.0425.

Anal. Calcd for $C_{10}H_6N_2O_2$: C, 64.52; H, 3.25; N, 15.05. Found: C, 64.12; H, 3.26; N, 14.72.

Supplementary Material Available: ^1H NMR spectra and spectral data of **8g**–**13g** and **15g**–**20g**; ^{13}C NMR spectra and spectral data of **8g**–**13g**, **15g**–**17g**, and **19g**; and COSY spectra of **8g**, **9g**, **11g**, **12g**, and **15g**–**17g** (35 pages). This material is contained in many 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.