excess of the most energetic photon (86 kcal/mol) observed in our spectrum. The value of ΔH_{rxn} (4b) is in excess of the estimated Si–H bond strength, 85 ± 10 kcal/mol,[25] There is also enough energy to populate the A state of HSiOH. Thus if R = SiH_2 and a reasonable fraction of the exothermicity were channeled into product electronic energy, a significant amount of predissociation could occur; this is consistent with our previous discussion. The presence of two mechanisms for the generation of H_2SiO might also account for the complexity of the observed chemiluminescence.

Precipitation. Finally, we report the deposition of a white, amorphous powder on the apparatus walls resulting from the low pressure gas-phase mixture of SiH_4 and O_3. An infrared spectrum of the powder indicates features attributable to O–H and Si–O vibrational frequencies. Investigation of the IR spectrum suggests that the powder is very similar to partially hydrated silica gel (amorphous SiO_2).

Upper Excited State Reactivity and Fluorescence of Fused 8-Cyanoheptafulvenes[†]

Yoshikazu Sugihara,[*‡] **Shigeharu Wakabayashi,**[‡] **Ichiro Murata,**[*‡] **Mamoru Jinguji,**[§] **Tomoo Nakazawa,**[§] **Gabriele Persy,**[⊥] **and Jakob Wirz**[*⊥]

Contribution from the Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan, the Department of Chemistry, Medical University of Yamanashi, Tamaho, Nakakoma, Yamanashi 409-38, Japan, and the Institut für Physikalische Chemie, Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland. Received February 8, 1985

Abstract: Fluorescence emission of 6-cyanotricyclo[5.5.0.0^{2,5}]dodeca-3,6,8,10,12-pentaene (1) is observed only from the second excited singlet states S_2 ($\phi_f = 3 \times 10^{-3}$, $\tau_f = 82$ ps) but not from S_1 in violation of Kasha's rule. Nonfused cyanoheptafulvenes are nonfluorescent due to a "free rotor effect" of the exocyclic double bond. The previously reported dependence of the photochemical valence isomerization of 1 on the excitation wavelength is, however, not due to the photoreactivity of an upper excited state but arises from "chemical" sensitization by an impurity absorbing below 320 nm.

In the course of our studies on valence isomers of nonalternant hydrocarbons,[1] we have recently reported the synthesis of 6-cyanotricyclo[5.5.0.0^{2,5}]dodeca-3,6,8,10,12-pentaene (1) and its isomerization to 1-cyanoheptalene (2).[2] The present work focuses

3 (R = H)
4 (R = CN)
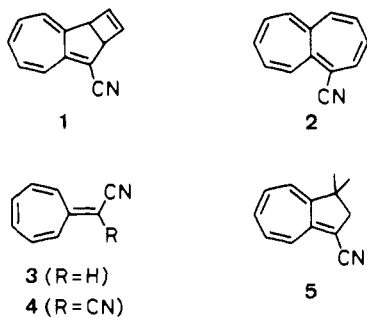
on the unusual photophysical and photochemical properties of 1, exclusive anti-Kasha fluorescence[3] from the second excited singlet state S_2 and the excitation wavelength dependence of the photoinduced valence isomerization 1 → 2. Simple rationalizations for these observations will be provided and supported by comparisons with reference compounds (3–5) and by standard PPP SCF CI[4] calculations.

Results and Discussion

Anti-Kasha Fluorescence. The fluorescence spectrum of 1 was found to be a close mirror image of the S_0–S_2 absorption band,

and the fluorescence excitation spectrum was in satisfactory agreement with the absorption spectrum below 400 nm (Figure 1). The fluorescence quantum yield, $\phi_f = 2.8 \times 10^{-3}$ (cyclohexane, room temperature), was not affected by degassing or oxygen saturation. Prolonged measurements did not produce any perceptible change in the fluorescence intensity or spectra. No fluorescence was observed to the red of the first absorption band, $\lambda > 658$ nm. PPP calculations predict that a considerable redistribution of charge is associated with S_0–S_2 excitation of the heptafulvene chromophore. This is born out by the complete loss of vibrational structure in the corresponding absorption and emission bands in polar media.

In order to exclude the remote possibility of an adventitious fluorescent impurity with these characteristics, we have determined the fluorescence lifetime of 1 by the time-correlated single-photon counting technique. The lifetime was very short, close to the time resolution of our setup. Deconvolution of the excitation pulse yielded $\tau_f = 82$ ps which may be considered as an upper limit. A calculated value of $\tau_f = 10$ ps was obtained from the relation $\tau_f = \phi_f/k_f$; this should be considered as a lower limit due to the inherent limitations of the Strickler–Berg relation[5] used to estimate k_f. We have recently obtained excellent agreement between calculated and experimental values for $\tau_f(S_2)$ in a related case,[6]

(1) Sugihara, Y.; Sugimura, T.; Murata, I. *J. Am. Chem. Soc.* **1981**, *103*, 6738-6739; **1982**, *104*, 4295-4296; **1984**, *106*, 7268-7269.
(2) Sugihara, Y.; Wakabayashi, S.; Murata, I. *J. Am. Chem. Soc.* **1983**, *105*, 6718-6719.
(3) Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125-145.
(4) Pariser, R.; Parr, R. G. *J. Chem. Phys.* **1953**, *21*, 466-471. Pople, J. A. *Trans. Faraday Soc.* **1953**, *49*, 1375-1385. Zahradnik, R. *Fortschr. Chem. Forsch.* **1968**, *10*, 1-58.
(5) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814-822.
(6) Leupin, W.; Wirz, J. *J. Am. Chem. Soc.* **1980**, *102*, 6068-6075. Leupin, W.; Berens, S. J.; Magde, D.; Wirz, J. *J. Phys. Chem.* **1984**, *88*, 1376-1379.
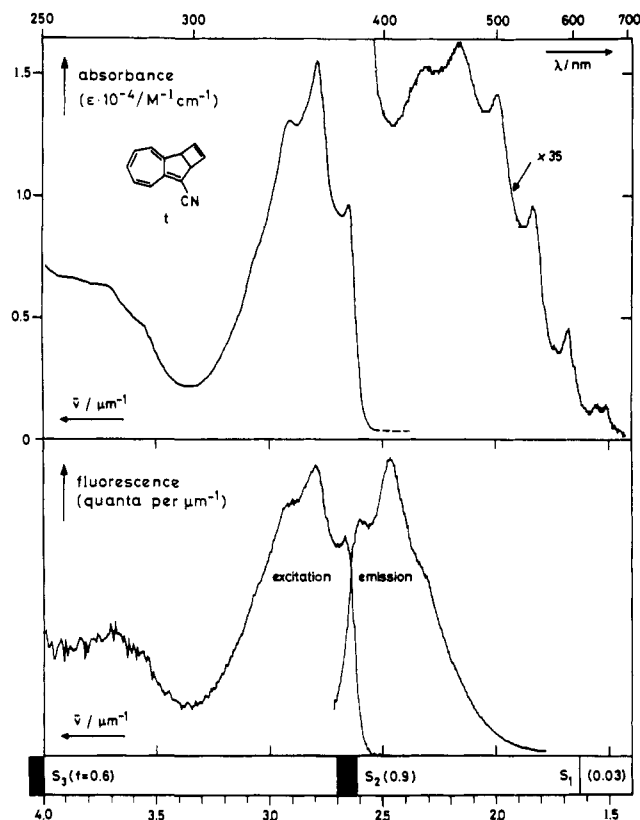
Figure 1. Absorption spectrum (upper half) and corrected fluorescence excitation and emission spectra (lower half) of **1** in cyclohexane solution at ambient temperature. Calculated transition energies and oscillator strengths *f* for the 8-cyanoheptafulvene chromophore are shown at the bottom (cf. Experimental Section).

but some discrepancies have also been noted.[7] In any case, much longer lifetimes would be expected for impurities with a high fluorescence efficiency.

8-Cyanoheptafulvene (**3**)[8] and 8,8-dicyanoheptafulvene (**4**)[9] did not give rise to any detectable fluorescence emission ($\phi_f \ll 10^{-4}$). This indicated that a "free rotor effect"[10] of the exocyclic double bond was responsible for a rapid radiationless deactivation of the S_2 state. Indeed, calculations predicted that the $C(1)-C(8)$ bond order was strongly reduced upon S_0-S_2 excitation of heptafulvenes ($\Delta p \cong 0.35$). To confirm this hypothesis, we have synthesized (vide infra) and examined another fused heptafulvene, 8-cyano-10,10-dimethylbicyclo[5.3.0]deca-1,3,5,7-tetraene (**5**). Except for a blue shift of ca. 10 nm, its S_2 absorption, emission, and excitation spectra were very similar ($\phi_f = 2.1 \times 10^{-3}$, $\tau_f = 78$ ps) to those of **1**. Nonradiative decay processes are predominant even in the fused systems **1** and **5**, but here the rate $k_{nr} \cong 1/\tau_f \cong 10^{10}$ s^{-1} is of the order of magnitude expected for S_2-S_1 internal conversion on the basis of energy gap law considerations.[11] *We conclude that S_2 emission from heptafulvenes is readily observable if the $C(1)-C(8)$ double bond is fused to a small ring*; in the parent heptafulvenes, radiationless deactivation of the S_2 state by rotational relaxation of the exocyclic double bond is fast even on a picosecond time scale.

Wavelength-Dependent Photoisomerization. Compound **1** is stable to irradiation through Pyrex, but it isomerizes to **2** upon irradiation through quartz.[2] Preparative photolyses with a low-

pressure mercury arc gave 40–70% isolated yields of **2**. Several photoinduced cycloreversion reactions have been reported to exhibit wavelength-dependent quantum yields.[3,12] Nevertheless, the following aspect of this observation was intriguing and called for further scrutiny. The preparative work suggested that the photoreaction took place with fair efficiency but only from an upper excited singlet state lying above S_2. Thus, the cycloreversion **1**** → **2** would have to be extremely fast to compete effectively with internal conversion to the nonreactive S_2 state.

Monochromatic irradiation of dilute solutions (1.3×10^{-4} M in CH_3CN) and spectrophotometric monitoring of the reaction progress confirmed the previous qualitative observation; the quantum yield $\phi(1 \rightarrow 2)$ was about 1×10^{-6} at 365 nm (S_2 excitation); it rose to 6×10^{-6} at 308 nm (XeCl excimer laser) and to nearly 10^{-4} at 254 nm. However, all these quantum yields were surprisingly low in view of the smooth reaction in the preparative runs. We therefore checked for a concentration dependence using samples of different path lengths (1 mm, 1 cm, and 2 cm) but identical absorbance ($A = 0.3$ at 308 nm, CH_3CN). The rate was found to be directly proportional to the initial concentration of **1** in the range of ca. $10^{-4}-10^{-3}$ M, and, furthermore, it hardly decreased at conversions up to ca. 50% although, of course, the absorbance of **1** decreased significantly during the photoreaction. Suppan et al. have recently shown that such behavior may arise from "chemical" sensitization by trace impurities which absorb at shorter wavelengths than the photochemical substrate.[13] Cyanoheptafulvenes may be expected to behave both as electron donors and acceptors since the ionization potential of **3** is found to be 7.94 eV and the electron affinities of **1** and **5** are estimated to be 0.90 and 0.98 eV, respectively (see Experimental Section). Thus, a reasonable mechanism for chemical sensitization in the present case would be that *the isomerization $1 \rightarrow 2$ proceeds via an exciplex or radical ion pair formed by the encounter of an electronically excited impurity with the substrate* **1**, a reaction with many authentic precedents.[14] Note that an imperceptible 0.01% contamination of **1** by an efficient chemical sensitizer would be sufficient to account for the observed quantum yields. Such a mechanism provides a natural explanation, as discussed previously,[13] for the photochemical rate dependence on the *initial*, but not on the *actual*, concentration. We can see no reasonable alternative, particularly since the very short lifetime of an upper excited state should preclude any bimolecular reactions initiated by **1**** in dilute solution.

We have made no attempts to identify or eliminate the hypothetical trace impurity. However, it was easily demonstrated that such a mechanism would be operative in the presence of virtually anything absorbing below 320 nm, Naphthalene, duroquinone, and *N*-methylindole happened to be on shelf. The deliberate addition of any of these compounds in trace quantities resulted in a marked rate increase of the photoreaction **1** → **2** (CH_3CN solution, 308-nm irradiation). In further support of the exciplex mechanism, we found that the reaction rate was much slower in cyclohexane as an apolar solvent. In this case, the quantum yield $\phi(1 \rightarrow 2)$ was not quite proportional to the initial concentration of **1**, leveling off at 1×10^{-6} in highly dilute solution. This indicates that a unimolecular valence isomerization does take place with very low efficiency (presumably from the fluorescent state S_2) which is however entirely swamped by impurity sensitization under preparative conditions. It seems likely that such effects may have passed unnoticed in related cases.

Synthesis of a Model Compound 5. The synthesis of **5** as a model of the fused heptafulvene is shown in Scheme I. The

(7) Eber, G.; Schneider, S.; Dörr, F. *Chem. Phys. Lett.* **1977**, *52*, 59-62. Plummer, B. F; Al-Saigh, Z. Y. *J. Phys. Chem.* **1983**, *87*, 1579-1582.

(8) Oda, M.; Kitahara, Y. *Chem. Commun.* **1969**, 352.

(9) Nozoe, T.; Mukai, T.; Osaka, K.; Shishido, N. *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1384-1390. Haug, E.; Föhlish, B. *Chem. Ber.* **1971**, *104*, 2670-2680. Hafner, K.; Riedel, H. W.; Danielisz, M. *Angew. Chem.* **1963**, *75*, 344-345.

(10) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718-3725.

(11) Siebrand, W. *J. Chem. Phys.* **1967**, *47*, 2411-2422. Gillispie, G. D.; Lim, E. C. *Chem. Phys. Lett.* **1979**, *63*, 193-198.

(12) Castellan, A.; Kolc, J.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 6687-6692.

(13) Suppan, P.; Huber, S.; Haselbach, E. *Helv. Chim. Acta* **1983**, *66*, 2579-2602.

(14) Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45-50. Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80-86. Jones, G., II; Becker, W. G. *J. Am. Chem. Soc.* **1983**, *105*, 1276-1283. Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6805-6808. Davis, H. F.; Das, P. K.; Reichel, L. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 6968-6973. Hasegawa, E.; Okada, K.; Mukai, T. *J. Am. Chem. Soc.* **1984**, *106*, 6852-6854.

Scheme I
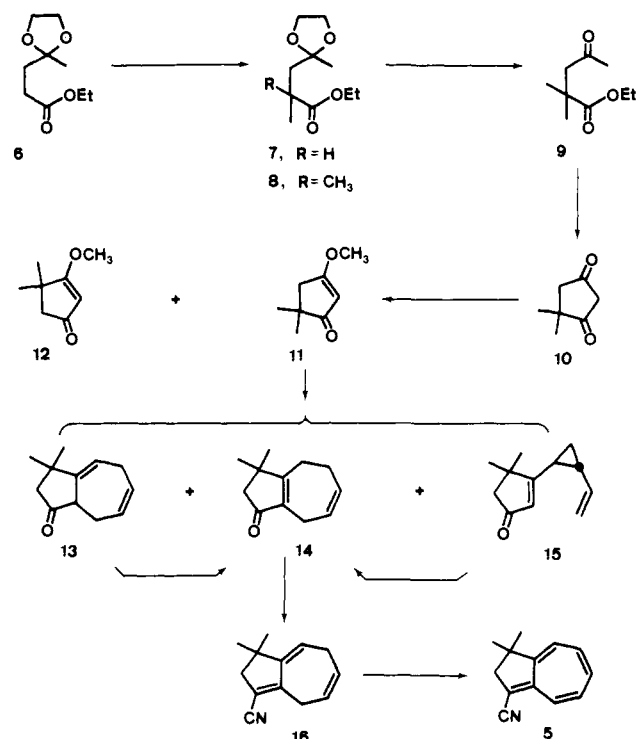
geminal dimethyl group was introduced so as to prevent aromatization under irradiation conditions. To prepare the required precursor, 5,5-dimethyl-3-methoxycyclopent-2-en-1-one (11), we initially tried to make use of the previously reported procedure.[15] However, owing to the rather low overall yield, we opted to carry out an intramolecular cyclization of ethyl 2,2-dimethyllevulinate (9) instead.

Ethyl levulinate 4-ethylene acetal (6) was methylated with lithium diisopropylamide (LDA) and methyl iodide to the monomethyl derivative 7 (84%), which on further methylation under the same conditions gave the dimethyl derivatives 8. The acetal 8 was then hydrolyzed to 9 in 88% yield from 7. Cyclization of 9 with 5 equiv of LDA in THF for 4 h at room temperature afforded 4,4-dimethylcyclopentane-1,3-dione (10) which upon methylation with diazomethane gave a mixture of 5,5-dimethyl-3-methoxycyclopent-2-en-1-one (11) and 4,4-dimethyl-3-methoxycyclopent-2-en-1-one (12) in 60% yield from 9. The mixture could be separated by repeated column chromatography on silica gel. Reaction of 11 with a mixture of *cis-* and *trans-*1-lithio-2-vinylcyclopropane and subsequent treatment with hydrochloric acid gave, after column chromatography on silica gel eluted with benzene and hexane (1:1), seven-membered annelated ketones 13 and 14 along with an uncyclized *trans-*cyclopropyl derivative 15 in 86.5% yield. The β,γ-unsaturated ketone 13 and the uncyclized cyclopropane 15 smoothly converted to the desired α,β-unsaturated ketone 14 upon rapid filtration through a short column of alumina (96% yield) and upon thermolysis (67% yield), respectively. Treatment of 14 with trimethylsilyl cyanide and zinc iodide followed by phosphoryl chloride in pyridine afforded the unsaturated nitrile 16 in 53% yield. Final dehydrogenation of 16 was performed in 30% yield with selenium dioxide in a mixture of dioxane and ethanol.

Experimental Section

General. All melting points are uncorrected. ¹H NMR (100 MHz) and ¹³C NMR (22.5 MHz) were recorded on a Varian XL-100 spectrometer and a JEOL FX-90Q spectrometer, respectively. Chemical shifts are given in parts per million (δ) downfield from TMS as internal standard and coupling constants are given in hertz. IR, UV, and MS spectra were obtained with JASCO A-100 spectrometer, Hitachi 340 spectrometer, and JEOL JMS-01SG-2 spectrometer, respectively.

(15) Landesberg, J. M.; Kellner, D. *J. Org. Chem.* **1968**, *33*, 3374-3382.

The fluorescence spectra were measured on a Spex Fluorolog Model 111C equipped with a multialkali R928 photomultiplier tube. Excitation spectra were corrected with the aid of a built-in Rhodamine 6G quantum counter, emission spectra with a calibration curve determined with a standard tungsten lamp.

Measurement of Fluorescence Lifetimes and Quantum Yields. The fluorescence lifetimes were measured by the time-correlated single-photon counting technique using a Spectra Physics argon-ion laser synchronously pumped, cavity-dumped dye laser as the excitation source. Samples were excited with the second harmonic of the dye (rhodamine 6G) laser at a repetition rate of 1 MHz. The fluorescence was dispersed with a Jobin Yvon H20 monochromator and detected by a Hamamatsu R106 photomultiplier. The fluorescence decay curves were deconvoluted and analyzed by a Sharp MZ80C personal computer. Quantum yields were determined by reference to 9,10-diphenylanthracene ($\phi_f = 0.86$).[16]

Quantum Yields for Isomerization 1 → 2. The reaction progress was monitored spectrophotometrically. Since the quantum yields were found to be concentration dependent, no great care was taken to obtain very reliable values for the absolute light intensities. The intensity of the 308-nm light pulses from a Lambda Physik EMG 101 MSC excimer laser operating on XeCl were measured with a calibrated Joulemeter Model ED-500 from Gentec. Monochromatic light at 254 and 365 nm was obtained by filtering the corresponding lines from a stabilized medium-pressure mercury arc Hanau St. 41. The light flux passing the sample cell was assumed to be the same as in previous calibrations of the same setup by ferrioxalate actinometry.

Measurement of Ionization Potential of 3. The He(1) photoelectron spectrum was recorded by Dr. I. Watanabe and Prof. S. Ikeda of Osaka University at a resolution of 22–24 meV. The calibration was done by mixing Xe gas (12.130 eV) as an internal reference during the measurement. The sample had to be heated to 38–39 °C because of the low vapor pressure of the sample. For 3, 7.94 eV was obtained as a vertical and adiabatic ionization potential.

Cyclic Voltammetry. The cyclic voltammetries were carried out in dimethylformamide at –60 °C with 0.1 M *n*-Bu₄ClO₄ as the supporting electrolyte, with a platinum working electrode and SCE reference electrode. Half-cell potentials for 1 and 5 are –1.51 and –1.59 V, respectively. The peak separation for the cathodic and anodic waves at sweep rate of 200 mV/s were 140 and 170 mV, respectively. Electron affinities were deduced based on the equation, EA $= -E_{1/2} +2.49$.[17]

Calculations. In the standard PPP SCF CI calculations, idealized geometries of regular planar polygons (bond lengths $r_{\mu\nu} = 140$ pm) and standard parameters were used: $r_{\mu\nu} = 1439.5/132.8 + r_{\mu\nu}$ (pm) eV, $I_N - I_C = 2.68$ eV, $\beta_{CC} = -2.318$ eV, $\beta_{CN} = -3.25$ eV, $\gamma_{CC} = 10.84$ eV, $\gamma_{NN} = 12.30$ eV, $Z_\mu{}^c = 1$. All singly excited configurations were included for CI.

Materials. 8-Cyanoheptafulvene (3)[8] and 8,8-dicyanoheptafulvene (4)[9] were prepared by following the literature procedures.

Preparation of 8-Cyano-10,10-dimethylbicyclo[5,3,0]deca-1,3,5,7-tetraene (5). A. Ethyl 2-Methyllevulinate 4-Ethylene Acetal (7), A solution of LDA (104 mmol) in dry tetrahydrofuran (THF) (150 mL) was prepared in the usual way. To the solution, ethyl levulinate 4-ethylene acetal (6) (18.0 g, 96 mmol) in dry THF (20 mL) was added dropwise at –78 °C, and the temperature was gradually raised to –25 °C over a period of 1 h. Methyl iodide (25 mL, 401 mmol) was added slowly, and the mixture was brought to room temperature. After 2.5 h of stirring, the mixture was diluted with ether and water. The aqueous layer was extracted 4 times with ether, and the combined ether layer was washed with water and brine and dried over magnesium sulfate. The dried solution was concentrated under a reduced pressure and distilled (3 mmHg, 66–68 °C) to give 7 (13.55 g, 84%): IR (neat) 1733 cm⁻¹; ¹H NMR (CDCl₃) δ 1.17 (d, 3 H, *J* = 6.5 Hz), 1.26 (t, 3 H, *J* = 7.0 Hz), 1.31 (s, 3 H), 1.66 (dd, 1 H, *J* = 14.0, 3.5 Hz), 2.27 (dd, 1 H, *J* = 14.0, 9.5 Hz), 2.45–2.80 (m, 1 H), 3.90 (s, 4 H), 4.13 (q, 2 H, *J* = 7.0 Hz); MS, *m/z* 203 (M⁺ + 1, 26%), 201 (18), 187 (100), 157 (100). Anal. Calcd for C₁₀H₁₈O₄: C, 59.38; H, 8.97. Found: C, 59.43; H, 9.04.

B. Ethyl 2,2-Dimethyllevulinate (9), A solution of LDA (87 mmol) in dry THF (150 mL) was prepared in an usual manner. To the solution, 7 (13.5 g, 67 mmol) in dry THF (20 mL) was added at –78 °C, and the temperature was gradually raised to –25 °C over the period of 1 h. Methyl iodide (21 mL, 337 mmol) was added slowly, and the mixture was brought to room temperature. After it was stirred for 2 h, the mixture was diluted with ether and water. The aqueous layer was extracted with ether, and the combined ether layer was washed with water and brine and dried over magnesium sulfate. The dried solution was concentrated under a reduced pressure to yield 8 (17.8 g). The crude 8

(16) Morris, J. V.; Mahaney, M. A.; Huber, J. R. *J. Phys. Chem.* **1976**, *80*, 969-974.

(17) Chen, E. C. M. *J. Chem. Phys.* **1975**, *63*, 3183-3191.

(17.8 g) in ether (50 mL) was treated with 2 N hydrochloric acid (50 mL) for 1.5 h at room temperature. The ether layer was separated and the aqueous layer was extracted 4 times with ether. The combined ether layer was washed successively with water, saturated aqueous sodium hydrogen carbonate, dilute aqueous sodium thiosulfate, water, and brine and dried over magnesium sulfate. The dried mixture was concentrated under a reduced pressure and distilled (3 mmHg, 55 °C) to give **9** (10.1 g, 88%): IR (neat) 1720 cm⁻¹; ¹H NMR (CDCl₃) δ 1.22 (s, 6 H), 1.22 (t, 3 H, *J* = 7.0 Hz), 2.10 (s, 3 H), 2.72 (s, 2 H), 4.12 (q, 2 H, *J* = 7.0 Hz); MS, *m/z* 172 (M⁺, 49%), 157 (8), 127 (100), 99 (77). Anal. Calcd for C₉H₁₆O₃: C, 62.76; H, 9.36. Found: C, 62.74; H, 9.44.

C. 5,5-Dimethyl-3-methoxycyclopent-2-en-1-one (11) and 4,4-Dimethyl-3-methoxycyclopent-2-en-1-one (12). To a solution of diisopropylamine (8.2 mL, 59 mmol) in dry THF (150 mL), *n*-butyllithium in hexane (1.41 N, 38.2 mL, 54 mmol) was added at −78 °C. A solution of **9** (2.03 g, 12 mmol) in dry THF (20 mL) was added dropwise at −78 °C, and the mixture was brought to room temperature over the period of 3 h. After an additional 4 h of stirring, the mixture was acidified with 6 N hydrochloric acid, concentrated to some extent under a reduced pressure, and extracted with ether. The ether layer was washed with water and brine and dried over magnesium sulfate. The dried solution was concentrated to give diketone **10** (1.825 g), which was dissolved in ether (20 mL) and treated with diazomethane in ether. The solvent was removed, and the residue was chromatographed over deactivated silica gel (3% H₂O, 33 g) with a mixture of benzene and ether (4:1 v/v) to yield **11** (257.5 mg), a mixture of **11** and **12** (600.9 mg), and **12** (142.2 mg). The mixture of **11** and **12** was separated by repeated column chromatography over silica gel (30 g). **11**: 30%; IR (neat) 1690, 1600 cm⁻¹; ¹H NMR (CDCl₃) δ 1.18 (s, 6 H), 2.46 (s, 2 H), 3.83 (s, 3 H), 5.15 (s, 1 H). **12**: 30%; IR (neat) 1685, 1590 cm⁻¹; ¹H NMR (CDCl₃) δ 1.25 (s, 6 H), 2.33 (s, 2 H), 3.83 (s, 3 H), 5.15 (s, 1 H).

D. Seven-Membered Ring Annelation on 11. To a solution of 1-bromo-2-vinylcyclopropane (790 mg, 5.37 mmol) in dry ether (6 mL), *sec*-butyllithium (1.70 N, 3.2 mL, 5.44 mmol) was added dropwise at −78 °C over the period of 5 min. After stirring for 1.5 h at −78 °C, a solution of **11** (507 mg, 3.62 mmol) in a mixture of dry ether (0.5 mL) and THF (0.5 mL) was added at −78 °C over the period of 10 min. The mixture was stirred for 1 h at −78 °C and then brought to room temperature and treated with 2 N hydrochloric acid (10 mL) for 15 min. The ether layer was separated, and the aqueous layer was extracted 4 times with ether. The combined organic layer was washed with water, saturated aqueous sodium hydrogen carbonate, and brine and dried over magnesium sulfate. The dried mixture was concentrated under a reduced pressure and chromatographed over deactivated silica gel (10% H₂O, 15 g) with a mixture of benzene and hexane (1:1 v/v) to give 10,10-dimethyl-bicyclo[5.3.0]deca-1,4-dien-8-one (**13**) (240 mg), 10,10-dimethyl-bicyclo[5.3.0]deca-1(7),4-dien-8-one (**14**) (118 mg), and 3-*trans*-(2-vinylcyclopropyl)-4,4-dimethylcyclopent-2-en-1-one (**15**) (106 mg) in a total yield of 86.5%. **13**: a yellow oil; IR (neat) 1740 cm⁻¹; ¹H NMR (CDCl₃) δ 1.23 (s, 6 H), 2.23-3.33 (m, 7 H), 5.50-5.83 (m, 3 H). **14**: a colorless oil; bp 65 °C (0.1 mmHg); IR (neat) 1700 cm⁻¹; ¹H NMR (CDCl₃) δ 1.19 (s, 6 H), 2.28 (s, 2 H), 2.30-2.62 (m, 4 H), 2.94-3.08 (m, 2 H), 5.64-6.02 (m, 2 H), the signal at δ 2.28 disappears after treatment with potassium carbonate in MeOD for 2.5 h; MS, *m/z* 176 (M⁺, 9%), 161 (9), 91 (100). Anal. Calcd for C₁₂H₁₆O: C, 81.77; H, 9.15. Found: C, 81.66; H, 9.26. **15**: a colorless oil; bp 70 °C (0.1 mmHg); IR (neat) 1688, 1600 cm⁻¹; ¹H NMR (CDCl₃) δ 1.30 (s, 6 H), 1.15-1.81 (m, 4 H), 2.30 (s, 2 H), 5.42 (s, 1 H), 4.93-5.69 (m, 3 H); MS, *m/z* 176 (M⁺, 3%),

161 (4), 91 (100). Anal. Calcd for C₁₂H₁₆O: C, 81.77; H, 9.15. Found: C, 81.48; H, 9.34. **13** (242 mg) was converted to **14** by filtration through deactivated alumina (3% H₂O, 8 g) with benzene in a yield of 96%. When a solution of **15** (150 mg) in carbon tetrachloride (5 mL) was heated at 180-200 °C for 5.5 h in a sealed tube, **14** was obtained in 67% yield.

E. 8-Cyano-10,10-dimethylbicyclo[5,3,0]deca-1,4,7-triene (16). In a 30-mL flask, **14** (350 mg, 1.99 mmol) and zinc iodide (catalytic amount) were placed, and trimethylsilyl cyanide (0.8 mL, 6.0 mmol) was added at room temperature with stirring. After 50 min, the solution was poured into a mixture of chloroform and cold water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layer was washed with water and brine and dried over magnesium sulfate. The dried solution was concentrated under a reduced pressure. The residue was dissolved in dry pyridine (3 mL) and treated with phosphoryl chloride (0.6 mL, 6.6 mmol) at 70 °C for 4 h. After cooling, the solution was poured into a mixture of ether and cold water. The organic layer was separated, and the aqueous layer was extracted 4 times with ether. The combined organic layer was washed with water, saturated aqueous sodium hydrogen carbonate, and brine and dried over magnesium sulfate. The dried solution was concentrated under a reduced pressure, and the residue was chromatographed over deactivated silica gel (10% H₂O, 10 g) with a mixture of benzene and hexane (1:1 v/v) to give **16** (197.5 mg, 53%) and **5** (2-3 mg). **16**: a pale orange oil: bp 80 °C (0.1 mmHg); IR (neat) 2200, 1592 cm⁻¹; ¹H NMR (CDCl₃) δ 1.08 (s, 6 H), 2.40 (brs, 2 H), 2.97 (dd, 2 H, *J* = 6.0, 5.5 Hz), 3.31 (dt, 2 H, *J* = 5.5, 1.9 Hz), 5.56-6.10 (m, 3 H); MS, *m/z* 185 (M⁺, 54%), 170 (34), 61 (100).

F. 8-Cyano-10,10-dimethylbicyclo[5,3,0]deca-1,3,5,7-tetraene (5). A suspension of **16** (126 mg, 0.68 mmol) and selenium dioxide (176 mg, 1.59 mmol) in a mixture of dioxane (4 mL) and ethanol (0.2 mL) was heated at 70 °C for 2.5 h with stirring. The precipitated selenium was filtered with a glass filter and washed with benzene. The combined organic layer was concentrated, and the residue was chromatographed 3 times over deactivated silica gel (10% H₂O, 4 g) with a mixture of benzene and hexane (1:1 v/v) to give **5**, which was recrystallized from hexane (37.0 mg, 30%): red leaflets; mp 71-72 °C under argon atmosphere; IR (KBr) 2180 cm⁻¹; ¹H NMR (CDCl₃) δ 1.13 (s, 6 H), 2.43 (s, 2 H), 5.63 (d, 1 H, *J* = 7.3 Hz), 5.70-6.10 (m, 3 H), 6.41 (dd, 1 H, *J* = 11.5, 1.3 Hz); ¹³C NMR (CDCl₃) δ 29.2, 43.0, 46.3, 97.8, 118.3, 122.9, 129.3, 129.9, 132.4, 133.4, 156.0, 164.0; UV (cyclohexane) λ_max (ε) 230 (12 600), 265 (sh, 5000), 333 (14 800), 347 (18 200), 364 (11 500), 428 (460), 456 (490), 494 (420), 537 (270), 586 (120), 640 (20) nm. Anal. Calcd for C₁₃H₁₃N: C, 85.20; H, 7.15; N, 7.64. Found: C, 85.21; H, 7.18; N, 7.64.