Photochemical Generation of Bicyclo[4.2.2]decapentaene from [4.2.2]Propellatetraene. Experimental and Theoretical Study of the π-Bond-Shift Isomers of Bicyclo[4.2.2]decapentaene, [4]Paracyclophane-1,3-diene, and 1,6-Ethenocycloocta-1,3,5,7-tetraene

Takashi Tsuji,*,† Shinya Nishida,† Masahiro Okuyama,† and Eiji Osawa‡

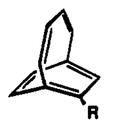
Contribution from the Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060, and Department of Knowledge-Based Information Engineering, Toyohashi University of Technology, Tempaku-Cho, Toyohashi 440, Japan

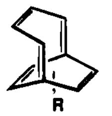
Received May 30, 1995®

Abstract: π-Bond shift isomerism in bicyclo[4.2.2]decapentaene provides two unique structures, [4]paracyclophane-1,3-diene **1** and 1,6-ethenocycloocta-1,3,5,7-tetraene **2**. The photochemical transformation of [4.2.2]propella-2,4,7,9-tetraene (**7a**) and its 7-(methoxycarbonyl) derivative (**7b**) into the corresponding bicyclo[4.2.2]decapentaenes has been examined. Irradiation of **7a** in MeOH affords an adduct of MeOH whose formation suggests the generation of bicyclo[4.2.2]decapentaene, but does not permit differentiation between the structural alternatives **1a** and **2a**. Photolysis of **7a** in the presence of cyclopentadiene provides adducts whose structures demonstrate that the intermediate is trapped in the form of **1**. The structures of cyclopentadiene adducts derived from **7b** also indicate the generation of the intermediate in the form of **1**. In no case was an adduct derived from the interception of the intermediates in the form of **2** detected. Electronic absorption spectra observed upon irradiation of **7a** and **7b** at 77 K are remarkably similar in shape to those of corresponding [4]paracyclophanes and thus substantiate again that the phototransformation of **7a** and **7b** leads to species whose structures are best represented by the form of **1**. The results of the geometrical optimization of **1a** and **2a** undertaken at the SCF level employing 3-21G and 6-31G* basis sets and also using semiempirical MNDO, AM1, and PM3 Hamiltonians are presented. The semiempirical methods as well as the ab initio calculations at 3-21G and 6-31G* levels predict that **1a** is 5.4−12.2 kcal/mol less stable than **2a**. With the application of the MP2 correlation energy treatment, however, the energy of **1a** relative to **2a** is remarkably lowered and **1a** is predicted to lie 4.5−4.7 kcal/mol below **2a**. The preparation of **7a** and **7b** from tetrahydrocinnamic acid in overall yields of 4.9% and 5.9%, respectively, is described.

Introduction

π-Bond shift isomerism in bicyclo[4.2.2]decapentaene provides a pair of unique structures, **1** and **2**, possessing novel and formally fully conjugated bicyclic 10-π-electron systems. Compound **1** may be viewed as [4]paracyclophane-1,3-diene in which the benzene ring is bridged at the para positions with a 1,3-butadiene chain and hence is extremely bent.[1] Compound **2** is 1,6-etheno-bridged cyclooctatetraene in which the bridgehead double bonds are constrained to interact through space and there may also be through-bond interaction.[2] This species also contains a hitherto unknown *cis,trans,cis,trans*-cyclooctatetraene structure.[3] It is of special interest whether bicyclo[4.2.2]decapentaene will exist as **1** and/or **2** or conceivably some structure of lower symmetry.


1a: R = H
1b: R = CO$_2$Me


2a: R = H
2b: R = CO$_2$Me

In the past 20 years, dramatic progress has been made in the synthesis of [*n*]paracyclophanes with ever smaller bridges, in pursuit of improved understanding of aromaticity and also driven by the challenges inherent in the synthesis of highly strained molecules.[4] Recently, generation of [4]paracyclophane **3**, the smallest member in the [*n*]paracyclophane series, was confirmed independently by us[5] and by Bickelhaupt and his co-workers.[6] This species is highly reactive and is observable only under matrix isolation at low temperature because of its high propen-

---

† Hokkaido University.

‡ Toyohashi University of Technology.

® Abstract published in *Advance ACS Abstracts,* September 15, 1995.

(1) For reviews of cyclophanes, see: (a) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1971,** *4,* 204−213. (b) *Cyclophanes*; Keehn, P. M., Rosenfeld, S. M., Eds.; Academic Press: New York, 1983. (c) Cyclophanes I and II. *Topics in Current Chemistry*; Vögtle, F., Ed.; Springer-Verlag: Berlin, 1983; Vols. 113 and 115. (d) Bickelhaupt, F.; De Wolf, W. H. *Recl. Trav. Chim. Pays-Bas* **1988,** *107,* 459−478. (e) Vögtle, F. *Cyclophan-Chemie*; B. G. Teubner Verlag: Stuttgart, 1990. (f) Bickelhaupt, F.; De Wolf, W. H. In *Advances in Strain in Organic Chemistry*; Holton, B., Ed.; JAI Press: Greenwich, CT, 1993; Vol. 3, p 185. (g) Tobe, Y. *Top. Curr. Chem.* **1994,** *172,* 1.

(2) For reviews of strained bridgehead double bond compounds, see: (a) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978. (b) Shea, K. J. *Tetrahedron* **1980,** *36,* 1683−1715. (c) Szeimies, G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: New York, 1983; Vol. 3, Chapter 5. (d) Warner, P. M. *Chem. Rev.* **1989,** *89,* 1067−1093. (e) Borden, W. T. *Ibid.* **1989,** *89,* 1095−1109. (f) Keese, R.; Luef, W. *Top. Stereochem.* **1991,** *20,* 231−318.

(3) For a theoretical study, see: Dewar, M. J. S.; Merz, K. M., Jr. *J. Chem. Soc., Chem. Commun.* **1985,** 343−344.

(4) (a) *Synthesis of Non-natural Products: Challenge and Reward (Tetrahedron Symposia-in-print No. 26)*; Eaton, P. E., Ed. *Tetrahedron* **1986,** *42,* 1549−1915. (b) The July/August 1989 issue of *Chemical Reviews* reports exclusively on strained organic compounds.

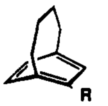
(5) Tsuji, T.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1987,** 1189−1190; *J. Am. Chem. Soc.* **1988,** *110,* 2157−2164.

(6) Kostermans, G. B. M.; Bobeldijk, M.; De Wolf, W. H.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1987,** *109,* 2471−2475.

0002-7863/95/1517-9804$09.00/0

sity for polymerization even in a dilute solution below −100 °C. It is of particular interest how the conjugated double bond system on the side chain of **1** modifies the structure and property of the extremely bent benzene, though the π-bond systems in the benzene ring and on the side chain are nearly orthogonal and thus appear to be essentially not conjugated to each other.

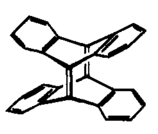
On the other hand, Wiseman[7] and Wiberg[8] have reported the preparation of anti-Bredt dienes **4** and **5**, respectively, in which nonconjugated double bonds are forced by their geometries to interact with each other. Both the compounds exhibit high reactivity toward oxygen but are isolable, and the latter has been analyzed by X-ray crystallography. Particularly intriguing is the property of the tetrabenzo derivative of **5** reported by Greene, Trefonas, and their co-workers.[9] Compound **6** is stable to heat, air, and moisture, despite the severe out-of-plane bending at the olefinic carbons. These results suggest that **2** may be much less prone to polymerization than **1** and may possibly be isolable, if the bicyclodecapentaene exists as **2**.



3a: R = H
3b: R = CO_2Me

4

5



6

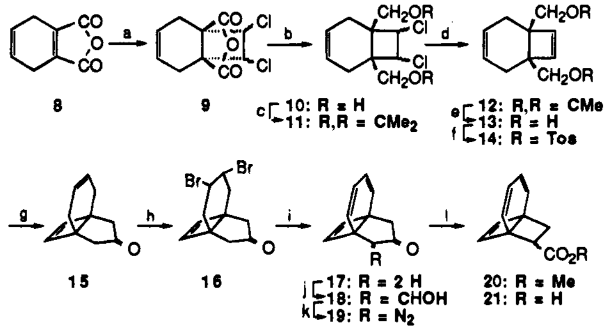
7a: R = H
7b: R = CO_2Me

In a preliminary account of this work[10] we reported the photochemical transformation of [4.2.2]propellatetraenes **7** into the corresponding bicyclo[4.2.2]decapentaenes whose structures were best represented by **1** rather than **2**. In the present paper we give the full account of the investigation including the theoretical study of **1a** and **2a**.

Results and Discussion

Preparation of [4.2.2]Propellatetraenes. When we embarked on the preparation of [4.2.2]propellatetraenes **7** some time ago, available methods for the synthesis of Dewar benzene derivatives seemed difficult to apply to that object. Accordingly, the development of a novel synthetic route was undertaken, and their preparations were eventually accomplished via the pathway outlined in Schemes 1 and 3,[11] though in rather low overall yields. Prompted by necessity to construct the [4.2.2]propellane skeleton more efficiently, an alternative procedure shown in Scheme 2 was later devised for the synthesis of **20**/**21**. In the latter process, **21** was obtained in 10.5% yield from **22** in eight steps, compared to the previous synthesis in 3.0% yield from **8** in twelve steps.[11]

Scheme 1



[a] Reagents and conditions: (a) $h\nu$/$Ph_2C{=}O$, $ClCH{=}CHCl$; (b) LAH; (c) $Me_2C(OMe)_2$, p-TsOH; (d) $Na/NH_3(l)$;[13] (e) 60% AcOH; (f) p-TsCl/C_5H_5N; (g) $MeSCH_2S(O)Me$ and BuLi/THF, H_2SO_4/EtOH; (h) $C_5H_5NHBr_3/CH_2Cl_2{-}C_5H_5N$; (i) LiCl and Li_2CO_3/HMPA; (j) HCO_2Et and $EtONa/C_6H_6$; (k) p-TsN_3 and Et_3N/Et_2O; (l) $h\nu$.

In the original preparation, readily accessible 3,6-dihydrophthalic anhydride **8**[12] was envisioned to be a convenient starting material to the [4.2.2]propellane framework. Thus, compound **8** was subjected to photocycloaddition with 1,2-dichloroethylene to afford a mixture of stereoisomeric adducts **9** (72%), from which diol **13** was prepared in 64% yield via a reaction sequence shown in Scheme 1. The conversion of **13** to the ester **14** smoothly proceeded, and treatment of the resulting **14** with lithiated methyl (methylsulfinyl)methyl sulfide, a carbonyl equivalent,[14] followed by hydrolysis furnished **15** in 64% yield. The bromination of **15** with pyridinium bromide perbromide in the presence of pyridine exclusively occurred at the cyclohexene double bond to give **16**, and the subsequent dehydrobromination with a mixture of LiCl and Li_2CO_3 in HMPA delivered **17** in 86% yield.[15] The trienone **17** was diazotized in the usual manner,[16] and subjected to the ring contraction reaction by the photo-Wolff rearrangement. Photolysis of **19** in methanol or in methylamine/ether, however, led to the formation of a large amount of tarry material and provided the ring-contracted ester **20** or amide as an about 6:1 mixture of stereoisomers in only 15% yield at best. The yield of the ring-contracted product **21** was improved to some extent in aqueous dioxane, but still was not better than 20%.

The multitude of reaction steps coupled with an unsatisfactory overall yield of **20**/**21** in the above preparation prompted us to develop an alternative procedure, and substantial improvement in those aspects could be achieved in the new procedure outlined in Scheme 2. Dihydroindan **24** has previously been prepared via a sequence including the cycloaddition of 2-(phenylthio)-2-cyclopentenone with butadiene.[17] This method, however, is laborious and not suitable for the preparation of a large quantity of **24**. We found that the tin(IV) chloride-catalyzed cyclization of acid chloride **23** in dichloroethane directly delivered **25** in a high yield. The subsequent transformation of **24** into **26** was carried out in the same manner as described for the conversion of **8** into **13**. The photo-Wolff rearrangement of **28** which was prepared in 83% yield from **26** in the usual manner[16] satisfactorily proceeded in methanol to afford **29** as a 5:2 mixture of stereoisomers in 86% yield. Regioselective bromination of **29** at the cyclohexene double bond with pyridinium bromide perbromide followed by dehydrobromination with $LiCl{-}Li_2CO_3$ in HMPA produced **21** in 39% yield (10.5% from **22**).

The carboxylic acid **21** was converted to the isocyanate

---

(7) Wiseman, J. R.; Vanderbilt, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 7730−7731.

(8) (a) Wiberg, K. B.; Matturro, M. G.; Okarma, P. J.; Jason, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 2194−2200. (b) Wiberg, K. B.; Adams, R. D.; Okarma, P. J.; Matturro, M. G.; Segmuller, B. *Ibid.* **1984**, *106*, 2200−2206.

(9) Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 4342−4343.

(10) Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1989**, *111*, 368−369.

(11) (a) Tsuji, T.; Komiya, Z.; Nishida, S. *Tetrahedron Lett.* **1980**, *21*, 3583−3586. (b) Tsuji, T.; Nishida, S. *Ibid.* **1983**, *24*, 3361−3364.

(12) Flaig, W. *Justus Liebigs Ann. Chem.* **1950**, *568*, 1−33.

(13) Allred, E. L.; Beck, B. R.; Voorhees, K. J. *J. Org. Chem.* **1974**, *39*, 1426−1427.

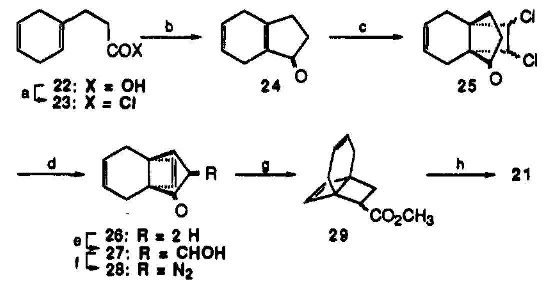
(14) Ogura, K.; Yamashita, M.; Furukawa, S.; Suzuki, M.; Tsuchihashi, G. *Tetrahedron Lett.* **1975**, 2767−2770.

(15) Paquette, L. A.; Wingard, R. E., Jr.; Photis, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 5801−5806.

(16) Regitz, M. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; J. Wiley & Sons: Chichester, 1975; Chaper 17.

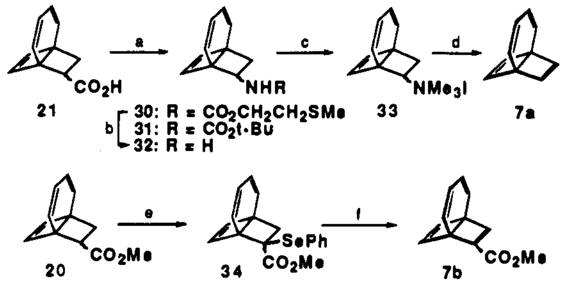
(17) (a) Monteiro, H. J. *J. Org. Chem.* **1977**, *42*, 2324−2326. (b) Knapp, S.; Lis, R.; Michna, P. *J. Org. Chem.* **1981**, *46*, 624−626.

Scheme 2



[a] Reagents and conditions: (a) NaOH, $(COCl)_2$; (b) $SnCl_4/C_2H_4Cl_2$; (c) $h\nu$/ClCH=CHCl; (d) $NaBH_4$, $Na/NH_3(l)$, $(COCl)_2$ and DMSO, Et_3N; (e) HCO_2Et and $EtONa/C_6H_6$; (f) p-TsN_3 and Et_3N/CH_2Cl_2; (g) $h\nu$/MeOH; (h) $C_5H_5NHBr_3/CH_2Cl_2-C_5H_5N$, LiCl and Li_2CO_3/HMPA, $NaOH/H_2O-MeOH$.

Scheme 3



[a] Reagents and conditions: (a) $(PhO)_2P(O)N_3$, $MeSCH_2CH_2OH/C_6H_6$; (b) Me_2SO_4 and $NaHCO_3$/MeOH, NaOH/MeOH, dilute HCl; (c) MeI and $NaHCO_3$/MeOH; (d) t-BuOK/DMF$-C_5H_{12}$; (e) LDA, $(PhSe)_2$/THF; (f) 15% H_2O_2/CH_2Cl_2.

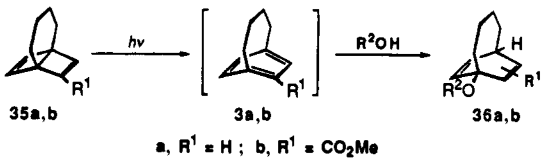
following the procedure of Yamada,[18] which was subsequently exposed to 2-(methylthio)ethanol to give the carbamate **30** (Scheme 3). Compound **30** was first treated with dimethyl sulfate and then with aqueous NaOH to produce carbamate salt, from which amine **32** was liberated in one pot through acidification and decarboxylation.[19] The quaternization of **32** with methyl iodide and treatment of the resultant salt **33** with t-BuOK in a DMF/pentane mixture provided the parent propellatetraene **7a** in an overall yield of 47% from **21** (4.9% from **22**).

Treatment of **20** with LDA followed by selenylation with diphenyl diselenide afforded **34** in 81% yield.[20] Oxidation of the selenide **34** to the selenoxide and the following elimination of benzeneselenenic acid smoothly proceeded to give **7b** in 69% yield. The spectroscopic properties of **7a** and **7b** were in full accord with their structures.

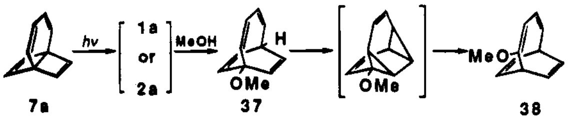
Electronic interaction among their three π-bond systems is of considerable interest. PE spectroscopic study, however, indicated that the interaction is rather weak at least in the ground state as reported elsewhere.[21]

Photolysis of 7a in Methanol. Previously we demonstrated that the production of alcohol adduct(s) **36** upon irradiation of **35** in an alcoholic medium resulted from its initial isomerization to [4]paracyclophane **3** followed by the addition of the alcohol to the extremely strained bridgehead carbons (Scheme 4).[5] If

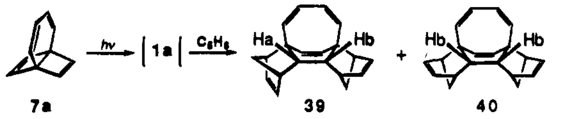
Scheme 4



Scheme 5



Scheme 6



the central σ-bond of **7a** is similarly cleaved photochemically to generate a highly strained bicyclo[4.2.2]decapentaene, a conversion into the corresponding adduct(s) in the alcoholic medium is reasonably expected.

Irradiation of **7a** in 1% CF_3CO_2H/methanol through Pyrex indeed led to the formation of a methanol adduct in 64% yield. The product, however, was found to be **38** rather than **37** on the basis of its spectroscopic property. Schröder and his coworkers have reported that bicyclo[4.2.2]deca-2,4,7,9-tetraenes bearing a substituent on one of the bridgehead carbons readily isomerize to the thermodynamically more stable 2-substituted derivatives at ambient or slightly higher temperature via the successive intramolecular [2 + 4] and retro-[2 + 4] processes (Scheme 5).[22] Since a direct photochemical process is difficult to conceive for the formation of **38** from **7a**, the methanol adduct would probably be derived through the rearrangement of the primary product **37** during the irradiation and/or the subsequent isolation process. The production of **38** thus suggested the occurrence of the photochemical cleavage of the central σ-bond of **7a**, but was not informative enough to permit the differentiation of the probable structural candidates **1a** and **2a**, because both species were expected to undergo the addition of methanol at the bridgehead carbons, thereby being effectively relieved from the steric strain inherent to the ring systems. To elucidate the structure of this reactive intermediate, the generation of the species under matrix isolation at low temperature and its chemical trapping with cyclopentadiene as a Diels–Alder adduct were next investigated.

Photolysis of 7 in the Presence of Cyclopentadiene. Chemical trapping of transient *anti*-Bredt bridgehead olefins with reactive conjugated dienes as Diels–Alder adducts is a well-established technique and provides reliable verification for their generation.[2] Fortunately, the electronic absorptions of **7a** and **7b** extend to wavelengths substantially longer than that of cyclopentadiene, enabling the selective excitation of the former in the presence of the latter. Irradiation of a mixture of **7a** and a large excess of cyclopentadiene in hexane through Pyrex cleanly afforded two 2:1 adducts of cyclopentadiene to **7a** in a ratio of ca. 2:1 for which the structures **39** and **40**, respectively, were assigned on the basis of their spectroscopic properties (Scheme 6). Virtually no volatile product other than those were detected in the photolysate. The strong electronic absorptions in the region of 250–300 nm exhibited by those products

---

(18) (a) Shioiri, T.; Ninomiya, K.; Yamada, S. *J. Am. Chem. Soc.* **1972**, *94*, 6203–6205. (b) Ninomiya, K.; Shioiri, T.; Yamada, S. *Tetrahedron* **1974**, *30*, 2151–2157.

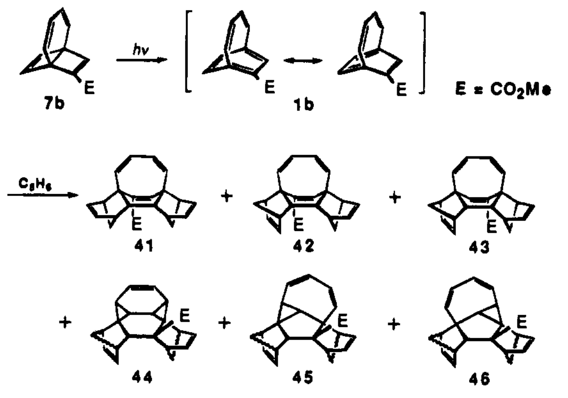
(19) (a) Amaral, M. J. S. A.; Barrett, G. C.; Rydon, H. N.; Willet, J. E. *J. Chem. Soc. C* **1966**, 807–813. (b) Kunz, H. *Chem. Ber.* **1976**, *109*, 3693–3706.

(20) Reich, H. J.; Renga, J. M; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5430–5447.

(21) Gleiter, R.; Krennrich, G.; Bischof, P.; Tsuji, T.; Nishida, S. *Helv. Chim. Acta* **1986**, *69*, 962–971.

(22) Camadi, H. D.; Hildenbrand, P.; Richter, J.; Schröder, G. *Justus Liebigs Ann. Chem.* **1978**, 2074–2087.

Scheme 7



substantiated the presence of a conjugated diene unit and effectively ruled out their derivation from **2a**. It should be noted that products resulting from the addition of cyclopentadiene to **2a** at the bridgehead double bonds should only possess isolated double bonds. The ^{1}H NMR spectra of the adducts were also incompatible with the structures expected for their formation from **2a** and cyclopentadiene. The preferential trapping of the decapentaene in the form of [4]paracyclophane-1,3-diene (**1a**) was thus confirmed.

The endo/exo stereochemistry of the addition of cyclopentadiene was elucidated by examining the magnitude of vicinal coupling between the bridgehead proton and the adjacent methine proton H_a or H_b in the norbornene moieties and the chemical shift of the latter. It is well documented that the exo proton in norbornene couples more strongly with the adjacent bridgehead proton than the endo proton and, moreover, resonates at a significantly lower field than the latter.[23] Consistent with the unsymmetrical structure, the relevant protons in the major product gave rise to a pair of doublets of doublets with $J = 2$ and 14 Hz and $J = 3$ and 14 Hz at δ 2.45 and 3.06, respectively. They were accordingly assigned to the endo and exo protons H_b and H_a, respectively. The minor product exhibited the signal of the corresponding protons at δ 2.50 as a singlet and thus was assigned as **40**, resulting from the addition of two molecules of cyclopentadiene to the bent benzene ring in the exo mode. The other possible symmetrical product, *endo,endo*-adduct, was not detected in the product mixture. Steric repulsion between the etheno bridges of the norbornene rings might hinder its formation.

Photolysis of **7b** in the presence of cyclopentadiene led to the formation of a rather complex product mixture, from which six major products were eventually isolated in 27% (37% by GLC) yield total and assigned as **41**−**46** on the basis of their spectroscopic properties (Scheme 7). The assignment of endo/exo stereochemistry of the addition of cyclopentadiene in **41**−**43** was made in the same manner as described for **39** and **40**. The differentiation of two isomeric *endo,exo*-adducts, **42** and **43**, from each other, however, has so far been unsuccessful. Together with **41**−**43**, three adducts assigned as **44**−**46** were isolated in low yields. These products apparently resulted from the addition of cyclopentadiene to the substituted side of the bent benzene ring of **1b** and, interestingly, had suffered secondary (photo)rearrangement. As illustrated in Scheme 8, their formation is rationalized in terms of the secondary di-π-methane rearrangement and [2 + 4] addition in the initial adduct(s) **47**, possibly facilitated by the accompanying relief of steric congestion. The mutual interconversion between **45** and **46** under preparative GLC conditions at 200 °C which apparently proceeded via 1,5-shifts of the strained cyclopropane bonds is in accord with their structural assignment.[24] The formation of products which could be derived from **2b** was not observed again, though it cannot be completely ruled out since a few very minor products remained unidentified.

Scheme 8

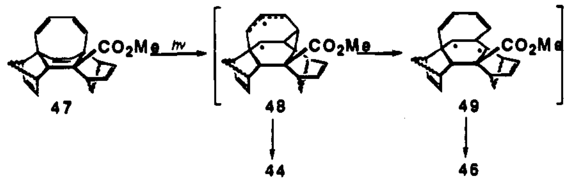


Table 1. Electronic Absorption Spectra of **1a**,**b** and **3a**,**b**[a]

species	λ, nm (log ε)	ref
1a	274 (3.7), 347 (3.3)[b]	this work
1b	291 (4.0), 345 (3.3), 415 (sh, 3.0)[b]	this work
3a	260, 330−340, 370−380[c]	5
3b	280, 348, 425[d]	5

[a] In rigid glass at 77 K. The quantitative conversion of **7a** and **7b** to **1a** and **1b**, respectively, was assumed for the estimation of molar absorptivity. [b] In a mixture of EPA.[25] [c] In a ca. 5:2:1 intensity ratio in EtOH. The band at the longest wavelength strongly overlaps with the neighboring band at 330−340 nm and does not give a distinct peak. [d] In a ca. 7:2:1 intensity ratio in EtOH.

Spectroscopic Detection of 1a and 1b in Rigid Glass at 77 K. As reported in the preliminary account, irradiation of **7a** and **7b** in rigid EPA[25] glass at 77 K with a 254 nm light source led to the development of UV/vis absorptions which were remarkably similar in shape to those of the corresponding [4]-paracyclophanes **3a** and **3b**, respectively.[10] On the basis of this similarity, it was concluded that the chromophores responsible for the absorptions were the severely bent aromatic rings of **1a** and **1b**, essentially unperturbed by the diene system on the four-carbon bridge, and thus the species generated from **7a** and **7b** in the glass at 77 K possessed the structure of **1** rather than that of **2**,[26] in accord with the results of the chemical trapping experiments at ambient temperature (Table 1).

Grimme indicated in his computational study that the main part of the experimental UV/vis spectrum of **3a** which we recently reported was reasonably accounted for in terms of the calculated excited-state energies, but commented that the origin of the lowest energy band seemed unclear.[29] Moreover, a strong red shift of this band observed for **3b**, not well reproduced by the calculations, was attributed to a strong solvent polarity effect or an impurity with a high extinction coefficient. Since the electronic absorption spectra observed upon irradiation of **7a** and **7b** provided important information on the geometries and electronic structures of the intermediates, the characteristics of the absorptions were reexamined. Irradiation of **7b** in pentane/isopentane glass at 77 K led to the development of absorption

---

(23) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon Press: Oxford, England, 1969.

(24) For 1,5-shifts in deuterated bicyclo[5.1.0]octa-2,4-diene, see: Grimme, W.; Doering, W. v. E. *Chem. Ber.* **1973**, *106*, 1765−1780.

(25) A 5:5:2 mixture of ether, isopentane, and ethanol.

(26) In **2**, the π-bonds overlap each other only weakly, and such a poorly conjugated system tends to exhibit a broad, weak absorption spectrum.[27] Cyclooctatetraene is a notable example,[28] and the π-bond system of **2** may be viewed as that of cyclooctatetraene perturbed by the etheno bridge double bond. It is reasonably expected that, if the species generated from **7a** and **7b** possessed the structures of **2a** and **2b**, respectively, the observed spectra would be much different from those of **3a** and **3b**.

(27) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1962; Chapter 15.

(28) (a) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *560*, 1. (b) Cope, A.; Bailey, W. J. *J. Am. Chem. Soc.* **1948**, *70*, 2305.

(29) Grimme, S. *J. Am. Chem. Soc.* **1992**, *114*, 10542−10547.

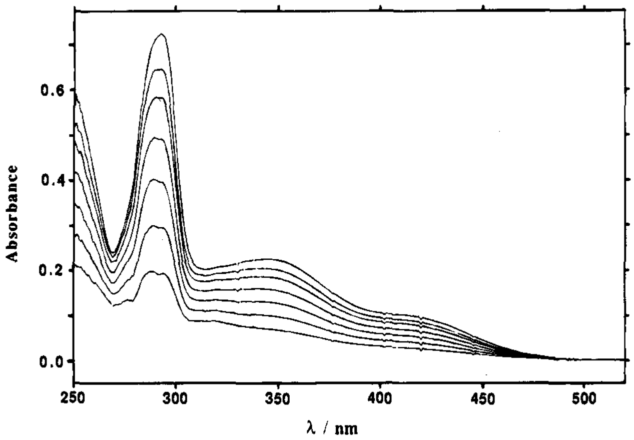
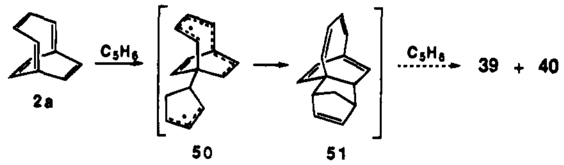


Figure 1. UV/vis absorption spectrum of **1b** and its decay by irradiation of >430 nm light in EPA glass at 77 K.

Scheme 9



almost indistinguishable from that observed in MeOH/EtOH or EPA glass at the same temperature. Although the effective polarity of rigid glass is difficult to evaluate, the close similarity of the spectra suggests that a solvent polarity effect upon the electronic transitions in **1b** is relatively minor. When the resultant glasses were irradiated with filtered light (>430 nm) by which only the species responsible for the longest wavelength band was excited, the observed three absorption bands proportionally decayed as shown in Figure 1. The bleaching of the absorption upon irradiation has been attributed to the photoreversion of **1b** to the starting **7b**.[10] This secondary photolysis experiment unambiguously demonstrates that the observed absorption in the range of 250–500 nm is due to a single species, **1b**. The electronic absorption spectrum of **1a** is also insensitive to the medium of glass, and the spectra observed in pentane/isopentane and MeOH/EtOH glasses are virtually superimposable on each other.

Photolysis of 7a in the Presence of Equimolar Amounts of Cyclopentadiene and Isoprene. The UV/vis spectroscopic investigation at low temperature as well as the chemical trapping experiments of the bicyclo[4.2.2]decapentaenes described above support a preference for the [4]paracyclophanediene structure **1** over the 1,6-ethenocyclooctatetraene structure **2**. One may argue, however, that the results of the trapping experiments are only superficial and the cyclopentadiene adducts might be derived stepwise from **2** via biradical intermediates as depicted in Scheme 9 rather than from **1** in a concerted manner. Such a possibility seems remote, but cannot be dismissed since, according to the theoretical analysis which we will discuss later, species **1a** and **2a** appear to represent energy minima on the potential energy surface of the bicyclo[4.2.2]decapentaene with a relatively small energy difference and, depending on the method of calculation, the predicted stabilomer changes between **1a** and **2a**.

It is known that the relative reactivity of conjugated dienes toward concerted [2 + 4] cycloaddition significantly differs from that toward free radical addition.[30] For example, isoprene is much less reactive than cyclopentadiene toward the former type of reactions, but about twice as reactive toward the stepwise cycloaddition with 1,1-dichloro-2,2-difluoroethylene.[31] To check the above possibility, **7a** was photolyzed in the presence of equimolar amounts of those dienes. Examination of the photolysate revealed the sole production of the cyclopentadiene adducts **39** and **40** without noticeable interference from isoprene, thus disproving the derivation of the adducts from **2a** via the biradical pathway. The stepwise cycloaddition of cyclopentadiene with alkenes tends to produce [2 + 2] adducts together with [2 + 4] adducts.[31] The observed [2 + 4] periselectivity was also in accord with the operation of the concerted mechanism.

Computational Analysis. The experimental observations unambiguously demonstrated that the reacting species photochemically generated from **7** possessed the structure of **1** rather than that of **2**. Those results, however, do not provide information concerning the latter. Moreover, a possibility that **2** is thermodynamically more stable than **1** cannot be rigorously ruled out on the basis of the chemical trapping experiments and/or the characteristics of the UV/vis absorption spectra. The photochemical transformation of **7** into **1** is an orbital-symmetry-allowed, four-electron disrotatory process, whereas that of **7** into **2** is a symmetry-forbidden reaction. The highly reactive **1**, once generated, might be intercepted by cyclopentadiene prior to its transformation into **2** owing to a substantial energy barrier dividing the former from the latter. By the same reasoning, in the glasses at low temperature the generated bicyclodecapentaene might be frozen in the form of **1**. It should be noted that the thermal interconversion between **1** and **2** is an orbital-symmetry-forbidden process.[32,33] To settle the above question and also to investigate the geometries and electronic states of those unique species, theoretical analyses were carried out by ab initio quantum mechanical methods as well as semiempirical procedures.

(1) **Geometry.** The geometrical optimizations of **1a** and **2a** were undertaken at the SCF level employing ab initio 3-21G and 6-31G* basis sets implemented in the Gaussian 86 and 92 programs[34] and also with semiempirical MNDO, AM1, and PM3 Hamiltonians in the MOPAC 5.0 program system.[35] An initial exploration of the potential energy surface of bicyclo[4.2.2]-decapentaene with the semiempirical methods furnished two local minima corresponding to the C_{2v} symmetric **1a** and the C_s symmetric **2a**. Thus, geometrical optimizations starting from the various less symmetrical structures led to either **1a** or **2a**. The optimizations of **1a** and **2a** with the 6-31G* basis set were

---

[30] (a) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779–807. (b) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon: Oxford, England, 1990. (c) Fringuelli, F.; Taticchi, A. *Dienes in The Diels-Alder Reaction*; J. Wiley & Sons: New York, 1990.

[31] Bartlett, P. D. *Q. Rev., Chem. Soc.* **1970**, *24*, 473–497.

[32] For π-bond shifting in cyclooctatetraenes, see: (a) Paquette, L. A. *Acc. Chem. Res.* **1993**, *26*, 57–62 and references cited therein. (b) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 5879–5881.

[33] According to recent theoretical calculations, the energy required for π-bond shifting in planar D_{4h} cyclooctatetraene (COT) is 3–4 kcal/mol which is in good agreement with the measured differences between the energies required for π-bond shifting and ring inversion in monosubstituted derivatives of COT.[32b]

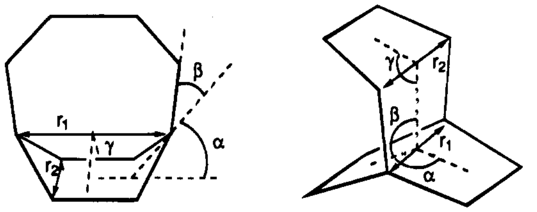
[34] (a) Gaussian 86: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Topial, S.; Pople, J. A., Carnegie-Mellon Quantum Chemistry Publishing Unit, Carnegie-Mellon University, Pittsburgh, PA, 1986. (b) Gaussian 92: Revision F. 3, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. A.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1992.

[35] Stewart, J. J. P. *QCPE Bull.* **1989**, *9*, 10. Hirano, T. *JCPE NewsLetter* **1989**, *1*, 36. Revised as Version 5.01 by J. Toyoda for Apple Macintosh.

Table 2. Comparison of Calculated Geometrical Parameters for **1a**, **2a**, and **3a**

computational method	α, deg	β, deg	α + β	γ, deg	r_1, Å	r_2, Å
			C_{2v} Symmetric Form **1a**			
6-31G*	29.0	44.8	73.8	147.5	2.645	2.390
3-21G	27.9	46.1	74.0	148.8	2.648	2.393
MNDO	39.5	33.9	73.4	137.3	2.560	2.446
AM1	37.2	36.3	73.5	139.8	2.565	2.431
PM3	37.4	35.8	73.2	140.0	2.542	2.429
			C_s Symmetric Form **2a**			
6-31G*	123.8	118.8		131.6	2.400	2.711
3-21G	123.5	119.0		129.6	2.405	2.660
MNDO	121.2	119.0		134.2	2.401	2.847
AM1	121.9	118.8		130.3	2.409	2.747
PM3	122.0	119.5		129.6	2.375	2.721
			[4]Paracyclophane (**3a**)[a]			
DZP[b]	29.7	38.2	67.9	145.9	2.657	2.374

[a] Parameters reported by Grimme.[29] [b] Double-ζ plus polarization basis set.



1a (**3a**) **2a**

Figure 2. Definition of the deformation angles α, β, and γ and the interatomic distances r_1 and r_2 for **1a** (**3a**) and **2a**.

accordingly performed within the constraint of C_{2v} and C_s symmetries, respectively.[36] The optimized geometrical parameters for **1a** and **2a** are summarized in Table 2 and Figure 3. For comparison, the data of **3a** from ref 29 are also listed in Table 2. The differences among the geometries optimized with the semiempirical MNDO, AM1, and PM3 Hamiltonians were relatively small, while the 3-21G geometry was close to that obtained with the 6-31G* basis set. Accordingly, only the geometrical parameters optimized at the 6-31G* level and with the PM3 method are given in Figure 3.

The most pronounced differences between the "ab initio" and "semiempirical" structures of **1a** are found in the deformation angles α and β, defined as illustrated in Figure 2, which give a measure of the degree to which the benzene ring is bent. The benzene ring in the former is substantially more flat than that in the latter, with α (γ) taking on the value 28.5 ± 0.6° (148.2 ± 0.7°) in the former and 38.0 ± 1.5° (139.0 ± 1.7°) in the latter. Interestingly, however, the total deformation angles (α + β) agree within 1° (73.6 ± 0.4°) in all the calculations. The out-of-plane bending of the benzylic C−C bond in the ab initio structure is accordingly more pronounced than that in the semiempirical structures. It has been pointed out that the semiempirical methods tend to overestimate the deformation angle α at the expense of β in [*n*]paracyclophanes.[29] The more pronounced deformation of the aromatic ring of **1a** as compared with **3a** ($\alpha + \beta = 67.9°$) is in line with the more pronounced bathochromic shifts of electronic absorption bands in the UV/vis spectrum of **1a** than in that of **3a**.[10] Compound **1a** thus represents the most strained of the [*n*]paracyclophanes ever prepared. Both **1a** and **3a** are, however, extremely labile, observable only in the rigid glass at low temperature, and the difference in their chemical reactivities was not discerned. In Figure 4A are shown torsion about the bond between C^1 and C^8 of **1a** (42.5°) and degrees of pyramidalization (out-of-plane bending)[37] at those aromatic carbons (46.0° and 26.7°, respectively). The pyramidalization at the aromatic methine carbons presumably is the consequence of maximization of favorable π-orbital overlap with the adjacent bridgehead carbon, and thus suggests the retention of aromatic conjugation in the severely bent benzene ring.[38] It is instructive that the corresponding unsaturated carbons of **2a** remain virtually planar (out-of-plane bending at $C^{7(8)}$ and $C^{9(10)}$ <2.2°). The bond alteration in the benzene ring of **1a** predicted by the ab initio calculations is $\Delta r = 0.010$ Å, surprisingly small for the extreme deformation of the ring. The semiempirical methods predict much larger differences, $\Delta r = 0.029{-}0.034$ Å. The most notable deformation in the 1,3-butadienylidene bridge of **1a** is the opening of the $C^2{-}C^3{-}C^4$ angle to about 137° at the 6-31G* level. The bond lengths are rather surprisingly normal, and the C−C bonds appear to suffer only slight elongation.

Structural parameters for the geometry-optimized C_s form **2a** are presented in Table 2 and Figure 3B. The bond alteration is more pronounced in the 6-31G* optimized structure than in that optimized by the semiempirical method. A separation between the bridgehead carbons C^1 and C^2 of ca. 2.40 Å suggests that there should be significant interaction between the π-electrons of the two bridgehead double bonds. The degrees of torsion about the bridgehead double bond (27.7°) and of pyramidalization at the terminal carbons C^1 and C^2 (40.3° and 24.8°, respectively) are shown in Figure 4B. Those deformation angles are substantially smaller than the corresponding values in **1a**, suggesting the superior kinetic stability of **2a**, apart from its thermodynamic stability compared with **1a**. The increased HOMO−LUMO energy gap in **2a** (0.445 au vs 0.355 au in **1a** at the 6-31G* level) reinforces the above expectation.

(2) Energy. In Tables 3 and 4 are listed total electronic energies of **1a** and **2a** calculated with the ab initio methods and heats of their formation with the semiempirical methods, respectively. Inspection of the tables reveals that the semiempirical methods as well as the ab initio calculations at the SCF level predict, contrary to the experimental observations, that the C_{2v} form **1a** is 5.4−12.2 kcal/mol less stable than the C_s form **2a**. The inclusion of polarization functions at the 6-31G* level leads to a somewhat smaller energy difference, but the calculated energy preference for **2a** does not fall below the above range. With the application of the second-order Møller−Plesset (MP2) correlation energy treatment, however, the energy of **1a** is remarkably lowered relative to **2a**, leading to the reversion of the relative stability of **1a** to **2a**. The C_{2v} form **1a** is now predicted to lie 4.5−4.7 kcal/mol below the C_s form **2a**.

Grimme has demonstrated in his high-level ab initio calculations for [4]paracyclophane (**3a**) and its valence isomers, the Dewar benzene **35a** and the prismane derivative, that the inclusion of electron correlation effects is essential to correctly evaluate the energy of **3a** relative to the isomers, and that the MP2 treatment adequately accounts for the correlation energy contribution to the **3a** → **35a** isomerization energy.[29] It seems reasonable to conclude that the thermodynamic stability of **1a** relative to **2a** is underestimated by the semiempirical methods as well as the ab initio calculations at the SCF level.

Conclusion

[4.2.2]Propella-2,4,7,9-tetraene (**7a**) and its 7-(methoxycarbonyl) derivative (**7b**) undergo photochemical transformation

---

(36) For the structural analysis of **1a** by force field calculations, see: Lee, O. S.; Lee, Y. H.; Osawa, E. *Bull. Korean Chem. Soc.* **1992**, *13*, 155−157.

(37) The deformation angles given in Figure 5 are dihedral angles. The real pyramidalization angles are slightly smaller.

(38) Haddon, R. C. *Acc. Chem. Res.* **1988**, *21*, 243−249.

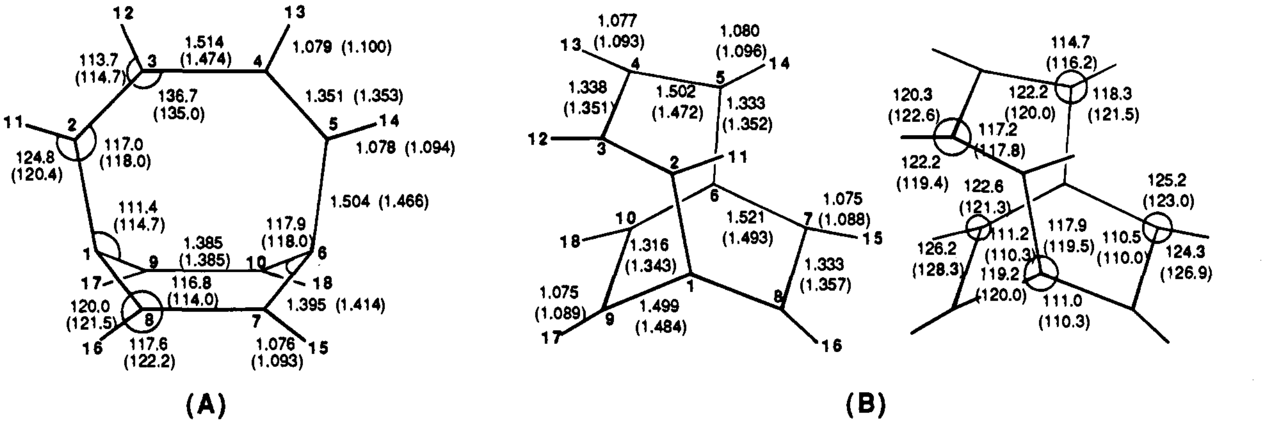


Figure 3. Theoretical molecular structures of **1a** (A) and **2a** (B) based on the SCF method employing the 6-31G* basis set. The semiempirical PM3 structures are given in parentheses.

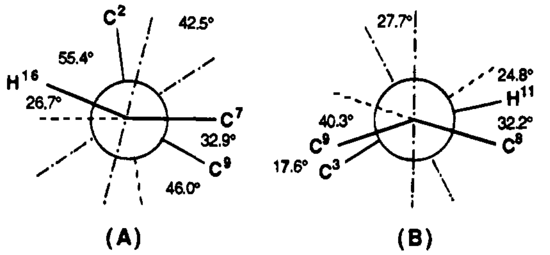


Figure 4. Twisting and out-of-plane bending (pyramidalization) at strained unsaturated carbons. Views (A) along the C^8–C^1 bond of **1a** and (B) along the C^1–C^2 bond of **2a** (6-31G* optimized).

Table 3. Total Energies of **1a** and **2a** As Obtained from ab Initio Calculations at Various Levels

computational level	total energy, au: 1a	total energy, au: 2a	energy difference, kcal/mol ($\Delta E = E$(**1a**) − E(**2a**))
3-21G	−380.980 11	−380.999 52	12.2
6-31G*//3-21G	−383.115 68	−383.129 28	8.5
6-31G*	−383.115 92	−383.130 00	8.8
MP2/6-31G*//3-21G[a]	−384.414 37	−384.406 90	−4.7
MP2/6-31G*//6-31G*[a]	−384.415 39	−384.408 29	−4.5

[a] The carbon 1s MOs were frozen in the MP2 calculations.

Table 4. Heats of Formation of **1a** and **2a** Calculated by Semiempirical Methods

method	ΔH_f, kcal/mol: 1a	ΔH_f, kcal/mol: 2a	energy difference, kcal/mol ($\Delta\Delta H_f = \Delta H_f$(**1a**) − ΔH_f(**2a**))
MNDO	150.1	144.7	5.4
AM1	155.4	149.0	6.4
PM3	151.6	141.8	9.8

into bicyclo[4.2.2]decapentaenes which possess the structure of [4]paracyclophane-1,3-diene **1** rather than that of its π-bond shift isomer 1,6-ethenocycloocta-1,3,5,7-tetraene **2**, as demonstrated by chemical trapping experiments and UV/vis spectroscopy at low temperature. Theoretical calculations reveal an extremely bent benzene ring for **1a**. The semiempirical methods as well as the ab initio calculations at the SCF level probably erroneously predict that **1a** is less stable by 5.5−12.2 kcal/mol than **2a**. By taking electron correlation energy into account at the MP2 level, **1a** is predicted to lie 4.5−4.7 kcal/mol below **2a** in accord with the experimental observations. The predicted small energy difference between **1a** and **2a** suggests that the structural preference may be electronically and/or sterically shifted to **2a** by the introduction of suitable substituents.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on JEOL FX-100 and FX-500 spectrometers in $CDCl_3$ unless otherwise indicated in the High-Resolution NMR Laboratory of Hokkaido University. IR spectra were taken on a Hitachi Model 215 grating spectrometer. Mass spectra were recorded on JEOL JMS-HX 110 and JMS-DX 303 spectrometers at an ionizing voltage of 70 eV unless otherwise indicated. UV/vis spectra were taken on a Hitachi U-4000 spectrophotometer. Elemental analyses were performed by the Center for Instrumental Analysis of Hokkaido University. Halos (Eiko-sha, Japan) 500 W high-pressure and 120 W low-pressure mercury lamps were employed as the light sources of photochemistry. A 500 W xenon lamp fitted with a Corning glass filter 3-72 was used as the >430 nm light source. 3,6-Dihydrophthalic anhydride,[12] tetrahydrocinnamic acid,[39] diphenylphosphoryl azide,[18] and *p*-toluenesulfonyl azide[40] were prepared following the known procedures. Other reagents and solvents were obtained from commercial sources and purified prior to use.

Cyclization of 22 into 4,7-Dihydroindanone (24). To 140 mL of 0.5 N aqueous NaOH was added 10.5 g of **22** (containing ca. 5% dihydrocinnamic acid, 67 mmol), and the resulting solution was evaporated in vacuo to give a colorless solid, which was dried at 120 °C (0.1 mmHg) for 2 h. The dried salt mixture was mixed with 380 mL of benzene, treated with 38 mL of oxalyl chloride (50 g, 0.40 mol) for 1 h at ambient temperature under argon, and then concentrated in vacuo to afford a mixture of acid chlorides, which was dissolved in 70 mL of 1,2-dichloroethane and cooled to 0 °C under argon. To the stirred solution was slowly added 12.8 mL of $SnCl_4$ (28.4 g, 0.109 mol). After 30 min at 0 °C, the resultant mixture was diluted with 1 L of ether, washed with 5% $NaHCO_3$ (5 × 100 mL) and brine (500 mL), dried with Na_2SO_4, filtered, and concentrated in vacuo to afford 10.0 g of crude product from which 7.70 g of colorless crystalline **24** (86%, 57 mmol) was isolated by chromatography on silica gel (20% AcOEt in hexane). The product was identical in all respects with **24** which was independently prepared by the known procedure.[17]

Conversion of 24 into Propelladienone 26. A solution of **24** (18.5 g, 0.138 mol) in 820 mL of 1,2-dichloroethylene was irradiated through Pyrex with a 450 W high-pressure mercury lamp under argon until **24** was largely consumed (26 h). After recovering excess dichloroethylene by distillation, the residue was dissolved in 500 mL of ether, washed with saturated $NaHCO_3$ (3 × 150 mL) and brine (150 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo to deliver 31.3 g of a crude mixture of three stereoisomers of **25**. The mixture was dissolved in 320 mL of dry methanol, cooled to 0 °C, and treated with $NaBH_4$ (10.3 g, 0.272 mol). After being stirred for 16 h at room temperature, the resulting mixture was concentrated in vacuo and the residue was dissolved in 600 mL of ether, washed successively with 150 mL portions of saturated NH_4Cl, $NaHCO_3$, and NaCl, dried with $MgSO_4$, filtered, and concentrated to give 28.3 g of oil.

In 1.2 L of liquid ammonia was dissolved 20.8 g of sodium (0.906 mol) in small portions at −78 °C. The above oily product was diluted with 200 mL of dry ether and added to the resulting deep blue solution. After stirring the mixture for 3.5 h, 48 g of solid NH_4Cl (0.90 mol)

---

(39) Snider, B. B.; Kirk, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2364−2368.

(40) Regitz, M.; Hocker, J.; Liedhegener, A. In *Organic Syntheses*; J. Wiley & Sons: New York, 1973; Collect. Vol. V, p 179.

was added in small portions to destroy excess sodium, and upon discharge of the blue color, the resultant suspension was evaporated to dryness. To the residue were added 500 mL portions of ether and water. The aqueous layer was separated from the ethereal layer and extracted with ether (3 × 200 mL). The extracts were combined with the ethereal layer, washed successively with 300 mL portions of saturated NH_4Cl, $NaHCO_3$, and NaCl, dried with $MgSO_4$, filtered, and concentrated in vacuo to provide 17.8 g of a mixture of [4.2.2]propelladienols, which was subjected to Swern oxidation without further purification.

To a stirred solution of oxalyl chloride (28.1 g, 0.221 mol) in dry CH_2Cl_2 (880 mL) were added DMSO (51.6 g, 0.661 mol) in CH_2Cl_2 (520 mL) and, after 30 min at −78 °C under argon, the crude propelladienols (17.8 g) in CH_2Cl_2 (180 mL). The reaction mixture was stirred for 2.5 h, treated with Et_3N (167 g, 1.65 mol), stirred for a further 20 min at −78 °C, and allowed to warm to room temperature. The resulting mixture was washed successively with 300 mL portions of water, dilute HCl (×5), saturated $NaHCO_3$, and brine, dried with $MgSO_4$, filtered, and concentrated in vacuo. The residual oil was subjected to Kugelrohr distillation to afford 12.7 g of **26** (bp 100 °C (17 mmHg), 58% from **24** in four steps). This procedure is essentially the same as that previously reported,[41] but is simplified and provides **26** in a somewhat improved yield.

Preparation of Diazoketone 28 from 26. To CH_3ONa which was prepared from 4.76 g of sodium (0.207 mol) and dried at 130 °C (0.1 mmHg) for 2 h were added 127 mL of dry benzene and 15.3 g of ethyl formate (0.207 mol). To the resulting suspension was slowly added a solution of 12.7 g of **26** (79 mmol) in 127 mL of benzene, and stirring was maintained for 18.5 h at 12 °C before the reaction was quenched with 100 mL of water. The reaction mixture was washed with ether (2 × 80 mL), and the washings were combined and extracted with water (4 × 25 mL). The washed reaction mixture was combined with the aqueous extracts, acidified with 26 mL of concentrated HCl, and extracted with ether (4 × 300 mL). The extracts were combined, dried with $MgSO_4$, filtered, and concentrated in vacuo to produce 12.5 g of oily **27**. The crude **27** (12.5 g) and 13.8 g of TsN_3 (70 mmol) were dissolved in 1.1 L of CH_2Cl_2 and treated with 13.9 g of Et_3N (0.138 mol) at 0 °C. After being stirred for 24 h at 20 °C, the reaction mixture was cooled to 0 °C, treated with 540 mL of 7% KOH, and allowed to separate into layers. The organic layer was washed with 300 mL portions of water and brine, dried with Na_2SO_4, filtered, and concentrated in vacuo. The residue was subjected to chromatography on silica gel (20% ether in hexane) to deliver 9.27 g of **28** (63%): ^1H NMR δ 2.17−2.32 (m, 4 H), 2.78 (d, J = 13.5 Hz, 1 H), 3.11 (d, J = 13.5 Hz, 1 H), 5.77−5.83 (m, 2 H), 6.11 (d, J = 2.7 Hz, 1 H), 6.21 (d, J = 2.7 Hz, 1 H); IR (neat) 3036, 2924, 2080, 1664, 1330, 1260, 1216, 876, 770, 662 cm^{-1}.

Photo-Wolff Rearrangement of 28. A solution of 4.60 g of **28** (24.6 mmol) and 1.4 g of Et_3N (14 mmol) in 600 mL of dry methanol was irradiated through Pyrex with a 450 W high-pressure mercury lamp until gas evolution ceased (24 h). After removal of the solvent in vacuo, the residue was dissolved in 500 mL of ether, washed successively with dilute HCl (2 × 150 mL), saturated $NaHCO_3$, and brine, dried with $MgSO_4$, filtered, and concentrated in vacuo. The residual oil was subjected to Kugelrohr distillation (110 °C (15 mmHg)) to give 4.04 g of **29** (86%) as a 5:2 mixture of stereoisomers: ^1H NMR (the major component) δ 2.10−2.28 (m, 6 H), 2.91 (dd, J = 10.5, 6 Hz, 1 H), 3.66 (s, 3 H), 5.83 (br t, J = 2.2 Hz, 2 H), 6.13 (d, J = 2.2 Hz, 1 H), 6.33 (d, J = 2.2 Hz, 1 H); IR (neat) 3028, 1738, 1198, 1174, 1048, 752, 662 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.75; H, 7.43. Found: C, 75.57; H, 7.55.

Preparation of 20 from 29. To a solution of 4.00 g of **29** (21.0 mmol) and 7.0 mL of pyridine in 90 mL of CH_2Cl_2 was added portionwise 7.3 g of pyridinium bromide perbromide (23.1 mmol) at 0 °C. The mixture was stirred for 3.5 h at 0 °C, diluted with 400 mL of CH_2Cl_2, washed successively with 150 mL portions of 5% $Na_2S_2O_3$, water, dilute HCl, water, saturated $NaHCO_3$, and brine, dried with $MgSO_4$, filtered, and concentrated in vacuo. The residual 6.89 g of colorless oil was dissolved in 98 mL of HMPA and added to a mixture of 9.69 g of LiCl (0.23 mol) and 14.7 g of Li_2CO_3 (0.20 mol) which had previously been dried at 150 °C (0.2 mmHg) for 6 h. The resulting suspension was stirred for 17 h at 40 °C, for 20 h at 80 °C, and for 5h at 100 °C. After being cooled to room temperature, the mixture was poured onto ice, diluted with water to 500 mL, and extracted with ether (5 × 250 mL). The ethereal extracts were combined, washed with water (2 × 300 mL), dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was flash-chromatographed on silica gel (5% ether in hexane) to deliver 1.52 g of **20** (39%) as a mixture of stereoisomers. The spectroscopic property of the product was essentially the same as that of **20** prepared from **19**: ^1H NMR (the major component) δ 2.34 (dd, J = 12, 7 Hz, 1 H), 2.46 (dd, J = 12, 10 Hz, 1 H), 3.34 (dd, J = 10, 7 Hz, 1 H), 3.60 (s, 3 H), 5.50−5.80 (m, 4 H), 6.08 (d, J = 2 Hz, 1 H), 6.22 (d, J = 2 Hz, 1 H); IR (CCl_4) 1730, 1435, 1295, 1200, 1170, 865, 695 cm^{-1}; MS m/z 188 (M, 4), 130 (11), 129 (100), 128 (38), 127 (13), 103 (11), 102 (96). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found for the mixture: C, 76.81; H, 6.53.

Hydrolysis of 20 To Give 21. To a solution of 1.52 g of **20** (8.1 mmol) in 20 mL of methanol was added 38 mL of 5% NaOH at 0 °C, and stirring was maintained for 6 h at 12 °C before the reaction was quenched with 200 mL of water. The resulting mixture was washed with ether (2 × 100 mL), acidified with concentrated HCl, and extracted with ether (4 × 100 mL). The ethereal extracts were combined, dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was subjected to Kugelrohr distillation (90 °C (4 × 10^{-3} mmHg)) to afford 1.41 g of **21** (100%). The spectroscopic property of the product was essentially the same as that of **21** obtained from **19**: ^1H NMR δ 2.42 (d, J = 7.5 Hz, 1 H), 2.52 (d, J = 10.5 Hz, 1 H), 3.52 (dd, J = 10.5, 7.5 Hz, 1 H), 5.65−5.75 (m, 4 H), 6.26 (d, J = 3.0 Hz, 1 H), 6.34 (d, J = 3.0 Hz, 1 H); IR (neat) 3028, 1706, 1422, 1294, 1234, 1218, 786, 760, 698 cm^{-1}; FI-MS m/z 175 (M + 1, 15), 174 (M, 100), 129 (7), 102 (7); HRMS for $C_{11}H_{10}O_2$, calcd 174.0680, found 174.0682.

Conversion of 21 into the Carbamate 30. A solution of **21** (450 mg, 2.6 mmol), Et_3N (400 mg, 4.0 mmol), and $(PhO)_2P(O)N_3$ (940 mg, 3.4 mmol) in 20 mL of dry benzene was refluxed for 20 h. GLC analysis of the resulting mixture indicated that **21** was largely converted to the corresponding isocyanate. 2-(Methylthio)ethanol (1.50 mL) was added, and the refluxing was continued for an additional 18 h. The mixture was cooled, diluted with 50 mL of ether, washed successively with water, dilute HCl, and saturated $NaHCO_3$, and dried with $MgSO_4$. After removal of the solvent, the residue was chromatograghed on Florisil (benzene, CH_2Cl_2) to give 580 mg of **30** (85%) as a >6:1 mixture of stereoisomers: ^1H NMR (the major component) δ 1.92 (dd, J = 13, 6 Hz, 1 H), 2.12 (s, 3 H), 2.67 (t, J = 7 Hz, 2 H), 2.78 (dd, J = 13, 4 Hz, 1 H), 4.18 (t, J = 7 Hz, 2 H), 4.20−4.45 (m, 1 H), 5.95 (br s, 1 H), 5.60−5.85 (m, 4 H), 6.16 (d, J = 2.5 Hz, 1 H), 6.40 (d, J = 2.5 Hz, 1 H); IR (neat) 3328, 1712, 1520, 1290, 776, 698 cm^{-1}; MS m/z 162 (3.8), 133 (3.6), 132 (14), 104 (13), 75 (100); FAB-MS m/z 264 (M + 1, 12), 219 (11), 154 (79), 136 (53), 102 (70), 75 (100); HRMS for $C_{14}H_{18}O_2NS$ (M + 1), calcd 264.1059, found 264.1059.

When the mixture containing the isocyanate was treated with t-BuOH (large excess)/DBU (1.4 equiv) and worked up as described above, **31** was obtained in 77% yield: ^1H NMR δ 1.42 (s, 9 H), 1.88 (dd, J = 12, 6 Hz, 1 H), 2.80 (dd, J = 12, 10 Hz, 1 H), 4.08−4.60 (m, 1 H), 4.60 (br s, 1 H), 5.50−5.98 (m, 4 H), 6.22 (d, J = 2.4 Hz, 1 H), 6.42 (d, J = 2.4 Hz, 1 H); IR (CCl_4) 3460, 1720, 1500, 1365, 1240, 1165 cm^{-1}. Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.05; H, 7.73; N, 5.80.

Conversion of 30 into Propellatetraene 7a. A mixture of **30** (810 mg, 3.1 mmol), $NaHCO_3$ (300 mg, 3.6 mmol), and Me_2SO_4 (1.33 g, 10.6 mmol) in 15 mL of MeOH was stirred at 35 °C for 40 h and then treated with NaOH (2.0 g, 50 mmol) in 30 mL of 50% MeOH. This mixture was stirred at 35−40 °C for 2 h, cooled in an ice bath, acidified with 4.5 mL of concentrated HCl, evaporated in vacuo, and washed with ether (2 × 5 mL) to remove nonbasic components including a trace amount of unreacted **30**. To the aqueous solution was added NaOH (15 g), and the liberated **32** was extracted with ether (4 × 50 mL). The combined extracts were dried with KOH and evaporated to give 330 mg of crude **32**, from which analytically pure sample was isolated by preparative GLC: ^1H NMR δ 1.53 (br s, 2 H), 1.86 (dd, J = 12, 5 Hz, 1 H), 2.76 (dd, J = 12, 9 Hz, 1 H), 3.69 (dd, J = 9, 5 Hz, 1 H), 5.62−5.73 (m, 3 H), 5.76−5.86 (m, 1 H), 6.27 (d, J = 2.5 Hz, 1 H), 6.48 (d, J = 2.5 Hz, 1 H); MS m/z 145 (M, 1.2), 144 (11), 130

---

[41] Ohkita, M.; Tsuji, T.; Suzuki, M.; Murakami, M.; Nishida, S. *J. Org. Chem.* **1990**, *55*, 1506−1513.

(2.2), 103 (3.2), 102 (100), 76 (2.0); HRMS for $C_{10}H_{11}N$, calcd 145.0892, found 145.0910.

A mixture of the crude **32** obtained above, MeI (1 mL, 16 mmol), and $NaHCO_3$ (0.6 g, 7 mmol) in 25 mL of MeOH was heated at 65 °C for 16 h and then evaporated to dryness. The residue was extracted with hot $CHCl_3$ (3 × 20 mL), and the combined extracts were evaporated to give 570 mg of crude ammonium salt **33**. This salt was dissolved in a mixture of 15 mL of DMF and 40 mL of pentane, and treated with 4.5, 4.5, and 2 mL of *t*-BuOK (0.80 M in DMF) after 0, 2, and 4.5 h at room temperature, respectively. After being stirred for 6 h, the mixture was poured into 100 mL of water, and the product was extracted with pentane (3 × 50 mL). The combined extracts were washed successively with water, dilute HCl, and saturated $NaHCO_3$, and dried with $MgSO_4$. The pentane was evaporated through a 10 cm Vigreux column to give ca. 2 mL of a concentrated solution of **7a** (220 mg by GLC, 55% from **30**), from which analytically pure **7a** was isolated by preparative GLC: mp 32–32.5 °C; ^{1}H NMR δ 5.52–5.74 and 5.78–6.00 (AA′XX′ m, 4 H), 6.43 (s, 4 H); ^{13}C NMR δ 56.1, 120.8, 124.2, 142.8; IR (CCl_4) 3100, 3040, 1378, 1265, 1195, 725, 672 cm^{-1}; UV (EtOH) λ_{max} 271 (ϵ 1900), 279 (2000), 289 (sh, 1600) nm; MS *m/z* 128 (M, 100), 127 (25), 102 (43), 76 (12), 51 (15). Anal. Calcd for $C_{10}H_8$: C, 93.71; H, 6.29. Found: C, 93.49; H, 6.31.

Preparation of Methyl [4.2.2]Propella-2,4,7,9-tetraene-7-carboxylate (7b) from 20. A solution of *i*-Pr_2NH (230 mg, 2.28 mmol) in 3 mL of THF was treated with 0.96 mL of BuLi (2.32 M in hexane, 2.23 mmol) at 0 °C to afford a LDA solution, to which **20** (350 mg, 1.86 mmol) in 3 mL of THF was added at −78 °C. After 20 min at −78 °C, a solution of $(PhSe)_2$ (720 mg, 2.31 mmol) in 3 mL of THF and 0.42 mL of HMPA was added. The resulting mixture was stirred for 20 min at −78 °C and 1 h at −40 °C, quenched with 5 mL of saturated $NaHCO_3$, and diluted with 50 mL of ether. The organic layer was washed with water (3 × 10 mL), dried with $MgSO_4$, filtered, and concentrated to give the crude product mixture, which was chromatographed on Florisil (hexane, hexane/benzene (1:1)) to give 0.515 g of **34** (81%) as a ~8:1 mixture of stereoisomers: ^{1}H NMR (the major component) δ 2.18 (d, *J* = 14 Hz, 1 H), 3.14 (d, *J* = 14 Hz, 1 H), 3.40 (s, 3 H), 5.45–5.70 (m, 4 H), 6.18 (d, *J* = 2 Hz, 1 H), 6.30 (d, *J* = 2 Hz, 1 H), 7.10–7.45 (m, 5H).

To a solution of **34** (515 mg, 1.50 mmol) in 10 mL of CH_2Cl_2 and 0.3 mL of pyridine was added 3 mL of 15% aqueous H_2O_2 (13 mmol). After being stirred for 0.5 h at 0 °C, the mixture was diluted with 25 mL of ether and washed successively with 10 mL portions of saturated $NaHCO_3$, water, 10% $Na_2S_2O_3$, water, and brine. To the ethereal solution were added 1 mL of pyridine and 2 g of $MgSO_4$. This mixture was refluxed for 40 min, cooled, washed successively with 10 mL portions of saturated $NaHCO_3$, water, dilute HCl, water, saturated $NaHCO_3$, and water, and dried with $MgSO_4$. After removal of the solvent, the residue was chromatographed on Florisil (hexane, benzene) and distilled (85–95 °C (bath temperature) (2 mmHg)) to give 194 mg of **7b** (69%): ^{1}H NMR δ 3.69 (s, 3 H), 5.48–6.02 (m, 4 H), 6.32 (d, *J* = 2 Hz, 1 H), 6.49 (d, *J* = 2 Hz, 1 H), 6.91 (s, 1 H); ^{13}C NMR 51.40, 53.09, 54.97, 121.58, 122.35, 122.48, 123.72, 142.17, 142.95, 145.75, 150.69, 162.19; IR (CCl_4) 1720, 1305, 1240, 1185, 1050, 685 cm^{-1}; UV (EtOH) λ_{max} 212 (ϵ 6640), 264 (sh, 2250), 274 (sh, 2040) nm; MS *m/z* 186 (M, 45), 155 (66), 128 (43), 127 (100), 102 (60). Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.32; H, 5.55.

Photolysis of 7a in 1% CF_3CO_2H/MeOH. A solution of **7a** (15 mg, 0.12 mmol) in 10 mL of 1% CF_3CO_2H/MeOH was placed in a Pyrex test tube, purged with Ar, irradiated at 12 °C with a high-pressure mercury lamp until 84% of **7a** was consumed, and poured into a mixture of 25 mL of hexane and 2 mL of saturated K_2CO_3. The organic layer was washed with water (2 × 10 mL) and dried with K_2CO_3. After removal of the solvent, the residue was subjected to preparative GLC to give 8.4 mg of **38** (45%; 58% by GLC) together with ca. 1 mg of naphthalene (12% by GLC). The GLC yields of **38** and naphthalene at the 68% conversion of **7a** were 64% and 12%, respectively. The former underwent slow secondary photolysis, and the yield dropped to 50% at the 93% conversion of **7a**. When CF_3CO_2H was not added, the yields of both the products were much lower. Data for **38**: ^{1}H NMR (C_6D_6) δ 2.95 (dt, *J* = 8, 6 Hz, 1 H), 3.07 (s, 3 H), 3.51 (td, *J* = 6, 1.5 Hz, 1 H), 4.89 (d, *J* = 8 Hz, 1 H), 5.57 (dd, *J* = 9, 6 Hz, 1 H), 5.62 (dd, *J* = 9, 6 Hz, 1 H), 5.75 (dd, *J* = 11, 8 Hz, 1 H), 5.78 (d, *J* = 8 Hz, 1 H); ^{13}C NMR δ 34.29, 41.05, 54.82, 95.07, 118.80, 121.75, 122.31, 126.84, 129.88; MS *m/z* 160 (M, 80), 159 (100), 145 (44), 144 (53), 129 (83), 128 (25), 117 (23); HRMS for $C_{11}H_{12}O$, calcd 160.0888, found 160.0883.

Photolysis of 7a in the Presence of Cyclopentadiene. A solution of **7a** (38 mg, 0.30 mmol) and freshly distilled cyclopentadiene (1.5 mL, 18 mmol) in 25 mL of hexane was irradiated through Pyrex under N_2. When 93% of **7a** was consumed, the irradiation was discontinued and the resulting mixture was filtered to remove the light brown precipitate. The filtrate was concentrated in vacuo and subjected to preparative GLC to give 40 mg of crystalline product which was found by ^{1}H NMR to consist of two isomeric 2:1 adducts of cyclopentadiene and **7a** in a ratio of ca. 1:2 (56%). The repeated crystallization of the mixture from MeOH afforded 12 mg of **39**. The residual product mixture was repeatedly chromatographed on a Lichroprep RP-8 column (90% MeOH) to give an additional 13 mg of **39** (32% in total, 41% by GLC) and 12 mg of **40** (16%, 22% by GLC). These were further purified by preparative GLC. Data for **39**: ^{1}H NMR δ 1.26 (dm, *J* = 8 Hz, 1 H), 1.49 (dt, *J* = 8, 2 Hz, 1 H), 1.51–1.55 (m, 2 H), 2.23 (br s, 1 H), 2.45 (dd, *J* = 14, 2 Hz, 1 H), 2.65 (br s, 1 H), 2.72 (br s, 1 H), 2.86 (br s, 1 H), 3.06 (dd, *J* = 14, 3 Hz, 1 H), 5.24 (d, *J* = 10 Hz, 1 H), 5.38 (d, *J* = 10 Hz, 1 H), 5.54–5.59 (m, 2 H), 5.60–5.66 (m, 1 H), 5.87–5.92 (m, 1 H), 5.90–5.96 (m, 2 H), 6.23 (dd, *J* = 6, 3 Hz, 1 H), 6.57 (dd, *J* = 6, 3 Hz, 1 H); ^{13}C NMR δ 44.05, 45.31, 47.83, 48.32, 49.87, 50.90, 52.56, 54.50, 56.31, 123.24, 123.62 (2 C), 123.76, 130.52, 133.62, 138.21, 143.07, 143.89, 145.50; IR (KBr) 3056, 3004, 2948, 2868, 798, 762, 740, 688, 648, 638 cm^{-1}; UV (hexane) λ_{max} 269 (ϵ 4100), 277 (sh, 3800) nm; MS *m/z* 260 (M, 4), 194 (62), 193 (59), 179 (69), 178 (55), 165 (43), 129 (54), 128 (100), 115 (38); HRMS for $C_{20}H_{20}$, calcd 260.1564, found 260.1552. In the ^{13}C NMR spectrum, only nine aliphatic carbon signals were observed. Presumably one of the quaternary carbon signals would accidentally overlap with one of the nine lines. Data for **40**: ^{1}H NMR δ 1.35 (d, *J* = 8 Hz, 2 H), 1.66 (d, *J* = 8 Hz, 2 H), 2.49 (br s, 2 H), 2.50 (s, 2 H), 2.72 (br s, 2 H), 5.45–5.51 (AA′ part of AA′XX′ m, 2 H), 5.56 (s, 2 H), 5.60–5.65 (XX′ part of the AA′XX′ m, 2 H), 5.99 (dd, *J* = 6, 3 Hz, 2 H), 6.55 (dd, *J* = 6, 3 Hz, 2 H); ^{13}C NMR δ 43.93, 44.90, 47.97, 52.01, 54.46, 123.47, 125.69, 130.75, 143.01, 144.82; IR (KBr) 3052, 1324, 792, 762, 744, 728, 688, 658, 636 cm^{-1}; UV (hexane) λ_{max} 271 (ϵ 3900), 278 (sh, 3600) nm; MS *m/z* 260 (M, 7), 194 (73), 193 (100), 179 (86), 178 (66), 165 (480, 129 (32), 128 (83), 115 (37); HRMS for $C_{20}H_{20}$, calcd 260.1564, found 260.1572.

Photolysis of 7b in the Presence of Cyclopentadiene. A solution of **7b** (100 mg, 0.54 mmol) and freshly distilled cyclopentadiene (3 mL, 36 mmol) in 30 mL of hexane was irradiated through Pyrex under N_2 at 12 °C. When 94% of **7b** was consumed, the irradiation was discontinued and the mixture was filtered to remove the brown precipitate. The filtrate was concentrated in vacuo and repeatedly chromatographed on a Lobar A column (1% ether/hexane) to give four fractions containing **41**/**42** (or **43**), **43** (or **42**), **44**, and **45**/**46**. The mixtures of **41**/**42** (or **43**) and **45**/**46** were further chromatographed on a Lobar A RP-8 column (1:6 water/MeOH) to separate the components from each other. The isolated adducts were further purified by preparative GLC to give 10 mg of **41** (6%), 15 mg of **42** (or **43**, 9%), 10 mg of **43** (or **42**, 6%), 3 mg of **44** (2%), and 6 mg of **45**/**46** (4%). The preparative GLC of **45** and **46** at 200 °C brought about their interconversion to afford the partially equilibrated mixtures. The GLC yield of the adducts was 37% in total. Data for **41**: ^{1}H NMR δ 1.38 (dd, *J* = 8, 2 Hz, 1 H), 1.40 (dd, *J* = 8, 2 Hz, 1 H), 1.46 (d, *J* = 8 Hz, 1 H), 1.55 (d, *J* = 8 Hz, 1 H), 2.54 (d, *J* = 14 Hz, 1 H), 2.55 (br s, 2 H), 2.67 (dd, *J* = 14, 2 Hz, 1 H), 2.82 (br s, 1 H), 3.59 (br s, 1 H), 3.76 (s, 3 H), 5.45 (dd, *J* = 12, 8 Hz, 1 H), 5.50 (dd, *J* = 12, 8 Hz, 1 H), 5.58 (d, *J* = 12 Hz, 1 H), 5.83 (d, *J* = 12 Hz, 1 H), 6.00 (dd, *J* = 5, 3 Hz, 1 H), 6.07 (dd, *J* = 5, 3 Hz, 1 H), 6.59 (dd, *J* = 5, 3 Hz, 1 H), 6.60 (s, 1 H), 6.62 (dd, *J* = 5, 3 Hz, 1 H); IR (KBr) 2964, 1716, 1242, 1222, 1098, 794, 750, 712 cm^{-1}; UV (hexane) λ_{max} 207 (sh, ϵ 14 000), 273 (3000), 279 (sh, 2800) nm; MS *m/z* 318 (M, 12), 193 (100), 192 (36), 191 (41), 186 (47), 179 (46), 178 (52), 165 (37), 115 (32); HRMS for $C_{22}H_{22}O_2$, calcd 318.1620, found 318.1590. Data for **42** or **43** (the major product): ^{1}H NMR δ 1.29 (dd, *J* = 8, 2 Hz, 1 H), 1.37 (d, *J* = 8 Hz, 1 H), 1.51 (dt, *J* = 8, 1 Hz, 1 H), 1.53 (d, *J* = 8 Hz, 1 H), 2.30

(br s, 1 H), 2.65 (dd, $J = 13, 2$ Hz, 1 H), 2.79 (br s, 1 H), 2.90 (br s, 1 H), 3.15 (dd, $J = 13, 3$ Hz, 1 H), 3.55 (br s, 1 H), 3.71 (s, 3 H), 5.53 (dd, $J = 12, 8$ Hz, 1 H), 5.57 (dd, $J = 12, 8$ Hz, 1 H), 5.83 (d, $J = 12$ Hz, 1 H), 5.85 (d, $J = 12$ Hz, 1 H), 5.99 (dd, $J = 5, 3$ Hz, 1 H), 6.02 (dd, $J = 5, 3$ Hz, 1 H), 6.31 (dd, $J = 5, 3$ Hz, 1 H), 6.48 (s, 1 H), 6.64 (dd, $J = 5, 3$ Hz, 1 H); ^{13}C NMR δ 45.19, 45.45, 48.06 (2 C), 48.38, 49.19, 47.75, 50.63, 51.33, 54.61, 57.68, 122.82, 124.64, 127.68, 131.19, 134.70, 135.43, 137.89, 141.37, 145.96 (2 C), 167.58; IR (KBr) 2972, 1710, 1240, 1106, 774, 746, 734, 720 cm^{-1}; UV (hexane) λ_{max} 211 (ϵ 15,000), 250 (sh, 4100), 260 (sh, 3200), 272 (3100), 279 (sh, 2800) nm; MS *m/z* 318 (M, 18), 193 (100), 192 (42), 191 (51), 189 (37), 188 (54), 179 (34), 178 (67), 165 (51), 129 (65), 128 (40), 115 (43); HRMS for $C_{22}H_{22}O_2$, calcd 318.1620, found 318.1626. Data for **43** or **42** (the minor product): ^{1}H NMR δ 1.31 (dd, $J = 8, 2$ Hz, 1 H), 1.37 (d, $J = 8$ Hz, 1 H), 1.53 (dt, $J = 9, 1$ Hz, 1 H), 1.55 (d, $J = 8$ Hz, 1 H), 2.29 (br s, 1 H), 2.52 (dd, $J = 14, 2$ Hz, 1 H), 2.76 (br s, 1 H), 2.90 (br s, 1 H), 3.19 (dd, $J = 14, 3$ Hz, 1 H), 3.44 (br s, 1 H), 3.74 (s, 3 H), 5.51−5.59 (m, 4 H), 5.92 (dd, $J = 5, 3$ Hz, 1 H), 5.95 (dd, $J = 5, 3$ Hz, 1 H), 6.07 (dd, $J = 5, 3$ Hz, 1 H), 6.43 (s, 1 H), 6.60 (dd, $J = 5, 3$ Hz, 1 H); IR (KBr) 2960, 1716, 1248, 750, 712 cm^{-1}; UV (hexane) λ_{max} 208 (ϵ 15 000), 272 (3300), 277 (sh, 3200) nm; MS *m/z* 318 (M, 8), 252 (32), 193 (100), 192 (37), 191 (40), 186 (41), 178 (51), 165 (40), 115 (33); HRMS for $C_{22}H_{22}O_2$, calcd 318.1620, found 318.1593. Data for **44**: ^{1}H NMR δ 0.87 (d, $J = 2$ Hz, 1 H), 1.00 (t, $J = 8$ Hz, 1 H), 1.29 (dd, $J = 8, 5$ Hz, 1 H), 1.46 (t, $J = 8$ Hz, 1 H), 1.54−1.59 (m, 2 H), 1.65 (d, $J = 8$ Hz, 1 H), 1.83 (d, $J = 8$ Hz, 1 H), 1.88 (dd, $J = 8, 5$ Hz, 1 H), 2.22 (br s, 1 H), 2.28 (br s, 1 H), 3.12 (br s, 1 H), 3.17 (br s, 1 H), 3.50 (s, 3 H), 5.65 (dd, $J = 11, 5$ Hz, 1 H), 6.00 (dd, $J = 11, 5$ Hz, 1 H), 6.07 (dd, $J = 5, 3$ Hz, 1 H), 6.18 (dd, $J = 5, 3$ Hz, 1 H), 6.22 (dd, $J = 5, 3$ Hz, 1 H), 6.27 (dd, $J = 5, 3$ Hz, 1 H); IR (KBr) 3020, 2965, 1738, 1162, 750, 674 cm^{-1}; MS *m/z* 318 (M, 8), 252 (30), 194 (18), 193 (100), 178 (24), 165 (15), 128 (13); HRMS for $C_{22}H_{22}O_2$, calcd 318.1620, found 318.1631. Data for **45** or **46** (the major product): ^{1}H NMR δ 1.17 (dd, $J = 9, 2$ Hz, 1H), 1.66 (dd, $J = 9, 2$ Hz, 1H), 1.74 (d, $J = 8$ Hz, 1 H), 1.81 (dt, $J = 8, 2$ Hz, 1 H), 2.06 (d, $J = 3$ Hz, 1 H), 2.17 (d, $J = 9$ Hz, 1 H), 2.59 (br s, 1 H), 2.72 (dd, $J = 9, 3$ Hz, 1 H), 2.75 (br s, 1 H), 2.94 (br s, 1 H), 3.37 (br s, 1 H), 3.69 (s, 3 H), 5.61 (dd, $J = 12, 6$ Hz, 1 H), 5.68 (d, $J = 12$ Hz, 1 H), 5.87 (dd, $J = 12, 6$ Hz, 1 H), 6.10 (dd, $J = 12, 4$ Hz, 1 H), 6.12 (dd, $J = 6, 3$ Hz, 1 H), 6.20 (dd, $J = 6, 3$ Hz, 1 H), 6.23 (dd, $J = 6, 3$ Hz, 1 H), 6.28 (dd, $J = 6, 3$ Hz, 1 H); IR (KBr) 3012, 2960, 1724, 1278, 1212, 1106, 730, 704, 674 cm^{-1}; UV (hexane) λ_{max} 262 (ϵ 3300) nm; MS *m/z* 318 (M, 7), 193 (100), 192 (29), 191 (32), 178 (49), 165 (31), 115 (25); HRMS for $C_{22}H_{22}O_2$, calcd 318.1620, found 318.1624. Data for **45** or **46** (the minor product): ^{1}H NMR δ 1.42 (d, $J = 8$ Hz, 1 H), 1.49 (dd, $J = 8, 2$ Hz, 1 H), 1.51 (dd, $J = 8, 2$ Hz, 1 H), 1.91 (dd, $J = 10, 2$ Hz, 1 H), 2.06 (d, $J = 4$ Hz, 1 H), 2.29 (dd, $J = 10, 4$ Hz, 1 H), 2.45 (d, $J = 8$ Hz, 1 H), 2.60 (br s, 1 H), 2.84 (br s, 1 H), 2.91 (br s, 1 H), 3.34 (br s, 1 H), 3.69 (s, 3 H), 5.70 (dd, $J = 12, 6$ Hz, 1 H), 5.82 (ddd, $J = 12, 6, 2$ Hz, 1 H), 5.90 (dd, $J = 6, 3$ Hz, 1 H), 5.94 (dd, $J = 12, 4$ Hz, 1 H), 5.98 (d, $J = 12$ Hz, 1 H), 6.13 (dd, $J = 6, 32$ Hz, 1 H), 6.22 (dd, $J = 6, 3$ Hz, 1 H), 6.38 (dd, $J = 6, 3$ Hz, 1 H).

Photolysis of 7a in the Presence of Equimolar Amounts of Cyclopentadiene and Isoprene. A solution of **7a** (2 mg, 15×10^{-3} mmol), octadecane (2 mg, as an internal standard), and cyclopentadiene (200 μL, 2.4 mmol) in 2 mL of hexane was nearly equally distributed between two Pyrex test tubes (A and B), which were sealed with rubber septa and filled with N_2. To tube B was added 120 μL of isoprene (1.2 mmol). Both the solutions were irradiated until ca. 90% of **7a** was consumed. The GLC yields of the cyclopentadiene adducts **39** and **40** in tubes A and B were 44% and 39% total, respectively. The GLC analysis of the photolysate in tube B showed that no isoprene adduct was produced in a detectable yield.

Acknowledgment. T.T. would like especially to thank Dr. Hiroshi Takeuchi for his help in performing the ab initio theoretical calculations at the Computer Center of the Institute for Molecular Science, Okazaki National Research Institutes, using the HITAC M-680H and S-820/80 and NEC SX-3/34R and HSP computers. This research was supported in part by a Grant-in-Aid for Scientific Research (04453018) from the Ministry of Education, Science, and Culture of Japan.

Supporting Information Available: Text describing the experimental procedure for the preparation of compounds **9−21** from **8** and spectral data for **9−21** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA9517532