Synthesis and Photochemical Reaction of [4.3.2]Propella-2,4,8,10-tetraen-7-one

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[4.3.2]Propella-2,4,8,10-tetraen-7-one (1) is synthesized from dihydroindanone in four steps in an overall yield of 10%. The electronic absorption spectrum of 1 suggests weak interactions among its π bonds, possibly longicyclic in mode. Direct photolysis of 1 leads to the formation of tricyclo[4.3.2.0^{1,4}]undeca-2,4,8,10-tetraen-7-one (18) and 6,7-benzobicyclo[3.2.0]hepta-3,6-dien-2-one (23) in aprotic solvents, presumably from its singlet excited state. The former product reverts to 1 upon irradiation. In methanol the interconversion between 1 and 18 is partially quenched and a labile methanol adduct, methyl 2-tricyclo[5.2.0.0^{1,3}]nona-4,6,8-trieneacetate (21), is produced from both 1 and 18. The transformation of 1 into 21 proceeds stereospecifically to give *endo*-21 at low temperature, which equilibrates with *exo*-21 at room temperature, presumably via a cyclobutadiene intermediate, methyl 6-bicyclo[5.2.0]nona-1(7),2,4,8-tetraeneacetate (22) ($15 < \Delta G^{\ddagger} < 22$ kcal/mol). The compound 21 undergoes only polymerization possibly via 22 in solution at ambient temperature but rearranges to methyl 1-indeneacetate (25) under GLC conditions above 150 °C.

Because of the specific manner in which three-ring systems are conjoined, propellanes are quite unique among polycyclic compounds. The informative conformational, reactivity, and electronic properties of this class of compounds have stimulated extensive studies.[1,2] Polyunsaturated propellanes are particularly interesting as has been demonstrated in a variety of studies,[1,2] since they provide opportunities to investigate interactions among π bonds in specific nonplanar arrangements. Moreover, their central σ bonds frequently participate in chemical transformation. The preparation of a fully unsaturated propellane, [4.4.2]propella-2,4,7,9,11-pentaene (3), was accomplished by Paquette and co-workers two decades ago.[3] Subsequent extensive study on 3 and the related compounds in their laboratory has proved highly fruitful.[4] The synthesis of a higher homologue of 3, [4.4.4]propella-2,4,7,9,11,13-hexaene (4), was also recently achieved

1

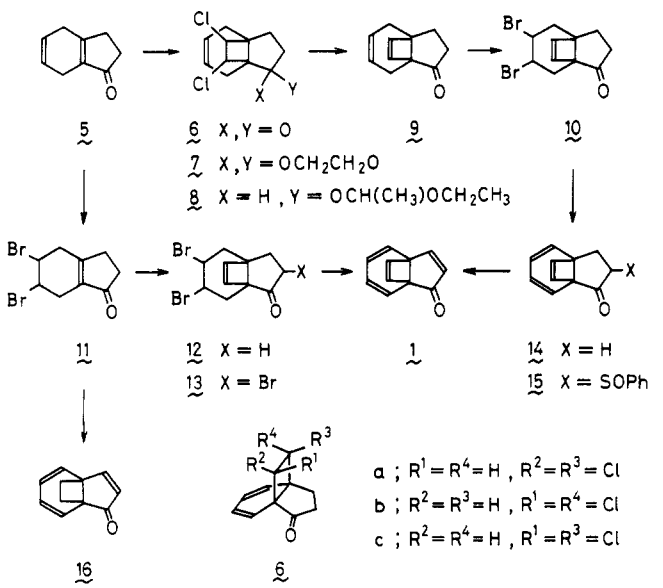
2

3

4

by Paquette and Waykole.[5] We have also been interested in learning of the chemistry of propellanes containing

Scheme I



unsaturated small rings and synthesized [4.2.2]propella-2,4,7,9-tetraene (2) and the substituted derivatives.[6] They were found to undergo interesting chemical transformations including thermal automerization via a cyclobutadiene intermediate[7] and photochemical rearrangement into extremely strained [4]paracyclopha-1,3-dienes.[8] In connection with the chemical behavior of 2, we have been drawn to investigate the chemistry of isoelectronic [4.3.2]propella-2,4,8,10-tetraen-7-one (1). In addition, 1 provides a chance to study photochemical behavior of polyunsaturated propellanones which has been relatively little explored so far. Herein we report the synthesis of 1 and give a detailed account of its photochemical behavior.

Results and Discussion

Preparation of 1 and the Related Compounds. The preparation of 1 was carried out by two different routes

(1) Ginsburg, D. *Acc. Chem. Res.* **1969**, *2*, 121; **1972**, *5*, 249.
(2) (a) Ginsburg, D. *Propellanes*; Verlag Chemie: Weinheim, 1975. (b) Ginsburg, D. *Propellanes, Sequel I*; Department of Chemistry, Technion: Haifa, 1981. (c) Ginsburg, D. *Propellanes, Sequel II*; Department of Chemistry, Technion: Haifa, 1985.
(3) (a) Paquette, L. A.; Philips, J. C. *J. Am. Chem. Soc.* **1969**, *91*, 3973. (b) Paquette, L. A.; Philips, J. C.; Wingard, R. E., Jr. *Ibid.* **1971**, *93*, 4516.
(4) (a) Gleiter, R.; Heilbronner, E.; Paquette, L. A.; Thompson, G. L.; Wingard, R. E., Jr. *Tetrahedron* **1973**, *29*, 565. (b) Paquette, L. A.; Wingard, R. E., Jr.; Photis, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 5801. (c) Paquette, L. A.; Micheli, R. P.; Photis, J. M. *Ibid.* **1977**, *99*, 7911. (d) Paquette, L. A.; Jelich, K.; Ohkata, K. *Tetrahedron Lett.* **1982**, *23*, 2749. (e) Paquette, L. A.; Ohkata, K.; Jelich, K.; Kitching, W. *J. Am. Chem. Soc.* **1983**, *105*, 2800. (f) Paquette, L. A.; Jendralla, H.; DeLucca, G. *Ibid.* **1984**, *106*, 1518. (g) Jendralla, H.; Jelich, K.; DeLucca, G.; Paquette, L. A. *Ibid.* **1986**, *108*, 3731. (h) Paquette, L. A.; Waykole, L.; Jendralla, H.; Cottrell, C. E. *Ibid.* **1986**, *108*, 3739.
(5) Waykole, L.; Paquette, L. A. *J. Am. Chem. Soc.* **1987**, *109*, 3174.
(6) (a) Tsuji, T.; Komiya, Z.; Nishida, S. *Tetrahedron Lett.* **1980**, *21*, 3583. (b) Tsuji, T.; Nishida, S. *Ibid.* **1983**, *24*, 3361. (c) Gleiter, R.; Krennich, G.; Bishop, P.; Tsuji, T.; Nishida, S. *Helv. Chim. Acta* **1986**, *69*, 962.
(7) Tsuji, T.; Nishida, S. *Tetrahedron Lett.* **1983**, *24*, 1269. *Chem. Lett.* **1986**, 1389.
(8) Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1989**, *111*, 368.

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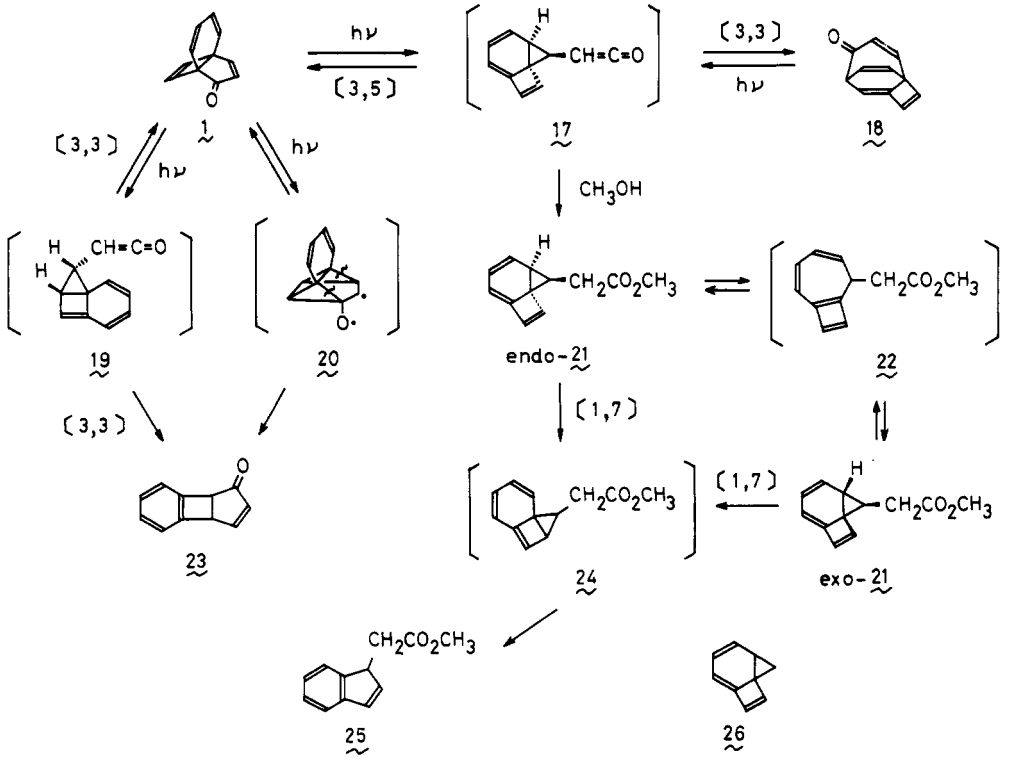
Scheme II



as outlined in Scheme I. The photocycloaddition of *trans*-1,2-dichloroethylene to bicyclo[4.3.0]nona-1(6),3-dien-7-one (**5**)[9] afforded a mixture of three isomeric [2 + 2] adducts, **6a**, **6b**, and **6c**, in a ratio of 66:21:13. The stereochemical assignment for the adducts was based on the magnitude of coupling constants between the cyclobutane ring protons (7.7 Hz in **6a**, 7.3 Hz, in **6b**, and 8.7 Hz in **6c**) and their reactivity toward acetalization. Thus, **6a** was readily acetalized under conventional reaction conditions, whereas both **6b** and **6c** were resistant to acetalization.[10] The diminished reactivity of **6b** and **6c** would result from the steric hindrance to the formation of acetal by one of the chlorine atoms (R^1 = Cl) located in the proximity of the carbonyl group. Reductive dechlorination of **7a** with sodium in liquid ammonia[11] and subsequent hydrolysis of the acetal afforded **9**. Attempts to photochemically add acetylene to **5** to give **9** met with failure, and a tetracyclo[2.2.2.$0^{2,7}$.$0^{3,5}$]octane derivative was obtained instead.[12] The successive bromination and dehydrobromination of **9** provided **14**.[13] The α-sulfenylation of **14** followed by oxidation with MCPBA to the sulfoxide **15** and subsequent treatment with triethyl phosphite in refluxing toluene afforded **1**.[14] This procedure for the preparation of **1**, however, was laborious and, moreover, poor in overall yield. Therefore, an alternative procedure was explored to obtain **1** in a sufficient amount to examine its chemistry.

In the second preparation of **1**, **5** was treated with an equivalent of pyridinium bromide perbromide to give **11** as a thermally unstable oil. With this reagent, the addition of bromine selectively occurred at the peripheral double bond. The photocycloaddition of acetylene to **11** at −60 °C, the treatment of the resultant **12** with isopropylidene dibromomalonate[15] to give **13**, and finally the dehydrobromination of **13** with LiCl/Li_2CO_3 in HMPA[13] afforded **1**. In this preparation, **1** was obtained in four steps from **5** in an overall yield of 10%. Partly saturated **16** was prepared by the photoaddition of ethylene to **11** followed by similar successive transformations. The spectroscopic properties of **1**, **16**, and the intermediate products were fully in accord with their structures.

The thermal stability of **1** was surprisingly high, and its heating in degassed benzene at 200 °C for 3 h resulted in a quantitative recovery. At higher temperatures **1** underwent decomposition, and only unidentified resinous material was produced.

Spectroscopic Property of 1. The electronic absorption spectrum of **1** in which three isolated chromophores are arrayed in a longicyclic topology[16] is worth noting. In Figure 1 are shown the spectra of **1** and the partially hydrogenated derivatives, **14** and **16**. Although the λ_{max} of $\pi \rightarrow \pi^*$ bands do not differ greatly from each other, the descending absorption curves in the spectra of **1** and **16** are shifted to the red by 15–20 nm in comparison with the spectrum of **14**. In addition, the spectrum of **1** shows the red-shift of $n \rightarrow \pi^*$ band by 20 nm in comparison with that of **16**. These red-shifts may arise from interactions among the chomorphores in **1** and **16**, possibly longicyclic in mode[16] in the case of **1**.

Photochemical Behavior of 1. The structure of **1** consists of the three different chromophores, and hence various intra- and interchromophore photochemical transformations are conceivable. The energies of the

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

(10) The conversion of **6b** and **6c** to **9** had to be carried out via their LAH reduction to the corresponding alcohols, the protection of hydroxyl groups with ethyl vinyl ether to give **8**, reductive elimination of chlorines from **8** with sodium in liquid ammonia, and finally the deprotection and subsequent PCC oxidation of the hydroxyl groups.

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

(12) (a) Askani, R. *Chem. Ber.* **1965**, *98*, 3618. (b) Klotzenberg, G.; Fuss, P. G.; Leitch, J. *Tetrahedron Lett.* **1966**, 3409.

(13) King, P. F.; Paquette, L. A. *Synthesis* **1977**, 279.

(14) Trost, B. M.; Salzmann, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887.

(15) Bloch, R. *Synthesis* **1974**, 140.

(16) Goldstein, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1971**, *93*, 6193.

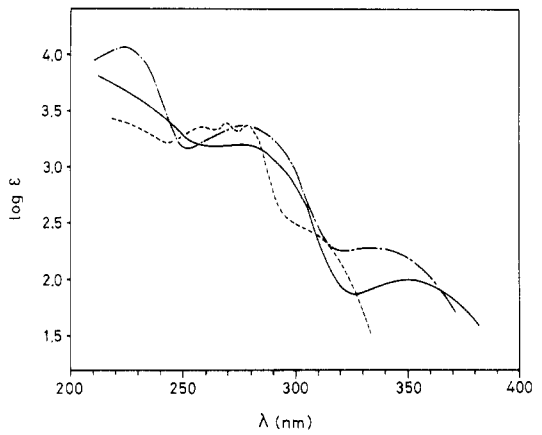


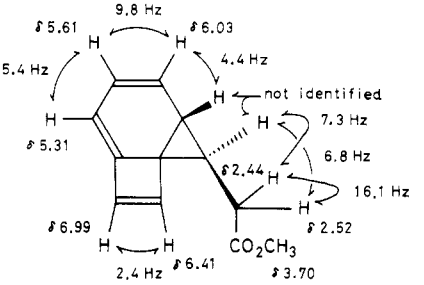
Figure 1. Electronic absorption spectra of 1 (—), 14 (- - -) and 16 (-·-).

lowest excited singlet and triplet states (E_S and E_T, respectively) of cyclohexadiene are 97 and 53 kcal/mol above the ground state,[17] respectively, and the corresponding energies of cyclobutene will be much higher. The E_T of cyclopentenone is 73–74 kcal/mol above the ground state[18,19] and the singlet–triplet splitting is thought to be quite small.[18,20] Therefore, the lowest excited singlet energy of **1** will mainly localize in the cyclopentenone ring, whereas the lowest triplet energy mainly in the cyclohexadiene moiety. In other words, the photoreaction of **1** in the singlet excited state will be dominated by transformation originating in the cyclopentenone moiety while that in the triplet excited state will be characteristic of cyclohexadiene.[21]

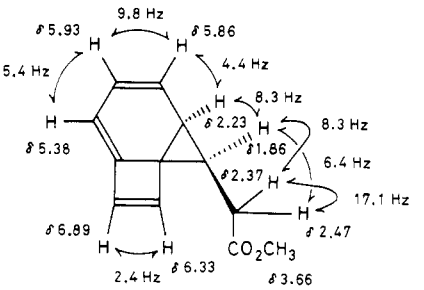
Irradiation of **1** in ether with a high-pressure mercury lamp through Pyrex afforded **18** and **23** in 31% and 26% yields, respectively, at the 46% conversion of **1** (see Scheme II). Since both products were photochemically reactive, prolonged irradiation resulted in their decreased yields and the formation of secondary products. The structural assignment for **18** which was configurationally strained and prone to polymerization was primarily based on its relatively simple ^{1}H NMR spectrum. The structure of **23** was confirmed by an independent synthesis.[22] When the photolysis of **1** was conducted in methanol, the yield of **23** remained virtually unchanged whereas that of **18** decreased to 7%. In addition to **18** and **23**, however, methyl 1-indeneacetate **25** was detected in the photolysate *by GLC*. The photochemical transformation of **1** to **18** is reversible, and irradiation of **18** in CH_2Cl_2 selectively produced **1** in 47% yield. In methanol, the yield of **1** decreased to 11%, and the formation of **25** in 36% yield was again indicated *by GLC*. The compound **23** also underwent secondary photolysis but gave neither **1** nor **18** in either methanol and CH_2Cl_2.

According to the GLC analysis, **25** appeared to be formed from both **1** and **18** in substantial amounts during their photolysis in methanol, but the HPLC analysis revealed that the amount of **25** in the photolysates was actually a mere trace at best, and a thermally labile product was produced instead. This product X decomposed in a dilute methanolic solution at room temperature with a half-life time of 5–20 h, which was dependent on the concentration; at a high concentration X was particularly liable to polymerize. The amount of **25** observed by GLC was found to be proportional to that of X by HPLC and decreased when the sample was allowed to stand at room temperature. Since **25** is thermally quite stable, this observation suggested that **25** was an artifact derived from X under GLC conditions.

Although X is so unstable that its isolation as a pure form has not yet been successfully accomplished, X could be obtained as a mixture with some other products by flash chromatography, and the ^{1}H NMR spectrum was recorded at 500 MHz with no delay. The spectrum of the mixture was recorded again after the sample had stood for several days at room temperature; during this period of time X largely decomposed. The examination of the two well-resolved spectra revealed that X would be a ca. 2:1 mixture of *endo*- and *exo*-**21**. Particularly interesting is the



exo-21

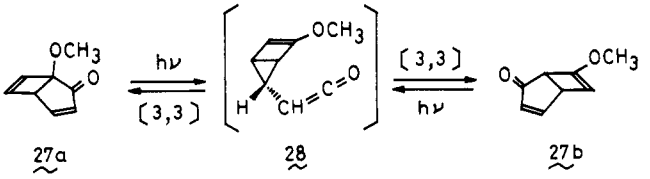


endo-21

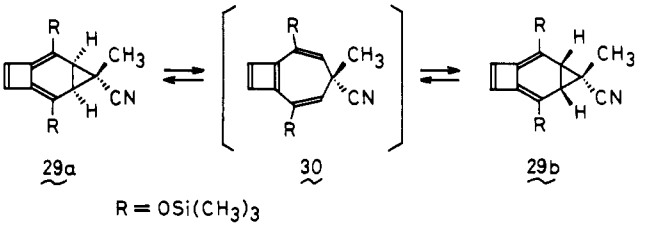
structure of **21** in which the configuration of norcaradiene is constrained by the antiaromaticity of cyclobutadiene. Thus, although norcaradiene itself is thermodynamically less stable than cycloheptatriene, the valence isomerization of **21** to a cycloheptatriene derivative, i.e. **22**, unavoidably generates a cyclobutadiene ring. The preparation of the parent compound **26** as an unisolable, unstable species has very recently been reported.[23] The chemical shifts and coupling constants of the ring protons of *endo*- and *exo*-**21** were in good agreement with those reported for **26**, and, therefore, we concluded that X was a mixture of *endo*- and *exo*-**21**.[24] The rearrangement of **21** to **25** under GLC conditions (>150 °C) was unambiguously demonstrated by injecting a solution of **21** into a gas chromatograph equipped with capillary columns. At room temperature,

(17) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.
(18) (a) Cargill, R. L.; Miller, A. C.; Pond, D. M.; de Mayo, P.; Tchir, M. F.; Neuberger, K. R.; Saltier, J. *Mol. Photochem.* **1969**, *1*, 301. (b) Bunting, J. R.; Filipescu, N. *J. Chem. Soc. B* **1970**, 1750. (c) Cargill, R. L.; Bundy, W. A.; Pond, D. M.; Sears, A. B.; Saltier, J.; Winterle, J. *Mol. Photochem.* **1971**, *3*, 123.
(19) Loutfy, R. O.; de Mayo, P. *J. Chem. Soc., Chem. Commun.* **1970**, 1040.
(20) Smith, A. B., III; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* **1970**, 466.
(21) Schryver, F. C.; Boens, N.; Put, J. *Adv. Photochem.* **1977**, *10*, 359.
(22) Ohkita, M.; Tsuji, T.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1989**, 924.
(23) Kawase, T.; Iyoda, M.; Oda, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 559.
(24) Under various HPLC conditions at ambient temperature was observed X as a single peak. Equilibration between *endo*- and *exo*-**21** (see text) might be fast enough not to allow their separation into two peaks.

Scheme III



Scheme IV



however, **21** underwent only polymerization and did not give **25**.

The photoreaction of **14** was also examined in methanol as well as in aprotic solvents such as acetone and ether. In all cases the only product found in the photolysate was 1-indanone, apparently the result of the loss of acetylene.

The reaction of **1** photosensitized by Michler's ketone in CH_2Cl_2 under nitrogen afforded neither **18** nor **23**, but only polymeric material. Therefore, it may be concluded that the photochemical transformation of **1** to **18** and **23** occurs from the singlet excited state.

Mechanistic Consideration for the Photoreaction of 1. The photochemical rearrangement of **1** may be rationalized in terms of initial [3,5] and [3,3] sigmatropic rearrangements involving the α-cleavage of the cyclopentenone ring in its singlet excited state, which lead to the formation of **17** and **19**, respectively (Scheme II). This type of photochemical transformation to give a cyclopropylketene is fairly common to conjugated-enone-bridged bicyclic compounds[25] and appears to persist in the present propellane system. In an aprotic solvent these ketenes rearrange to **18** and **23** or revert to **1**.[26] In methanol, however, a major fraction of **17** undergoes the addition of a solvent molecule to give **21**. Thus the sigmatropic rearrangements in **17** to give **1** and **18** would be slow enough to allow the interception of **17** by methanol. On the other hand, the fact that **25** was not produced in an appreciable yield as a primary product in methanol suggests that **19** rearranged faster than it reacted with methanol, otherwise **25** would be produced in a substantial yield via subsequent ring enlargement in the resultant ester. In this respect it should be noted that a related ketene **28** has been known to rearrange to **27** so fast that it cannot be intercepted by methanol (Scheme III).[27] The virtual absence of **25** in the product mixture also implies that the rearrangement of **19** to **23** would be faster than the ring enlargement in the former to give 1-indenylketene. For the formation of **23**, an alternative pathway via concurrent or successive oxadi-π-methane and di-π-methane bridging to give **20** followed by ring cleavage may also be conceivable. In cyclic unsaturated systems, however, those bridging processes generally occur from triplet excited states.[25a,b,28] Since the formation of **23** was observed only upon direct irradiation of **1**, the involvement of **20** in the present reaction seems rather unlikely. The present photoreaction of **1** is characteristic of conjugated enone rather than cyclohexadiene, and its occurrence in the singlet excited state of **1** is in accord with the conjecture made in the beginning of the previous section.

The thermal rearrangements postulated above for **17** and **19** require their stereoselective formation in the endo forms. In the analogous photoisomerization of polyunsaturated bicyclic ketones, the endo-selective formation of cyclopropylketenes has, in fact, commonly been observed.[25,29] The ^1H NMR spectrum of **21**, however, showed that the ester was a ca. 2:1 mixture of the endo and exo isomers. An interesting possibility for the formation of an epimeric mixture of **21** is that the initially produced *endo*-**21** might be equilibrated with the endo isomer via reversible valence isomerization to the cyclobutadiene intermediate **22**. To examine this possibility, **1** was irradiated at −80 °C in CD_3OD, and the resultant photolysate was analyzed by ^1H NMR spectroscopy at the same temperature, which cleanly demonstrated the formation of **21** almost exclusively in the endo form. After 2 h at room temperature, **21** was already a 1.8:1 mixture of the endo and exo isomers, and the ratio did not change further. Photolysis of **18** at −80 °C in CD_3OD also gave *endo*-**21** with 95% isomeric purity. The epimerization in **21** is possible only by reversible cleavage of one of the cyclopropane bonds, and the only reasonable mechanism seems to be one involving the valence isomerization of **21** to **22**. Since *endo*-**21** was configurationally stable at −80 °C, the activation free energy for the epimerization of **21** to **22** is in a range of $15 < \Delta G^{\ddagger} < 22$ kcal/mol. The values of negative resonance energy for cyclobutadiene calculated or experimentally obtained are divergent and vary between 0 and −35 kcal/mol.[30] Recently Klärner and co-workers, however, estimated the value at −21 kcal/mol on the basis of $\Delta G^{\ddagger} = 26$ kcal/mol for the interconversion between **29a** and **29b** (Scheme IV).[31] Taking into account the higher degree of configurational distortion in **21** than in **29** and the seemingly comparable strain energies of **22** and **30**, therefore, the energy barrier presently estimated for the epimerization in **21** is also consistent with the intermediacy of **22**.

In contrast to the photolysis at ambient temperature, neither the formation of **18** from **1** nor the reversion was observed at −80 °C in CD_3OD. The sigmatropic rearrangements in **17** to give **1** and **18** would presumably require substantial thermal activation and hence would be overshadowed by the competing methanolysis to give *endo*-**21** at a low temperature. These observations also suggest that a direct interconversion between **1** and **18** via acyl [1,3] shifts would not occur to any appreciable degree in the photochemistry of **1** and **18**.

The rearrangement of **21** into **25**, which was observed under GLC conditions above 150 °C but not in a solution

(25) (a) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1. (b) Schuster, D. I. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Essay 17. (c) Uyehara, T.; Ogata, K.; Yamada, J.; Kato, T. *J. Chem. Soc., Chem. Commun.* **1983**, *17* and references cited therein.

(26) The orbital-symmetry-forbidden reversion of **17** to **1** may also be involved. For ready thermal [3,5] rearrangement in a closely related system, see: (a) Battye, P. J.; Jones, D. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1807. (b) Battye, P. J.; Jones, D. W.; Tucker, H. P. *Ibid.* **1988**, 495.

(27) Chapman, O. L.; Lassila, J. D. *J. Am. Chem. Soc.* **1968**, *90*, 2449.

(28) (a) Hixon, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531. (b) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Essay 16.

(29) (a) Chapman, O. L.; Kane, M.; Lassila, J. D.; Loeschen, R. L.; Wright H. E. *J. Am. Chem. Soc.* **1969**, *91*, 6856. (b) Kende, A. S.; Goldschmidt, Z.; Izzo, P. T. *Ibid.* **1969**, *91*, 6858.

(30) (a) Masamune, S.; Bally, T. *Tetrahedron* **1980**, *36*, 343. (b) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 309.

(31) Klärner, F.-G.; Schmidt, E. K. G.; Rahman, M. A. A.; Kollmar, H. *Angew. Chem., Int Ed. Engl.* **1982**, *21*, 139.

at ambient temperature, is of considerable interest. Although substantiating observations have not been made, the reaction seems to be most satisfactorily rationalized in terms of initial [1,7] walk rearrangement to give **24**,[32] which would proceed either concertedly or stepwise via a biradical, and subsequent ring enlargement to give **25**. The suppression of the intermolecular reaction of **21** possibly via **22** owing to the extremely low concentration under GLC conditions and concomitant thermal activation might enable **21** to rearrange to **24**.

Experimental Section

Melting points are uncorrected. Unless otherwise specified, all ^1H and ^{13}C NMR were recorded with a JEOL FX-100 spectrometer in $CDCl_3$ in the High-Resolution NMR Laboratory Hokkaido University; the chemical shifts are given in ppm relative to tetramethylsilane. IR spectra were taken on Hitachi Model 215 and 270-30 grating spectrometers. Mass spectra were recorded on JEOL Model JMS-D300 and DX303 spectrometers at an ionization voltage of 70 eV unless otherwise indicated; ions of each spectrum were normalized to the most intense ion set equal to 100, and the relative intensities are given in parentheses. UV spectra were taken on a Cary Model 17 spectrometer. Elemental analyses were performed by the Center for Instrumental Analysis of Hokkaido University. GLC work was done on Hitachi 063 and 163 gas chromatographs with helium as a carrier gas. Following columns were used: A, 20% polyethylene glycol (PEG) 20M, 1 m; B, 5% PEG 20M, 1 m; C, 10% Silicone SE-30, 1 m; D, PEG 20M capillary column, 30 m; E, Silicone OV-1 capillary column, 50 m. Preparative chromatography was performed on Merck Kieselgel 60 (70–230 mesh). HPLC analysis was conducted on a Hitachi Model 635 liquid chromatograph using a 3.9 mm × 30 cm column packed with μ-Porasil. The light source for photochemistry was a Halos (Eiko-sha, Japan) 450-W high-pressure Hg lamp. Pyridinium chlorochromate (PCC),[33] pyridinium bromide perbromide,[34] isopropylidene dibromomalonate,[15] perbenzoic acid,[35] and bicyclo[4.3.0]nona-1(6),3-dien-7-one[9] were prepared following the known procedures. Other reagents and solvents were obtained from commercial sources and purified prior to use.

Photocycloaddition of *trans*-1,2-Dichloroethylene to 5. A solution of 7.8 g of **5** (58 mmol) in 150 mL of *trans*-1,2-dichloroethylene was placed in a Pyrex vessel, bubbled with argon for 5 min, and irradiated with a high-pressure Hg lamp at ambient temperature. The starting enone was consumed within 6 h to give a mixture of three adducts, **6a–c**, in a ratio of ca. 10:4:3 in an almost quantitative yield. After the recovery of excess dichloroethylene by distillation, a part of the residue was subjected to preparative GLC to isolate the adducts. **6a**: ^1H NMR δ 1.67–2.98 (m, 8 H), 4.24 (d, J = 7.8 Hz, 1 H), 4.34 (d, J = 7.8 Hz, 1 H), 5.70–6.08 (m, 2 H); IR (KBr) 1740, 1650 cm^{-1}; MS m/z 230 (M^+, 1.2), 197 (28), 195 (83), 159 (17), 133 (100). Anal. Calcd for $C_{11}H_{12}OCl_2$: C, 57.17; H, 5.23; Cl, 30.68. Found: C, 56.76; H, 5.33; Cl, 31.04. **6b**: ^1H NMR δ 1.34–3.06 (m, 8 H), 4.28 (d, J = 8.7 Hz, 1 H), 4.55 (d, J = 8.7 Hz, 1 H), 5.79–6.15 (m, 2 H); IR (KBr) 1740, 1640 cm^{-1}. **6c**: ^1H NMR δ 1.67–2.87 (m, 8 H), 4.10 (d, J = 7.3 Hz, 1 H), 4.37 (d, J = 7.3 Hz, 1 H), 5.87–5.97 (m, 2 H); IR (KBr) 1730, 1640 cm^{-1}.

Acetalization of 6. A mixture of 13.9 g of **6** (a mixture of the three isomeric adducts, 61 mmol), 7 g of ethylene glycol (112 mmol), and 0.1 g of toluenesulfonic acid in 300 mL of benzene was heated under reflux, and water which was formed was removed as an azeotrope with benzene through a 30-cm packed column. GLC analysis showed that the acetalization of **6a** was almost complete within 4.5 h, but **6b** and **6c** remained virtually unchanged. The reaction mixture was washed with aqueous Na_2CO_3, dried with K_2CO_3, concentrated, and subjected to chromatography on silica gel eluted with ether/hexane (1:1) to give 5.2 g of **7a** (42% from **5**) and 3.0 g of a mixture of **6b** and **6c** (29% from **5**). The isomers **6b** and **6c** were quite reluctant to undergo acetalization and attempts to acetalize them under a variety of conditions (ethylene glycol/AcOH/BF_3 etherate, ethylene glycol/toluene/TsOH, and $CH(OCH_3)_3$/Amberlist-15) met with failure.

Reductive Elimination of Chlorines from 7a. To 300 mL of liquid ammonia was added 2.1 g of sodium (91 mmol) at ca. −70 °C, and the resultant deep blue solution was stirred for 20 min. A solution of 5.2 g of **7a** (19 mmol) in 50 mL of dry ether was added over a period of 15 min. After 1 h at the above temperature, the excess sodium was destroyed with 4.8 g of NH_4Cl, and the ammonia was evaporated. The residue was dissolved in ether, washed with water, and dried with K_2CO_3. After removal of the solvent, the crude product was hydrolyzed in 30 mL of 60% AcOH at 45 °C for 1 h, and the liberated ketone was extracted with ether. The ethereal extract was washed successively with water, dilute NaOH, and water and dried with $MgSO_4$. The crude product was distilled at 120–135 °C (bath temperature, 20 Torr) to give 2.33 g of **9** (77%): ^1H NMR δ 1.63 (ddd, J = 8, 12, 13 Hz, 1 H), 1.93–2.52 (m, 6 H), 3.02 (ddd, J = 9, 12, 18 Hz, 1 H), 5.63–5.95 (m, 2 H), 6.02 (d, J = 2.7 Hz, 1 H), 6.26 (d, J = 2.7 Hz, 1 H); IR (neat) 1730, 1650 cm^{-1}; MS m/z 160 (M^+, 18), 132 (100), 131 (45), 118 (23), 117 (77), 115 (32), 105 (23), 104 (40), 103 (26), 91 (80). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.68; H, 7.74.

Conversion of 6b and 6c into 9. A solution of 3.0 g of a mixture of **6b** and **6c** (13 mmol) in 20 mL of dry ether was added to 0.41 g of $LiAlH_4$ (11 mmol) in 40 mL of ether. The resultant suspension was stirred for 1 h at room temperature and then treated successively with 0.41 mL of water, 0.41 mL of 15% NaOH, and 1.23 mL of water. The suspension was filtered, and the salts were washed with ether (2 × 50 mL). The ethereal solution was dried with $MgSO_4$, filtered, and concentrated to yield 2.9 g of a mixture of alcohols, which was dissolved in a mixture of 10 mL of ethyl vinyl ether and 0.1 g of toluenesulfonic acid. After 29 h at room temperature, the solution was diluted with 30 mL of ether, washed with 20 mL of 5% $NaHCO_3$, dried with K_2CO_3, and concentrated to give 2.7 g of **8** (68%).

To a solution of 1.1 g of sodium (48 mmol) in 150 mL in liquid ammonia was added 2.7 g of **8** (8.8 mmol) in 40 mL of ether at −78 °C. After 1 h, 2.5 g of NH_4Cl was added to destroy excess sodium, a cooling bath was removed, and the ammonia was allowed to evaporate. To the residue were added 100-mL portions of ether and water, and the aqueous layer which was separated from the organic layer was extracted with ether (2 × 50 mL). The ethereal layer was combined with the extracts, washed with water, dried with K_2CO_3, and concentrated to give 1.3 g of oil, which was dissolved in 10 mL of 60% AcOH. After 1.5 h at 50 °C, the solution was poured into 30 mL of water and the hydrolyzed product was extracted with ether (3 × 20 mL). The combined extracts were washed with dilute NaOH and water, dried with $MgSO_4$, and concentrated to give 0.99 g of a mixture of alcohols, which was dissolved in 15 mL of CH_2Cl_2 and added to a suspension of 1.43 g of PCC (6.7 mmol) and 1.1 g of AcONa (1.3 mmol) in 20 mL of CH_2Cl_2. After 3 h at room temperature, 200 mL of ether was added, and the mixture was filtered through a short pad of Florisil. The filtrate was washed with water, dried with $MgSO_4$, concentrated, and distilled at 120–140 °C (bath temperature, 20 Torr) to give 0.70 g of **9** (50% from **6**).

Preparation of [4.3.2]Propella-2,4,10-trien-7-one (14). To a solution of 2.29 g of **9** (14 mmol) in 80 mL of CH_2Cl_2 and 4 mL of pyridine was portionwise added 5.38 g of pyridinium bromide perbromide (16.8 mmol) at room temperature. After 40 min, the pale yellow solution was washed successively with 30-mL portions of 5% $Na_2S_2O_3$, dilute HCl, 5% $NaHCO_3$, and water and dried with $MgSO_4$. After removal of the solvent, the residual oil (4.02 g) was dissolved in 80 mL of dry HMPA and added to a mixture of 5.95 g of LiCl and 10.4 g of Li_2CO_3, which had previously been dried at 140 °C for 3 h in vacuo. The resultant suspension was stirred under nitrogen for 90 min at 80 °C, cooled to room temperature, and poured into a mixture of 150 mL of water and 200 mL of ether. The organic layer was separated, washed with water (3 × 50 mL), and dried with $MgSO_4$. After removal of the solvent,

(32) For [1,7] walk rearrangements in bicyclo[6.1.0]nona-2,4,6-trienes, see: Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981.
(33) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.
(34) Fieser, L. F. *Organic Experiments*; D. C. Heath: Boston, 1964; p 68.
(35) Ogata, Y.; Sawaki, Y. *Tetrahedron* **1967**, *23*, 3327.

the residue was subjected to chromatography on silica gel eluted with ether/hexane (1:1). The eluent containing the product was concentrated and distilled at ca. 110 °C (bath temperature, 12 Torr) to give 840 mg of **14**: ^{1}H NMR δ 1.51–1.85 (m, 1 H), 1.85–2.25 (m, 2 H), 2.69–3.09 (m, 1 H), 5.83–5.99 (m, 5 H), 6.30 (d, J = 2.7 Hz, 1 H); IR (neat) 3045, 1730, 1410, 1220, 990, 760, 700 cm^{-1}; UV λ_{max} (EtOH) 259 (ε 2200), 270 (2400), 281 (2300), 302 nm (280, sh); MS m/z 158 (M^+, 52), 130 (27), 129 (54), 128 (26), 116 (100), 115 (66), 103 (22), 102 (39). Anal. Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.73; H, 6.21.

Preparation of [4.3.2]Propella-2,4,8,10-tetraen-7-one (1) from 14. Diisopropylamine (0.25 mL, 1.78 mmol) in 3 mL of THF was treated with 0.82 mL of 1.96 M butyllithium (1.61 mmol) in hexane at −78 °C to generate i-Pr_2NLi, to which a solution of 101 mg of **14** (0.64 mmol) in 2 mL of THF was added. After 30 min at −78 °C, the resultant solution was transferred through a double-ended needle to a flask containing 0.19 g of PhSSPh (1.15 mmol) and 1 mL of HMPA. The reaction was stirred for 1 h at room temperature and quenched with wet ether. The mixture was washed successively with 2 N HCl, 5% $NaHCO_3$, and water, and dried with $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel. Elution with ether/hexane (1:9) afforded 75 mg of a 1:4 epimeric mixture of the α-phenylthio derivatives of **14** (44%). In the ^{1}H NMR spectrum of the mixture, α-protons in the cyclopentanone rings of the major and minor products were observed at δ 4.31 (dd, J = 9, 12 Hz) and 3.63 (dd, J = 6, 7 Hz), respectively. The mixture was oxidized to **15** without separating the epimers.

To a solution of 75 mg of the above product (0.28 mmol) in 4 mL of CH_2Cl_2 was added 62 mg of MCPBA (80% purity, 0.28 mmol) in 3 mL of CH_2Cl_2 at −78 °C under nitrogen over a period of 3 min. After 5 min, the reaction was quenched with 5 mL of aqueous Na_2SO_3 and warmed up to room temperature. The organic solution was separated from the aqueous layer, washed successively with 5% $NaHCO_3$ and water, and dried with $MgSO_4$. After removal of the solvent, the residual 70 mg of crude sulfoxide was dissolved in a mixture of 5 mL of toluene and 80 μL of triethyl phosphite. The mixture was refluxed for 6 h, concentrated in vacuo, and subjected to preparative GLC to give 11 mg of **1**: ^{1}H NMR δ 5.76–5.99 (m, 4 H), 6.23 (d, J = 2.5 Hz, 1 H), 6.24 (d, J = 6.0 Hz, 1 H), 6.51 (d, J = 2.5 Hz, 1 H), 7.54 (d, J = 6.0 Hz, 1 H); ^{13}C NMR δ 58.2, 58.9, 123.3, 123.6, 124.9, 125.1, 134.7, 138.3, 145.0, 163.2, 206.2; IR (neat) 3050, 1706, 1640, 1580, 1570, 1544, 1340, 1224, 772, 740, 686 cm^{-1}; UV λ_{max} (EtOH) 270 (ε 1600), 278 (1600), 355 nm (80); MS m/z 156 (M^+, 43), 128 (100), 127 (27), 102 (34). Anal. Calcd for $C_{11}H_8O$: C, 84.59; H, 5.16. Found: C, 84.39; H, 5.10.

Preparation of 3,4-Dibromo[4.3.2]propell-10-en-7-one (12). To a magnetically stirred solution of 1.73 g of **5** (12.9 mmol) in 100 mL of CH_2Cl_2 containing 5 mL of pyridine was portionwise added 4.13 g of pyridinium bromide perbromide (12.9 mmol) at 0 °C. Within 30 min, the solution became pale yellow and GLC analysis (column A, 170 °C) showed that **5** was largely consumed. The reaction mixture was poured into 5% $Na_2S_2O_3$, and the product was extracted with 400 mL of ether. The ethereal extract was washed successively with 5% HCl, water, 5% $NaHCO_3$, and water and dried with $MgSO_4$. The removal of the solvent at 0 °C in vacuo yielded **11** as a colorless oil, which was immediately diluted with 180 mL of acetone and used without purification in the next step because of its thermal instability. **11**: ^{1}H NMR δ 2.45–2.56 (m, 4 H), 2.75–3.66 (m, 4 H), 4.63–4.66 (br s, 2 H); IR (neat) 2925, 1700, 1655, 1270, 880 cm^{-1}.

The acetone solution of **11** was cooled to −70 °C in a dry ice/methanol bath, and acetylene was condensed in it until the volume of the solution became about 300 mL. The mixture was photolyzed through Pyrex with a high-pressure Hg lamp at −60 °C. After 2 h, GLC analysis (column A, 170 °C) showed the complete consumption of **11**. The cooling bath was removed, boiling stones were added, and excess acetylene was allowed to evaporate. After the evaporation of acetylene ceased, the residual solution was dried with $MgSO_4$ and concentrated to yield 3.9 g of pale yellow oil, which was subjected to chromatography on silica gel eluted with ether/hexane (1:9) to give 1.74 g of **12** (42% from **5**) as a colorless solid. Crystallization from ether at −20 °C afforded analytically pure **12**: mp 54–55 °C; R_f (CH_2Cl_2) 0.52; ^{1}H NMR δ 1.60–2.55 (m, 3 H), 2.65–2.85 (m, 4 H), 2.90–3.19 (m, 1 H), 4.50–4.68 (m, 2 H), 6.12 (d, J = 2.7 Hz, 1 H), 6.45 (d, J = 2.7 Hz, 1 H); IR (KBr) 3070, 1725, 1430, 1288, 1248, 1042, 880, 758 cm^{-1}; UV λ_{max} (hexane) 208 (ε 2900), 301 nm (120); MS m/z 322 (M^+ + 4, 2.5), 320 (M^+ + 2, 5), 318 (M^+, 2.5), 159 (31), 131 (100), 91 (45). Anal. Calcd for $C_{11}H_{12}OBr_2$: C, 41.28; H, 3.78; Br, 49.94. Found: C, 41.34; H, 3.87; Br, 49.93.

Preparation of 3,4,8-Tribromo[4.3.2]propell-10-en-7-one (13). A mixture of 1.34 g of **12** (4.2 mmol) and 1.26 g of isopropylidene dibromomalonate (4.2 mmol) in 30 mL of CCl_4 was stirred at 60 °C under argon. After 29 h, TLC analysis showed the almost complete consumption of **12**. The reaction mixture was then diluted with 150 mL of ether, washed with 5% $NaHCO_3$ and water, and dried with $MgSO_4$. After removal of the solvent, the residual oil was chromatographed on silica gel. Elution with ether/hexane (1:19) afforded 0.98 g of **13** (58%) as a colorless solid. Crystallization from methanol afforded analytically pure **13**: mp 112–112.5 °C; R_f (CH_2Cl_2) 0.63; ^{1}H NMR δ 2.14 (dd, J = 11.3, 13.3 Hz, 1 H), 2.69–2.96 (m, 5 H), 4.58–4.79 (m, 2 H), 5.09 (dd, J = 8.3, 11.3 Hz, 1 H), 6.19 (d, J = 2.7 Hz, 1 H), 6.51 (d, J = 2.7 Hz, 1 H); IR (KBr) 3010, 2950, 2930, 1745, 1442, 1428, 942, 880, 780, 740 cm^{-1}; UV λ_{max} (EtOH) 307 nm (ε 140); MS m/z 402 (M^+ + 6, 2), 400 (M^+ + 4, 6), 398 (M^+ + 2, 6), 396 (M^+, 2), 319 (20), 157 (22), 129 (100), 104 (27), 91 (26), 77 (22). Anal. Calcd for $C_{11}H_{11}OBr_3$: C, 33.12; H, 2.78; Br, 60.09. Found: C, 33.30; H, 2.81; Br, 60.06.

Preparation of 1 from 13. A solution of 160 mg of **13** (0.40 mmol) in 7 mL of dry HMPA was added to a mixture of LiCl (260 mg, 6.1 mmol) and Li_2CO_3 (450 mg, 6.1 mmol), which had been dried at 140 °C (2 Torr) for 4 h. The resultant suspension was stirred at 140 °C for 2.5 h under argon. The reaction mixture was cooled to room temperature, poured into 50 mL of water, and extracted with ether (3 × 50 mL). The ethereal extracts were combined, washed well with water, and dried with $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel. Elution with ether/hexane (1:9) afforded 35 mg of crude **1**, which was further purified by preparative GLC (column B, 170 °C) to give 27 mg of pure **1** (43%) as a colorless oil. The obtained product was identical in all respects with **1**, which was prepared from **14**.

Preparation of [4.3.2]Propella-2,4,8-trien-7-one (16). The dibromide **11**, which was prepared from 2.26 g of **5** (17 mmol), was dissolved in 300 mL of CH_2Cl_2 and placed in a Pyrex vessel. The solution was cooled to −78 °C, saturated with ethylene, and irradiated below −50 °C while a slow stream of ethylene was maintained. GLC analysis (column C, 100–220 °C) showed the complete consumption of **11** after 2 h. The photolyzed mixture was warmed up to room temperature, dried with $MgSO_4$, and concentrated to give 4.6 g of residue, which was chromatographed on silica gel. Elution with ether/hexane (3:17) produced 2.81 g of a mixture of two isomeric ethylene adducts (ca. 1:6, 52%): ^{1}H NMR δ 1.74–2.19 (m, 6 H), 2.24–2.50 (m, 2 H), 2.59–2.84 (m, 4 H), 4.43–4.62 (m, 2 H); IR (KBr) 1718 cm^{-1}.

A solution of 2.81 g of the ethylene adducts (8.7 mmol) and 2.63 g of isopropylidene dibromomalonate (8.7 mmol) in 30 mL of CCl_4 was stirred at 60 °C under nitrogen. After 39 h, the mixture was cooled to room temperature, diluted with 100 mL of CH_2Cl_2, washed with 5% $NaHCO_3$ and water, and dried with $MgSO_4$. After removal of the solvent, the residue was subjected to chromatography on silica gel eluted with ether/hexane (1:19) to afford 1.63 g of a mixture of tribromides (47%): mp 84–88 °C; R_f (CH_2Cl_2) 0.64; ^{1}H NMR δ 1.73–3.25 (m, 11 H), 4.43–4.76 (m, 2 H), 4.90 (dd, J = 9.8, 11.0 Hz, 1 H).

To a mixture of 4.31 g of LiCl (101 mmol) and 7.51 g of Li_2CO_3 (101 mmol) which had been dried at 140 °C (2 Torr) for 3 h was added a solution of 1.63 g of the tribromo compounds (4.1 mmol) in 200 mL of HMPA, and the resultant suspension was heated at 135 °C. After 1.5 h the reaction mixture was cooled to room temperature, poured into 400 mL of water, and extracted with ether (4 × 100 mL). The ethereal extracts were combined, washed with water (3 × 150 mL), dried with $MgSO_4$, and concentrated to give 0.74 g of crude product, which was chromatographed on silica gel. Elution with ether/hexane (1:9) afforded 0.50 g of crude **16**, which was further purified by preparative GLC (column B, 170 °C) to give 373 mg of pure **16** (58%): ^{1}H NMR δ 1.93–2.24 (m, 2 H), 2.49–2.77 (m, 2 H), 5.61–5.79 (m, 4 H), 6.53 (d, J = 5.6 Hz, 1 H), 7.69 (d, J = 5.6 Hz, 1 H); ^{13}C NMR δ 33.3, 36.4, 49.3,

49.6, 121.7, 122.4, 125.0, 125.8, 135.5, 167.3, 211.8; IR (neat) 3030, 2935, 1705, 1635, 1580, 1560 cm^{-1}; UV λ_{max} (EtOH) 222 (ϵ 9700), 270 (2000), 286 (1800, sh), 299 (1000, sh), 335 nm (170); MS m/z 158 (M^+, 15), 130 (100), 102 (44); HRMS calcd for $C_{11}H_{10}O$ 158.0732, found 158.0733.

Photolysis of 1 in Aprotic Solvents. A solution of 50 mg of 1 (0.32 mmol) in 25 mL of CH_2Cl_2 was placed in a Pyrex test tube (18 mm × 18 cm), bubbled with argon for 20 min at 0 °C, and irradiated with a high-pressure Hg lamp at 12 °C. The reaction was monitored by GLC (column A, 200 °C), which showed the formation of two volatile products. After 30 min the irradiation was discontinued, and the photolyzed mixture was concentrated. The residue was chromatographed on silica gel and eluted with ether/hexane to give fractions containing a mixture of 1 and 18 and crude 23, which were subjected to preparative GLC (column B, 125 °C) to give 30 mg of 1, 6 mg of 18 (30%), and 5 mg of 23 (25%). Photolysis of 1 in ether gave a similar result (18 and 23 in 31% and 26% yields, respectively, by GLC). 18: ^1H NMR δ 4.16 (dddd, J = 1.0, 1.7, 6.3, 6.6 Hz, 1 H), 5.51 (dd, J = 1.7, 10.6 Hz, 1 H), 5.71 (d, J = 6.3 Hz, 1 H), 6.32 (dd, J = 6.6, 7.6 Hz, 1 H), 6.52 (d, J = 2.2 Hz, 1 H), 6.62 (dd, J = 1.0, 7.6 Hz, 1 H), 7.02 (d, J = 2.2 Hz, 1 H), 7.08 (d, J = 10.6 Hz, 1 H); IR (neat) 1684, 1658, 1288, 834, 788, 706, 678 cm^{-1}; UV λ_{max} (EtOH) 228 (ϵ 3100), 290 (200, sh), 360 nm (50); MS (23 eV) m/z 156 (M^+, 7), 128 (100); HRMS calcd for $C_{11}H_8O$ 156.0575, found 156.0574. 23: mp 110.5–111 °C; ^1H NMR δ 4.15 (d, J = 2.7 Hz, 1 H), 4.65 (dd, J = 2.9, 7.7 Hz, 1 H), 6.05 (d, J = 5.6 Hz, 1 H), 7.17–7.26 (m, 4 H), 7.81 (dd, J = 2.9, 5.6 Hz, 1 H); IR (KBr) 1688, 1572, 1454, 1180, 918, 806, 764, 742 cm^{-1}; UV λ_{max} (EtOH) 224 (ϵ 6100, sh), 261 (840, sh), 269 (840), 277 (680), 330 nm (80); MS m/z 156 (M^+, 59), 129 (11), 128 (100), 127 (18), 123 (13). Anal. Calcd for $C_{11}H_8O$: C, 84.59; H, 5.16. Found: C, 84.72; H, 5.03.

Photolysis of 1 in Methanol. A solution of 90 mg of 1 (0.58 mmol) in 100 mL of methanol was placed in a Pyrex vessel, deaerated by bubbling argon, and irradiated with a high-pressure Hg lamp at 12 °C. The reaction was monitored by GLC (column B, 160 °C), which showed the 65% consumption of 1 after the 10 min irradiation and formation of 18 (7%) and 23 (23%) together with two products which were later identified as 21[36] (20%) and methyl 2-indeneacetate 31 (5%). After removal of the solvent in vacuo, the residue was chromatographed on silica gel. Elution with ether/hexane (1:9) produced a mixture of 1, 21, and 31, which was further chromatographed on silica gel (Merck Lobar A, ether/hexane, 1:15) to give 3 mg of 31. Elution with ether/hexane (1:4) produced a mixture of 1, 18, and 23, which was subjected to preparative GLC to give 14 mg of 1, 4 mg of 18, and 18 mg of 23. The compound 21 which is liable to polymerize particularly in a concentrated solution largely decomposed during the workup and could not be isolated. The formation of 21 in the photolysis of 1 in methanol, however, was substantiated by ^1H NMR measurements. The yield of 21 was determined by assuming its quantitative isomerization to 25 under the GLC conditions. The compound 25 was independently obtained by photolyzing 23 in methanol.[37] In the present photolysis of 1 in methanol, the yield of 25 which would presumably be produced via 23 was less than 1 mg. A control experiment showed that 31 would also be a secondary product derived from 23. 25: ^1H NMR (500 MHz) δ 2.41 (dd, J = 9.3, 16.1 Hz, 1 H), 2.75 (dd, J = 6.9, 16.1 Hz, 1 H), 3.76 (s, 3 H), 3.86 (dddd, J = 1.5, 1.5, 6.9, 9.3 Hz, 1 H), 6.54 (dd, J = 1.5, 5.4 Hz, 1 H), 6.83 (dd, J = 1.5, 5.4 Hz, 1 H), 7.19 (dd, J = 7.3, 7.3 Hz, 1 H), 7.28 (dd, J = 7.3, 7.3 Hz, 1 H), 7.36 (d, J = 7.3 Hz, 1 H), 7.39 (d, J = 7.3 Hz, 1 H); IR (neat) 3075, 2952, 1738, 1462, 1438, 1354, 1236, 1166, 780 cm^{-1}; UV λ_{max} (EtOH) 252 (ϵ 6000), 282 (950, sh), 288 nm (700, sh); MS m/z 188 (M^+, 48), 129 (100), 128 (78). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; MW 188.0837. Found: C, 76.01; H, 6.27; MW 188.0844. 31: ^1H NMR (CD_3CN) δ 3.43 (br s, 2 H), 3.53 (br s, 2 H), 3.67 (s, 3 H), 6.69 (br s, 1 H), 7.11–7.38 (m, 4 H); IR (neat) 3025, 2952, 1738, 1464, 1438, 1258, 1202, 1170, 754, 718 cm^{-1}; UV λ_{max} (EtOH) 257 (ϵ 12800), 281 (1300, sh), 288 nm (500, sh); MS m/z 188 (M^+, 29), 129 (100), 128 (81). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.40; H, 6.44.

(36) The compound 21 underwent thermal rearrangement to 25 under the GLC conditions and was observed at 25 by GLC (see text).

(37) Ohkita, M.; Tsuji, T.; Nishida, S., unpublished result.

Photolysis of 1 Sensitized by Michler's Ketone. A solution of 11 mg of 1 (0.07 mmol) and 90 mg of Michler's ketone (0.34 mmol) in 2 mL of CH_2Cl_2 was deaerated by bubbling nitrogen for 10 min at 0 °C and irradiated with a high-pressure Hg lamp through Pyrex. The reaction was monitored by GLC. After 2 h, 60% of 1 had been consumed, but the formation of monomeric rearranged products including 18 and 23 was not observed.

Photolysis of 18. A 10^{-2} M solution of freshly purified 18 in methanol or CH_2Cl_2 containing tetraglyme as an internal standard was placed in a Pyrex test tube, deaerated by bubbling argon for 10 min at 0 °C, and irradiated with a high-pressure Hg lamp at 10–12 °C. The reaction was monitored by analyzing aliquots intermittently by capillary GLC (column D, 170 °C). The irradiation of 18 in CH_2Cl_2 led to the formation of 1 in 47% yield as a single volatile product at the 22% conversion of 18. In methanol, 1 and 21 were formed in 11% and 36% yields, respectively, at the 31% conversion of 18.

Measurement of ^1H NMR Spectrum of 21. A solution of 20 mg of 1 (0.13 mmol) in 20 mL of methanol in a Pyrex test tube (18 mm × 18 cm) was deaerated by bubbling argon for 10 min and irradiated with a high-pressure Hg lamp for 10 min. Toluene and a small amount of hydroquinone as an inhibitor were added, and the mixture was concentrated in vacuo. The residue was subjected to chromatography on silica gel (Merck Lobar A) eluted with ether/hexane (1:9). The eluent containing the desired product, to which hydroquinone was added, was concentrated in vacuo. The residual crude product was dissolved in a small amount of CCl_4, and the solution was concentrated again in vacuo. The residue was dissolved in $CDCl_3$ and filtered into an NMR tube, and the spectrum was recorded at 500 MHz with no delay. The measurement was repeated after allowing the sample to stand for 5 days at room temperature and then heating it 40 h at 50 °C. The examination of the two well-resolved spectra showed that a couple of products having closely related structures in a ratio of ca. 1:2 were consumed between the two measurements. On the basis of two sets of signals which disappeared, the structures of *endo*- and *exo*-21 were assigned to the major and minor components of the thermally labile photoproducts, respectively. The stereochemical assignment for *endo*-21 was made primarily on the basis of the magnitude of coupling (8.3 Hz) between the vicinal cyclopropane protons. For the parent compound 26, corresponding vicinal coupling constants for the exo and endo protons have been reported to be 8.5 and 3.5 Hz, respectively.[23] Unfortunately signals due to the cyclopropane ring protons of *exo*-21 could not be identified owing to their overlap with those due to impurities.

Stereoselective Formation of *endo*-21 at Low Temperature and Its Thermal Equilibration with *exo*-21. (a) Photolysis of 1 in CD_3OD at −80 °C. A solution of 9 mg of 1 in 0.6 mL of CD_3OD in an NMR tube was irradiated with a high-pressure Hg lamp through Coaning 7-60 and 7-54 filters (366-nm light) for 20 min at −80 °C. Since HPLC analysis showed that the conversion of 1 was low, the filters were replaced by a Pyrex filter and the irradiation was continued for 10 min while the temperature of a cooling bath briefly rose to −60 °C. The ^1H NMR spectrum (400 MHz) of the photolysate recorded at −80 °C after 2 h at −90 °C in the dark showed the formation *endo*- and *exo*-21-d_4 in a ratio of 92:8. When the measurement was repeated after allowing the sample to stand for 2 h at room temperature, the ratio was found to be 9:5. The spectrum also showed the formation of 23, but none of 18 was detected. *endo*-21-d_4: ^1H NMR (400 MHz, CD_3OD) δ 1.83 (dd, J = 6.5, 8.5 Hz, 0.3 H), 1.84 (dd, J = 8.5, 8.5 Hz, 0.7 H), 2.20 (dd, J = 4.2, 8.5 Hz, 1 H), 2.28 (d, J = 8.5 Hz, 0.7 H), 2.44 (d, J = 6.5 Hz, 0.3 H), 5.37 (d, J = 5.4 Hz, 1 H), 5.83 (dd, J = 4.2, 9.6 Hz, 1 H), 5.90 (dd, J = 5.4, 9.6 Hz, 1 H), 6.35 (d, J = 2.4 Hz, 1 H), 6.95 (d, J = 2.4 Hz, 1 H).

(b) Photolysis of 18 in CD_3OD at −80 °C. Ca. 6 mg of 18, which was freshly purified by preparative GLC, was dissolved in 0.5 mL of CD_3OD, placed in an NMR tube, and irradiated with a high-pressure Hg lamp throughg a Corning 7-60 filter (366 nm) for 25 min at −80 °C. The ^1H NMR spectrum (400 MHz) of the photolysate recorded at −80 °C after 1 h at the same temperature in the dark showed the formation of *endo*- and *exo*-21-d_4 in a ratio of 95:5. When the measurement was repeated after 3 h at room temperature, the ratio was 9:5. The ratio did not change further upon allowing the sample to stand at room temperature while

21 underwent gradual decomposition. The spectrum also showed that 1 was not formed in a detectable amount.

Rearrangement of 21 to 25 under GLC Conditions. A ca. 3×10^{-2} M solution of 18 in methanol was irradiated through Pyrex to give 21 and the resultant photolysate which was kept at 22–24 °C was intermittently analyzed by HPLC (μ-Porasil, ether/hexane, 1:9) and capillary GLC (columns D and E, 150-170 °C) to monitor the decomposition of 21 at 22–24 °C and its rearrangement to 25 under the GLC conditions. The relative amounts of remaining 21 (1.00 at 0 h) determined by HPLC after 3, 18, and 40 h were 0.77, 0.51, and 0.26, respectively. The amount of 25 observed by the capillary GLC decreased in parallel with that of 21 and was found to be 80%, 45%, and 27% of the initial amount after 3, 18, and 40 h, respectively, despite of its perfect stability in methanol and under the analysis conditions. Moreover, the HPLC analysis showed that 25 was not formed upon standing the solution of 21 at 22–24 °C. When the above experiment was repeated on purified 21, good reproducibility was observed. These observations clearly demonstrate that 21 undergoes rearrangement to 25 under the GLC conditions, but not in a solution at ambient temperature.

Photolysis of 14. A solution of 10 mg of 14 in 7 mL of methanol was deaerated by bubbling nitrogen and irradiated with a high-pressure Hg lamp through Pyrex at 12 °C. GLC analysis showed the formation of a single volatile product, which was identified as 1-indanone (ca. 20% by GLC). The photochemical formation of 1-indanone from 14 was also observed in ether (20% by GLC) and in acetone (50% by GLC).

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Alkynyliodonium Salts as Alkynylating Reagents: Direct Conversion of Alkynylphenyliodonium Tosylates to Dialkyl Alkynylphosphonates with Trialkyl Phosphites

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The treatment of various alkynyl(phenyl)iodonium tosylates 1 (R = *t*-Bu, *s*-Bu, *i*-Pr, cyclopentyl, Ph, and *p*-MeC_6H_4; X^- = OTs^-) with neat trimethyl phosphite gave the dimethyl alkynylphosphonates **4a** and **4d–h** in isolated yields ranging from 34 to 90%. Similar treatment of 1 (R = *t*-Bu, X^- = OTs^-) with neat triethyl and triisopropyl phosphites gave the diethyl and diisopropyl alkynylphosphonates **4b** (81%) and **4c** (58%). The byproducts of these reactions are alkyl tosylates and iodobenzene. The high yields of iodobenzene, determined by GC analysis for the reactions of 1 (R = *s*-Bu, *p*-tolyl; X^- = OTs^-) with trimethyl phosphite, indicate that the cleavage of the alkynyl(phenyl)iodonium ions with trialkyl phosphites proceeds with high regioselectivity at the alkynyl ligand.

The recent development of general methods for the synthesis of alkynylphenyliodonium salts 1[1,2] has stimulated interest in their use as alkynylating reagents. Stang and co-workers have employed 1 (X^- = OTs^-) as precursors to the first examples of alkynyl tosylates,[1d,e] alkynyl carboxylates,[3] and alkynyl phosphates[3a,4] and for the preparation of conjugated enynes by the treatment of 1 with vinylcopper reagents.[5] The photochemical production of alkynylphosphonium salts from 1 (X^- = BF_4^-) with triphenylphosphine has also been described.[6] Not all nucleophilic species are alkynylated with 1. 2-Lithiofuran and 2-lithiothiophenes displace the *tert*-butylethynyl ligand from iodine in various aryl(*tert*-butylethynyl)iodonium tosylates to give aryl(2-furyl)- and aryl(2-thienyl)iodonium salts.[7] Azide ion[8] and β-dicarbonyl anions[9] add to 1 in Michael fashion to give products consistent with intermediate vinylideneiodinanes 2 and vinylidenes 3.

$$\underset{\mathbf{1}}{RC{\equiv}\overset{+}{C}IPh},\ X^- \qquad \underset{\mathbf{2}}{R(Nu)C{=}\overset{+}{C}IPh} \qquad \underset{\mathbf{3}}{R(Nu)C{=}C:}$$

We now report that alkynylphenyliodonium tosylates react with trialkyl phosphites in formal Arbusov fashion to give alkynylphosphonates 4, eq 1. For example, when

$$\underset{\mathbf{1}}{RC{\equiv}\overset{+}{C}IPh},\ OTs^- + P(OR')_3 \rightarrow \underset{\mathbf{4}}{R{-}C{\equiv}CP(O)(OR')_2} + R'OTs + PhI \quad (1)$$

an excess of neat trimethyl phosphite was added to solid (*tert*-butylethynyl)phenyliodonium tosylate (1, R = *t*-Bu, X^- = OTs^-) at room temperature, heat was evolved and the iodonium salt rapidly (within 1 min) disappeared. Concentration of the resulting solution and chromatography of the residual oil on silica gel gave methyl tosylate (96%) and a 90% yield of dimethyl (*tert*-butylethynyl)-phosphonate (**4a**, R = *t*-Bu, R′ = Me). Similar treatment of 1 (R = *t*-Bu, X^- = OTs^-) with triethyl phosphite (at 85–7

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