over sodium sulfate and concentrated in vacuo. The residue was taken up in 15 mL of dioxane, 27 mL of methyl iodide was added, and the mixture was heated at reflux for 24 h. The solvents were evaporated in vacuo; the residue was washed with 16 mL of ether (8×) and then taken up in 8 mL of a 8% sodium bicarbonate solution and 72 mL of ethyl acetate. The suspension was stirred for 30 min, the organic phase was separated, and a new portion of 45 mL of ethyl acetate was added to the water layer. After the mixture was stirred for 30 min, the combined ethyl acetate solutions were dried on magnesium sulfate and the solvent was removed in vacuo. The residue was taken up in 1 mL of benzene containing 2 mg of p-toluenesulfonic acid and 5 μL of water. The mixture was stirred for 24 h at room temperature. Purification by column chromatography on silica gel using 30% acetone–isooctane yielded 15 mg (17%) of (±)-carpesiolin (**6**), which was recrystallized from chloroform–hexane: mp 145–148 °C (sublimes); IR (KBr) 3500, 1765, 1730, 1270, 1130, 1100, 1070, 980, 955 cm^{-1}; NMR δ 6.23 (d, J = 4.5 Hz, 1 H), 6.01 (d, J = 3.2 Hz, 1 H), 4.39 (ddd, J = 2.8, 10.0, and 12.0 Hz, 1 H), 4.02 (br d, J = 8.8 Hz, 1 H), 1.10 (d, J = 6.6 Hz, 3 H), 1.04 (s, 3 H); MS m/z (rel intensity) 264 (M^+, 1), 246 (22), 189 (22), 147 (22), 119 (20), 105 (24), 97 (100), 95 (20), 91 (22), 79 (28), 77 (24), 69 (20), 67 (26), 55 (38), 44 (22), 43 (30), 41 (58), 39 (24), 32 (24).

Acknowledgment. We are indebted to the "Nationaal Fonds voor Wetenschappelijk Onderzoek" and the "Ministerie voor Wetenschapsbeleid" for financial support to the laboratory. We acknowledge the help of H. De Wilde and R. Myngheer for large-scale preparations of starting materials.

Registry No. **1**, 62990-80-1; **6**, 71698-61-8; **9**, 71599-18-3; **11**, 71661-77-3; **12**, 71661-78-4; **13**, 71661-79-5; **14**, 71661-80-8; **16**, 71661-81-9; **17**, 71661-82-0; **18**, 71661-83-1; **19**, 71661-84-2; ethylene glycol, 107-21-1.

Ring Size Effect on the Photoreaction of [n.3.2]Propellanones Involving a Cyclobutanone Ring

Yoshihiro Fukuda,* Toshihiko Negoro, Yoshito Tobe, Koji Kimura, and Yoshinobu Odaira

Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Received May 30, 1979

In the photoreactions in methanol of [n.3.2]propellanones **1–4** and [n.3.2]propellanediones **5–8** involving a cyclobutanone ring, cycloelimination products show increasing predominance over ring-expansion products with increasing third-ring size. In addition, in the case of **5–8**, the yield of the syn-form acetals **16a–19a** was slightly more than the yield of the anti-form acetals **16b–19b**, and the syn/anti ratio increases by degrees as the third ring changes from a five- to an eight-membered ring. These ring size effects are discussed.

Recently, the chemistry of propellanes has attracted much attention, especially in view of structure–reactivity relationships,[1] and we have been deeply interested in these relationships on [n.3.2]propellane derivatives.[2] In this ring system, the bicyclo[3.2.0]heptane moiety has a rigid boat geometry independent of the conformational flexibility of the third alicyclic ring. Therefore, the tricyclo[n.3.2.0] ring system serves as a good model for examination of the steric effect of the third alicyclic ring. We have previously reported on the remarkable effect of the ring size on the stereoselectivity in the hydride reduction of [n.3.2]propellanones[2g] and also on the chromic acid oxidation of [n.3.2]propellanols[2h] and have pointed out that the ring size effect is attributable to the steric effect associated with the conformational flexibility of the third alicyclic ring.

In order to explain the size effect of another alicyclic ring on the photochemical behavior of the cyclobutanone moiety incorporated into a propellane system, we have now selected as suitable model compounds [n.3.2]propellanones **1–4** or [n.3.2]propellanediones **5–8** involving a cyclobutanone, a cyclopentane, or a cyclopentanone ring and a five- to eight-membered alicyclic ring.

As is well-known,[3] three major processes in the photochemical behavior of cyclobutanones are (i) ring expansion (formation of an oxacarbene), (ii) cycloelimination (formation of an olefin and ketene), and (iii) decarbonylation. Therefore, our attention has been focused on the steric effect of the third alicyclic ring on these major processes in the photoreaction of [n.3.2]propellanones.

[n.3.2]Propellanones involving a cyclobutanone ring were synthesized as shown in Scheme I. On irradiation of the bicyclic enones **20–23** with a large excess of vinyl acetate[4] in ether at −70 °C, the respective cycloadducts were afforded in good yields. These cycloadducts were converted in moderate yields to cyclobutanols by tosylhydrazone reduction or Wolff–Kishner reduction. Finally, Jones oxidation of the cyclobutanols produced the desired cyclobutanones **1–4** in fair yields.

When 10^{-2} M solutions of [n.3.2]propellanones **1–4** in methanol were irradiated in Pyrex tubes at 20 °C with a

---

[1] For a review see: Ginsburg, D. "Propellanes, Structure and Reactions"; Verlag Chemie: Weinheim/Bergstr., Germany, 1975. See also: Paquette, L. A.; Photis, J. M.; Micheli, R. P. *J. Am. Chem. Soc.* **1977**, *99*, 7899 and references cited therein.

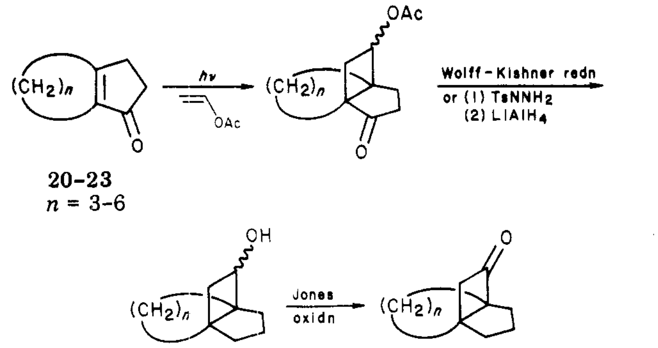
[2] (a) Kunai, A.; Yorihiro, K.; Hirata, T.; Odaira, Y. *Tetrahedron* **1973**, *29*, 1679. (b) Kunai, A.; Ishii, T.; Odaira, Y. *Chem. Lett.* **1974**, 315. (c) Tobe, Y.; Omura, H.; Kunai, A.; Kimura, K.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 319. (d) Tobe, Y.; Doi, A.; Kunai, A.; Kimura, K.; Odaira, Y. *J. Org. Chem.* **1977**, *42*, 2523. (e) Tobe, Y.; Kimura, K.; Odaira, Y. *Ibid.* **1978**, *43*, 3776. (f) Tobe, Y.; Hoshino, T.; Kawakami, Y.; Sakai, Y.; Kimura, K.; Odaira, Y. *Ibid.* **1978**, *43*, 4334. (g) Tobe, Y.; Doi, A.; Kimura, K.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 639. (h) Tobe, Y.; Kimura, K.; Odaira, Y. *J. Org. Chem.* **1979**, *44*, 639.

[3] (a) McDaniel, D. M.; Turro, N. J. *Tetrahedron Lett.* **1972**, 3035. (b) Morton, D. R.; Turro, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 3947. (c) Turro, N. J.; Dalton, J. C.; Dawes, K.; Farrington, G.; Hautala, R.; Morton, D. R.; Niemczyk, M.; Schore, N. *Acc. Chem. Res.* **1972**, *5*, 92. (d) Yates, P.; Loutfy, R. O. *Ibid.* **1975**, *8*, 209. (e) Yates, P. *J. Photochem.* **1976**, *5*, 91. (f) Stohrer, W. D.; Jacobs, P.; Kaiser, K. H.; Weich, G.; Quinkert, G. *Top. Curr. Chem.* **1974**, *46*, 181 and references cited therein. (g) Jones II, G.; McDonnell, L. P. *J. Am. Chem. Soc.* **1976**, *98*, 6203. (h) Kimura, K.; Koshibe, S.; Juro, M.; Fukuda, Y.; Odaira, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 741. (i) Kimura, K.; Masuda, T.; Fukuda, Y.; Odaira, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 787.

[4] Liu, H. J.; Ogino, T. *Tetrahedron Lett.* **1973**, 4937. Mori, K.; Sasaki, M. *Ibid.* **1979**, 1329.

0022-3263/79/1944-4557$01.00/0

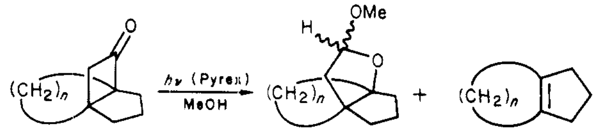
Scheme I



20–23
n = 3–6

1, n = 3 (five-membered third ring)
2, n = 4 (six-membered third ring)
3, n = 5 (seven-membered third ring)
4, n = 6 (eight-membered third ring)

Scheme II. Percent Yields of the Products from the Photolysis of [n.3.2] Propellanones 1–4 in MeOH



1, n = 3	**9**, 74	other products[a]
2, n = 4	**10**, 95[b]	**13**, trace
3, n = 5	**11**, 88[b]	**14**, 10
4, n = 6	**12**, 55[b]	**15**, 45

[a] See ref 5 and Experimental Section. [b] A mixture of two epimers.

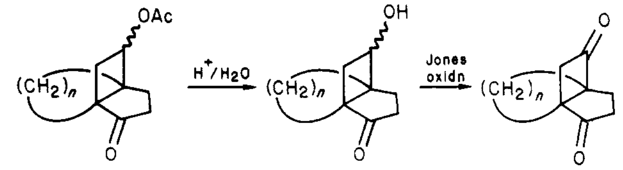
high-pressure Hg lamp, both ring expansion via an oxacarbene intermediate and cycloelimination proceeded smoothly to afford ring-expanded acetals **9–12** and bicyclic olefins **13–15**, but no decarbonylation occurred at all (Scheme II).[5]

From the above result, it is obvious that, with increased third-ring size, the formation of bicyclic olefin increases remarkably, while the formation of ring-expanded acetal, on the other hand, decreases in turn. Although each acetal **10–12** was composed of a pair of syn and anti epimers, most of them were indistinguishable by GLC analysis except for the epimers of **12**, and, as a result, their stereochemistry was not definable. On that account, the interesting question of the ring size effect on the formation of the two epimers still remains open. In order to solve this problem, the photoreaction of [n.3.2]propellanediones **5–8**, involving a cyclobutanone ring, was undertaken. These compounds **5–8** were synthesized by hydrolysis followed by Jones oxidation of the above-mentioned photocycloadducts as shown in Scheme III.

Similar irradiation of [n.3.2]propellanediones **5–8** in methanol gave a pair of epimers of ring-expanded acetals **16a–19a** and **16b–19b** and the corresponding bicyclic enones **20–23** in high efficiency (Scheme IV).[6]

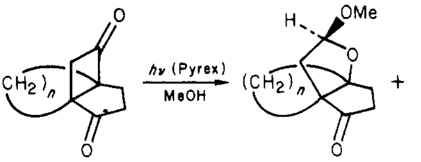
As shown in Scheme IV, cycloelimination predominated over ring expansion with increasing size of the third ring, in analogy with the case of [n.3.2]propellanones, and, especially, in the case of [6.3.2]propellanedione (**8**); the bicyclic enone **23** was afforded in 86% yield from **8**. As might be expected, four pairs of epimers, **16a–19a** and **16b–19b** could be readily separated by GLC analysis, and their configuration with respect to the methoxyl group was determined by an LIS NMR study using Eu(dpm)$_3$ in the following way. Taking the case of **17a** or **17b** as an example (Table I), the β-hydrogen adjacent to the methoxyl group is the most deshielded hydrogen of all hydrogens in **17a** or **17b**. Therefore, it is evident that the coordination to the LSR occurs wholly at the carbonyl function. Moreover, for the two possible positions of the methoxyl group, the degree of deshielding in the case of the syn form should be higher than that in the case of the anti form by adding Eu(dpm)$_3$. This is expressed in the terms of the S value[7] and is summarized in Table I. Consequently, **16a–19a** were assigned as the syn-form acetals and **16b–19b** as the anti-form ones.

Scheme III

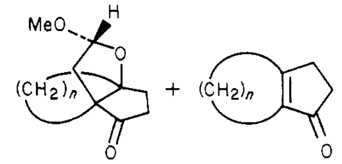


5–8, n = 3–6

Scheme IV. Percent Yields of the Products from the Photolysis of [n3.2] Propellanediones 5–8 in MeOH

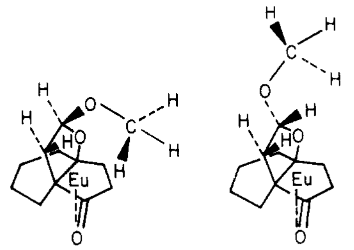


	syn form
5, n = 3	**16a**, 40
6, n = 4	**17a**, 25
7, n = 5	**18a**, 22
8, n = 6	**19a**, 9



anti form	
16b, 35	**20**, 13
17b, 16	**21**, 59
18b, 13	**22**, 65
19b, 5	**23**, 86

Table I. S Values of Methoxyl Protons in the LIS NMR Spectra of Acetals 17a and 17b



syn-**17a** *anti*-**17b**

acetal	S^a	acetal	S^a
17a	2.16	17b	1.64

[a] [Eu(dpm)$_3$]/[acetal] = 0.2–0.8.

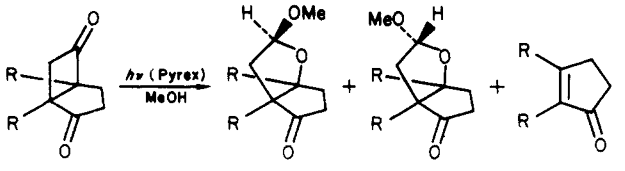
Interestingly, the syn-form epimer was afforded in a larger quantity than the anti epimer regardless of the third-ring size of **5–8**, and the syn/anti ratio of obtainable

---

(5) The esters **1d** and **1e** seem to be formed by way of the ring cleavage of **1**, owing to the fairly large strain of **1**.

(6) The cyclopentanone moiety of **5–8** and **25** was little reacted under these conditions, but further irradiation gave rise to the cleavage of the cyclopentanone ring to afford aldehydes and acetals.

Scheme V. Percent Yields of the Products from the Photolysis of Bicyclo[3.2.0]heptane-2,6-diones 24 and 25 in MeOH



24, R = H
25, R = Me

syn form
26a, 24
27a, 42

anti form
26b, 57
27b, 25

28, trace
29, 33

acetals **16a**–**19a** and **16b**–**19b** increases by degrees from 1.1 to 1.8 as the third ring changes from a five- to an eight-membered ring.

Furthermore, for the sake of elucidation of the structural feature of the propellane system on the photochemical behavior of cyclobutanones, the photoreaction of bicyclo[3.2.0]heptane-2,6-diones **24** and **25** was examined under similar conditions. The result is shown in Scheme V.

In the case of nonsubstituted **24**, the anti ring-expanded acetal **26b** was formed in preference to the syn one, **26a**, along with a trace of cyclopentenone. On the other hand, dimethyl derivative **25** trended toward a similar result to that obtained in the case of propellanedione **6** or **7**. It is unambiguous that the two methyl substituents of **25** at the bridgehead positions play a similar role to the third ring (six- or seven-membered ring) in [*n*.3.2]propellanediones.

The facts mentioned above indicate obviously that, in both [*n*.3.2]propellanones and [*n*.3.2]propellanediones, the third ring has a much greater influence on the photochemical processes than on the syn/anti ratio of the ring-expanded acetals.

However, there seems to be little or no distinction between the excited states of **5** and **8** because the quantum yield for the disappearance of **5** is 0.21 and that for **8** is 0.22 (Table II).[8]

In previous papers, the concept of the steric effect associated with the conformational flexibility of the third ring has been applied to account for the distinctions in various reactions of a series of [*n*.3.2]propellanes. However, since the eminent distinctions observed in the present case are not sufficiently interpreted by this concept, it seems reasonable to assume that these differences are attributable to the distinction in the degree of rigidity or flexibility of a radical at the bridgehead position of a bicyclic ring system in a 1,4-acylbicycloalkyl singlet biradical generated photochemically by the initial cleavage via n–π* excitation of the carbonyl group of a cyclobutanone ring.

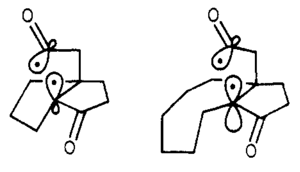
For example, the bridgehead radical **30** generated from **5** may be constrained to a nonplanar state and predominantly participates in the formation of an oxacarbene with relief of ring strain, since the conformation of bicyclo[3.3.0]octane ring system is very rigid and fixed. On the contrary, the nonplanar bridgehead radical **31** formed from **8** is flexible enough to be inverted to the more stable planar one[9] because of the conformational flexibility of the bicyclo[6.3.0]undecane ring system. In sum, the efficiency of cycloelimination via a planar radical may be enhanced with the increase of the conformational flexibility of the bicyclo[*n*.3.0] ring system (Chart I).

Table II. Products Ratio and Syn/Anti Ratio of Acetals in the Photoreaction of 5–8

[*n*.3.2]-propel-lane-dione	ring size of third ring	ring expansion product/cycloelimination product	syn/anti	Φ_d[a]
5	5	5.8	1.1	0.21
6	6	0.7	1.6	
7	7	0.5	1.7	
8	8	0.2	1.8	0.22

[a] Quantum yield for disappearance of **5** or **8**.

Chart I



30
most rigid

31
most flexible

In addition, the conformational flexibility of the third ring appears to play a key role in determination of the syn/anti ratio of the obtainable acetals. This is because the steric hindrance to the approach of methanol to an oxacarbene intermediate from the third-ring side may become larger with increasing conformational flexibility of the third alicyclic ring.

Further work on the photolysis of the above [*n*.3.2]-propellanones in an aprotic solvent, which may demonstrate the striking effect of propellane structure, is in progress and will be reported shortly.

Experimental Section

General Procedures. Melting points were measured in a sealed tube and are uncorrected. Infrared spectra were recorded on a JASCO IR-G spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained on JEOL JNM-PS-100 and JEOL JNM-FX60S spectrometers, respectively, using CCl_4 or $CDCl_3$ as a solvent and Me_4Si as an internal standard. Mass spectra were determined with a Hitachi RMU-6E spectrometer. UV spectra were recorded on a Hitachi 356 spectrometer. Analytical GLC was carried out on a Hitachi 163 gas chromatograph (1 m × 3 mm columns: A, 10% FFAP; B, 5% SE-30; C, 5% OV-17), and preparative GLC separation was undertaken on a Varian Aerograph 90-P or 920 gas chromatograph (5 ft × 0.25 in. columns: D, 10% FFAP; E, 5% SE-30; F, 5% OV-17).

General Procedure for Photocycloaddition of Enones with Vinyl Acetate. Bicyclic enones **20**–**23**,[10] 2,3-dimethylcyclopentenone[11] (0.2 M solution), and a 20 molar excess of vinyl acetate in ether were irradiated with a 500-W high-pressure Hg lamp through a Pyrex filter under N_2 at −70 °C, and the irradiation was continued until the enones were almost consumed (monitored by GLC; >95%). After evaporation of unreacted vinyl acetate and ether, the cycloadducts were obtained in 70–96% yields by distilling the residue under reduced pressure (1 mmHg). The carbonyl absorptions in the IR spectra of the cycloadducts, which may be composed of four isomers, were at 1725 cm^{-1}.

General Procedure for Synthesis of [*n*.3.2]Propellanones. The cycloadducts of bicyclic enone **20** or **21** with vinyl acetate

---

[7] Cockerill, A. F.; Rackham, D. M. *Tetrahedron Lett.* **1970**, 5149.

[8] The quantum yields were not affected by added 1,3-pentadiene; therefore, the present photoreaction occurred from the n–π* singlet state.

[9] Greene, F. D.; Lowry, N. N. *J. Org. Chem.* **1967**, *32*, 875. Bartlett, P. D.; Pincock, R. D.; Rolston, J. H.; Schindel, W. G.; Singer, L. A. *J. Am. Chem. Soc.* **1965**, *87*, 2590.

[10] The enones **20**–**22** were prepared according to the procedure reported by Kulkarni and Dev,[10a] by Dev,[10b] and by Plattner and Büchi,[10c] respectively, and **23** was prepared by a method similar to that used for **22**. (a) Kulkarni, S. B.; Dev, S. *Tetrahedron* **1968**, *24*, 553. (b) Dev, S. *J. Indian Chem. Soc.* **1957**, *34*, 169. (c) Plattner, P. A.; Büchi, G. *Helv. Chim. Acta* **1946**, *29*, 1608.

[11] Varech, D.; Ouannes, C.; Jacques, J. *Bull. Soc. Chim. Fr.* **1965**, *32*, 1662.

were dissolved in 200 mL of MeOH. A 50% excess of tosylhydrazine was added and the resultant solution was refluxed for 3 h. After removal of MeOH, the residue was redissolved in 200 mL of THF, and a 20% excess of $LiAlH_4$ in limited amounts was added to the solution during 1 h. Then the mixture was refluxed for 12 h. After the mixture was cooled and 200 mL of 6 N H_2SO_4 was added, the mixture was extracted with ether. The extract was washed sequentially with dilute aqueous $NaHCO_3$ and saturated NaCl solution, dried (Na_2SO_4), and evaporated in vacuo to afford the cyclobutanols in 58 or 52% yield, respectively. However, in the case of **21**, the cyclobutanols, that is, the [4.3.2]propellanols, contained the unsaturated homologues in a 40% ratio, which were not separable by preparative GLC, so diimide reduction of the mixture was carried out by the use of 30 mL of 90% hydrazine hydrate, 0.3 mL of 5% copper sulfate solution, and bubbling of air in ethanol solution; the pure saturated cyclobutanols were obtained by column chromatography on silica gel in 63% yield. For the cycloadducts of bicyclic enones **22** and **23** with vinyl acetate, the Wolff-Kishner reduction procedure of Huang-Minlon was employed. The cyclobutanols were afforded in 87 and 61% yields, respectively. Although the Wolff-Kishner reduction of the cycloadducts given from **20** and **21** was attempted, it resulted in decomposition and contamination of the products. Jones oxidation of the obtainable cyclobutanols gave the desired [*n*.3.2]propellanones involving a cyclobutanone ring (**1**-**4**) in 32-62% yields. The propellanones were purified by column chromatography on silica gel (the eluent was composed of 3% ether and 97% petroleum-ether) and analyzed by GLC (column A, B, or C). Analytical and spectroscopic samples were obtained by preparative GLC (column D or F).

[3.3.2]Propellan-9-one (1). From enone **20** (8.0 g, 64 mmol), cyclobutanone **1** (2.7 g, 18 mmol) was obtained (the overall yield based on the reacted enone was 29%). **1**: mp 99-100 °C; IR (KBr) 1770 cm^{-1}; MS *m/e* 150 (M^+), 122, 108 (base); ^1H NMR (CCl_4) δ 1.30-2.20 (m, 12 H), 2.77 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.93 (t), 34.05 (t), 38.27 (t), 48.67 (s), 54.97 (t), 83.43 (s), 217.34 (s); UV (MeOH) λ_{max} 304 nm (ϵ 35). Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.56; H, 9.19.

[4.3.2]Propellan-10-one (2). From enone **21** (10.0 g, 73.5 mmol), cyclobutanone **2** (1.9 g, 12 mmol) was obtained (overall yield 16%). **2**: mp 29-30 °C; IR (neat) 1770 cm^{-1}; MS *m/e* 164 (M^+), 136, 122 (base); ^1H NMR (CCl_4) δ 1.20-2.20 (m, 14 H), 2.72 (d of d, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.08 (t), 20.60 (t), 24.95 (t), 27.48 (t), 32.49 (t), 37.10 (t), 38.66 (s), 40.48 (t), 55.36 (t), 69.72 (s), 217.20 (s); UV (MeOH) λ_{max} 298 nm (ϵ 41). Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.08; H, 9.98.

[5.3.2]Propellan-11-one (3). From enone **22** (10.5 g, 70.0 mmol), cyclobutanone **3** (3.2 g, 18 mmol) was obtained (overall yield 26%). **3**: mp 27-28 °C; IR (neat) 1770 cm^{-1}; MS *m/e* 178 (M^+), 150, 136 (base); ^1H NMR (CCl_4) δ 1.20-2.20 (m, 16 H), 2.70 (d of d, 2 H); UV (MeOH) λ_{max} 302 nm (ϵ 32). Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.61; H, 10.29.

[6.3.2]Propellan-12-one (4). From enone **23** (6.7 g, 41 mmol), cyclobutanone **4** (1.8 g, 9.4 mmol) was obtained (overall yield 23%). **4**: mp 73-74 °C; IR (KBr) 1770 cm^{-1}; MS *m/e* 192 (M^+), 164, 150 (base); ^1H NMR (CCl_4) δ 1.20-2.12 (m, 18 H), 2.68 (s, 2 H); UV (MeOH) λ_{max} 304 nm (ϵ 34). Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.33; H, 10.66.

General Procedure for Synthesis of [*n*.3.2]Propellanediones and Bicyclo[3.2.0]heptane-2,6-diones. Method A. The above-mentioned cycloadducts and the cycloadducts of 2,3-dimethylcyclopentenone with vinyl acetate were dissolved in 160 mL of THF, 3 N HCl (60 mL) was added, and the resultant solution was refluxed for 12 h. After the solution cooled and the THF was evaporated, the residue was extracted with ether. The ethereal layer was washed sequentially with dilute aqueous $NaHCO_3$ and saturated NaCl solution, dried (Na_2SO_4), and evaporated in vacuo to afford the keto cyclobutanols in 64-89% yields, which were isolated by distillation or column chromatography on silica gel. The keto cyclobutanols were oxidized with Jones reagent to give [*n*.3.2]propellanediones **5**-**8** and the bicyclic dione **25** in 33-45% yields. The products were purified by distillation, column chromatography on silica gel, or preparative GLC.

Method B. Photocycloaddition of cyclopentenone or bicyclic enone **23** with about a fivefold excess of diethoxyethylene in *n*-pentane was carried out at -70 °C by using a 500-W high-pressure Hg lamp through a Pyrex filter for 11 h under N_2. After evaporation of the reaction mixture, the distillation of the residue under reduced pressure gave the cycloadducts in 50 or 92% yield, respectively. The cycloadducts were hydrolyzed in 3 N HCl-THF solution, and after treatment as mentioned above, [6.3.2]propellanedione **8** or bicyclo[3.2.0]heptane-2,6-dione **24** was obtained in 36 or 33% yield, which was purified by silica gel column chromatography or distillation employing a spinning-band distillation column.

[3.3.2]Propellane-2,10-dione (5). From enone **20** (3.3 g, 27 mmol), 1.1 g (6.7 mmol) of **5** was obtained (overall yield 25%). **5**: mp 66-67 °C; IR (KBr) 1770, 1720 cm^{-1}; MS *m/e* 164 (M^+), 136, 122 (base); ^1H NMR (CCl_4) δ 1.40-3.00 (m, 10 H), 3.04 (d of d, 2 H); UV (MeOH) λ_{max} 298 nm (ϵ 52). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.13; H, 7.37.

[4.3.2]Propellane-7,10-dione (6). From enone **21** (6.7 g, 49 mmol), 1.9 g (11 mmol) of **6** was obtained (overall yield 22%). **6**: mp 54-55 °C; IR (KBr) 1770, 1730 cm^{-1}; MS *m/e* 178 (M^+), 150, 136 (base); ^1H NMR (CCl_4) δ 1.00-2.70 (m, 12 H), 3.00 (d of d, 2 H); UV (MeOH) λ_{max} 289 nm (ϵ 60). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.93. Found: C, 73.87; H, 8.27.

[5.3.2]Propellane-8,11-dione (7). From enone **22** (6.8 g, 45 mmol), 2.2 g (12 mmol) of **7** was obtained (overall yield 27%). **7**: mp 69-70 °C; IR (KBr) 1770, 1730 cm^{-1}; MS *m/e* 192 (M^+), 164, 150 (base); ^1H NMR (CCl_4) δ 1.20-2.60 (m, 14 H), 2.92 (d of d, 2 H); UV (MeOH) λ_{max} 296 nm (ϵ 51). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.15; H, 8.67.

[6.3.2]Propellane-9,12-dione (8). From enone **23** (6.8 g, 41 mmol), 2.6 g (13 mmol) of **8** was obtained (method B, overall yield 32%). **8**: mp 106-108 °C; IR (KBr) 1770, 1720 cm^{-1}; MS *m/e* 206 (M^+), 178, 164 (base); ^1H NMR (CCl_4) δ 1.00-2.60 (m, 16 H), 2.94 (s, 2 H); UV (MeOH) λ_{max} 291 nm (ϵ 56). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.30; H, 8.70.

Bicyclo[3.2.0]heptane-2,6-dione (24).[12] From 5.8 g (71 mmol) of cyclopentenone, 1.7 g (14 mmol) of **24** was obtained (method B, overall yield 20%). **24**: IR (neat) 1770, 1720 cm^{-1}; MS *m/e* 124 (M^+), 96, 82 (base); ^1H NMR (CCl_4) δ 2.00-2.50 (m, 4 H), 2.76-3.04 (m, 2 H), 3.32-3.92 (m, 2 H); UV (MeOH) λ_{max} 292 nm (ϵ 37).

1,5-Dimethylbicyclo[3.2.0]heptane-2,6-dione (25). From 4.9 g (44 mmol) of 2,3-dimethylcyclopentenone, 2.4 g (16 mmol) of **25** was obtained (overall yield 36%). **25**: mp 45-46 °C; IR (KBr) 1770, 1730 cm^{-1}; MS *m/e* 152 (M^+), 124, 110 (base); ^1H NMR (CCl_4) δ 1.16 (s, 3 H), 1.24 (s, 3 H), 1.40-1.74 (m, 1 H), 2.10-2.60 (m, 3 H), 2.96 (s, 2 H); UV (MeOH) λ_{max} 294 nm (ϵ 51). Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.65; H, 7.91.

General Irradiation Procedure in Methanol. Irradiation of 10^{-2} M methanol solutions of [*n*.3.2]propellanones **1**-**4**, [*n*.3.2]propellanediones **5**-**8**, and bicyclo[3.2.0]heptane-2,6-diones **24** and **25** was carried out in Pyrex tubes by using a 500-W high-pressure Hg lamp at 20 °C under N_2, and irradiation was continued for 1-3 h until the cyclobutanones were almost consumed (monitored by GLC; >95%). After removal of methanol, the residue was analyzed by GLC (column A or C) and the products were isolated by preparative GLC (column D, E, or F). Yields of the products were determined by GLC analysis on the basis of the reacted cyclobutanones at 20-30% conversion.

Irradiation of 1. Irradiation of **1** (120 mg, 0.8 mmol) gave 143 mg of a mixture of products composed of **9** (74%) and two esters, which were methyl 5-methylbicyclo[3.3.0]octane-1-carboxylate (**32**) (15%) and methyl 5-methylenecyclooctane-1-carboxylate (**33**) (10%). No cycloelimination product, i.e., bicyclo[3.3.0]oct-1-(5)-ene, was detected.

9: IR (neat) 1080, 1030 cm^{-1}; MS *m/e* 182 (M^+, no peak), 150, 121 (base); ^1H NMR (CCl_4) δ 1.16-2.10 (m, 14 H), 3.20 (s, 3 H), 4.90 (d, 1 H). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.33; H, 10.11.

32: IR (neat) 1720, 1180 cm^{-1}; MS *m/e* 182 (M^+), 150, 122, 79 (base); ^1H NMR (CCl_4) δ 0.96 (s, 3 H), 1.20-2.08 (m, 12 H), 3.60 (s, 3 H). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.29; H, 10.14.

---

(12) Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.

33: IR (neat) 3070, 1730, 1630, 1160, 880 cm^{-1}; MS *m/e* 182 (M$^+$), 150, 122, 81 (base); ^{1}H NMR (CCl$_4$) δ 1.40–2.30 (m, 12 H), 2.60 (m, 1 H), 3.56 (s, 3 H), 4.78 (s, 2 H). Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.89; H, 10.08.

Irradiation of 2. Irradiation of **2** (140 mg, 0.85 mmol) gave 157 mg of a product mixture composed of **10** (95%) and a trace of olefin **13**, which was identical with an authentic sample by GLC. **10**: IR (neat) 1090, 1030 cm^{-1}; MS *m/e* 196 (M$^+$, no peak), 164, 135 (base); ^{1}H NMR (CCl$_4$) δ 1.10–2.20 (m, 16 H), 3.24 (s, 3 H), 4.88 (t, 1 H). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.25; H, 10.39.

Irradiation of 3. Irradiation of **3** (135 mg, 0.76 mmol) gave 140 mg of a product mixture composed of **11** (88%) and **14** (10%), which was identified by comparing its retention time of GLC and IR spectra with those of an authentic sample.[13] **11**: IR (neat) 1090, 1040 cm^{-1}; MS *m/e* 210 (M$^+$, no peak), 178, 149 (base); ^{1}H NMR (CCl$_4$) δ 1.20–2.30 (m, 18 H), 3.22 (s, 3 H), 4.80 (m, 1 H). Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.08; H, 10.69.

Irradiation of 4. Irradiation of **4** (108 mg, 0.56 mmol) gave 86 mg of a product mixture composed of **12** (55%) and **15** (45%), which was identified by comparing its retention time of GLC and IR spectra with those of an authentic sample.[2e] **12**: IR (neat) 1095, 1040 cm^{-1}; MS *m/e* 224 (M$^+$, no peak), 192, 163, 149 (base); ^{1}H NMR (CCl$_4$) δ 1.30–2.40 (m, 20 H), 3.20 (s, 3 H), 4.76 (m, 1 H). Anal. Calcd for $C_{14}H_{24}O_2$: C, 75.07; H, 10.82. Found: C, 74.73; H, 10.58.

Irradiation of 5. Irradiation of **5** (140 mg, 0.85 mmol) gave 145 mg of a product mixture composed of a pair of epimers, **16a** (40%) and **16b** (35%), and bicyclic enone **20** (13%), which was identified by comparing its retention time of GLC and IR spectra with those of an authentic sample. In the following cases, the identification of the enones was undertaken in a similar manner. **16a** and **16b**: IR (neat) 1730, 1090 cm^{-1}; MS *m/e* 196 (M$^+$), 164, 136, 108 (base); ^{1}H NMR (CCl$_4$) δ 1.40–2.70 (m, 12 H), 3.23 (syn, **16a**) and 3.26 (anti, **16b**) (s, 3 H), 4.92 (m, 1 H). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.19; H, 8.42.

Irradiation of 6. Irradiation of **6** (170 mg, 0.96 mmol) gave 160 mg of a product mixture composed of a pair of epimers, **17a** (25%) and **17b** (16%), and bicyclic enone **21** (59%). **17a** and **17b**: IR (neat) 1730, 1090 cm^{-1}; MS *m/e* 210 (M$^+$), 178, 150, 122 (base); ^{1}H NMR (CCl$_4$) δ 1.00–2.60 (m, 14 H), 3.16 (syn, **17a**) and 3.24 (anti, **17b**) (s, 3 H), 4.72 (anti, **17b**) and 4.80 (syn, **17a**) (d, 1 H). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.76; H, 8.82.

Irradiation of 7. Irradiation of **7** (123 mg, 0.64 mmol) gave 120 mg of a product mixture composed of a pair of epimers, **18a** (22%) and **18b** (13%), and a bicyclic enone **22** (65%). **18a** and **18b**: IR (neat) 1730, 1090 cm^{-1}; MS *m/e* 224 (M$^+$), 192, 164, 136 (base); ^{1}H NMR (CCl$_4$) δ 1.40–2.80 (m, 16 H), 3.20 (syn, **18a**) and 3.25 (anti, **18b**) (s, 3 H), 4.78 (m, 1 H). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.68; H, 9.15.

Irradiation of 8. Irradiation of **8** (144 mg, 0.70 mmol) gave 132 mg of a product mixture composed of a pair of epimers, **19a** (9%) and **19b** (5%), and bicyclic enone **23** (86%). **19a** and **19b**: IR (neat) 1730, 1095, 1045 cm^{-1}; MS *m/e* 238 (M$^+$), 206, 178, 150 (base); ^{1}H NMR (CCl$_4$) δ 1.00–2.60 (m, 18 H), 3.18 (syn, **19a**) and 3.23 (anti, **19b**) (s, 3 H), 4.72 (m, 1 H). Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.55; H, 9.31. Found: C, 70.41; H, 9.27.

Irradiation of 24. Irradiation of **24** (115 mg, 0.93 mmol) afforded mainly a pair of epimers, **26a** (24%) and **26b** (57%). A trace of cyclopentenone **28** generated through cycloelimination and small amounts of the further reaction products,[3c] which were aldehydes and acetals formed by cleavage of the cyclopentanone ring of acetals **26a** and **26b**, were detected. **26a** and **26b**: IR (neat) 1725, 1195, 1080 cm^{-1}; MS *m/e* 156 (M$^+$), 124, 96, 68 (base); ^{1}H NMR (CCl$_4$) δ 1.80–2.64 (m, 7 H), 3.15 (syn, **26a**) and 3.20 (anti, **26b**) (s, 3 H), 4.64–4.88 (m, 2 H). Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.20; H, 7.93.

Irradiation of 25. Irradiation of **25** (180 mg, 1.18 mmol) gave 190 mg of a product mixture composed of a pair of epimers, **27a** (42%) and **27b** (25%), and bicyclic enone **29** (33%). **27a** and **27b**: IR (neat) 1735, 1250 cm^{-1}; MS *m/e* 184 (M$^+$), 152, 124, 96 (base); ^{1}H NMR (CCl$_4$) δ 0.94 (syn, **27a**) and 0.98 (anti, **27b**) (s, 3 H), 1.20 (syn, **27a**) and 1.34 (anti, **27b**) (s, 3 H), 1.60–2.70 (m, 6 H), 3.16 (syn, **27a**) and 3.24 (anti, **27b**) (s, 3 H), 4.68 (d, 1 H). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.30; H, 8.89.

Quantum Yield Measurement. The quantum yields for disappearance of **5** and **8** were measured according to the method of Jones et al.[3g] employing a merry-go-round apparatus and valerophenone as the actinometer.[14]

Registry No. **1**, 71734-13-9; **2**, 71734-14-0; **3**, 71734-15-1; **4**, 71734-16-2; **5**, 71734-17-3; **6**, 71734-18-4; **7**, 71734-19-5; **8**, 71734-20-8; **9**, 71734-21-9; **10**, epimer 1, 71734-22-0; **10**, epimer 2, 71772-40-2; **11**, epimer 1, 71734-23-1; **11**, epimer 2, 71772-41-3; **12**, epimer 1, 71734-24-2; **12**, epimer 2, 71772-42-4; **14**, 7125-60-2; **15**, 25107-10-2; **16a**, 71734-25-3; **16b**, 71772-43-5; **17a**, 71734-26-4; **17b**, 71772-44-6; **18a**, 71734-27-5; **18b**, 71772-45-7; **19a**, 71734-28-6; **19b**, 71772-46-8; **20**, 10515-92-1; **21**, 22118-00-9; **22**, 769-32-4; **23**, 38262-50-9; **24**, 932-38-7; **25**, 71734-29-7; **26a**, 71734-30-0; **26b**, 71772-47-9; **27a**, 71734-31-1; **27b**, 71772-48-0; **29**, 1121-05-7; **32**, 71734-32-2; **33**, 53343-46-7; vinyl acetate, 108-05-4; diethoxyethylene, 16484-86-9; pentane, 109-66-0; cyclopentenone, 930-30-3.

---

(13) Mayer, R.; Töpelmann, W. *Chem. Ber.* **1958**, *91*, 1764.

(14) Wagner, P. J.; Kelso, P. A.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 7480.