stages with isotropic and anisotropic thermal parameters. Difference maps were used to locate the hydrogen atoms, which were then refined with isotropically thermal parameters.

Because of the size of the structure and limitations in computer core space, the least-squares refinements were carried out by a blocked full-matrix method, using the computer program SHELX. The scattering factors were taken from the "International Tables", Vol. 4, pp 99 and 149. The weighting scheme used was $W_F = K/(\sigma_F)^2$, where $\sigma_F = {}^1/_2[\{\sigma^2 + (0.04P)^2\}/[(P)(L_p)]]^{1/2}$ and $\sigma = T^{1/2}v$, where v = scan speed, $T = P_k + 4(R + L)$, $P = [P_k - 2(R + L)]v$, P_k = peak height, R = right background, L = left background, L_p = Lorentz and polarization. The factor K was redetermined after each structure factor calculation and was 0.134 after the final cycle of refinement.

The variance was calculated as shown by

$$v = \{M\sum[W_F(|F_o| - |F_c|)^2]/N\sum W_f\}^{1/2}$$

where N is the number of reflections in a group, M is the total number of reflections, the sum in the numerator is over all the reflections in a group, and the sum in the denominator is over all the reflections. An analysis of the variance in terms of the parity of the reflection indices, sin θ, and $[F_o/F_{max}]^{1/2}$ showed no significant variation of v for various ranges of the functions tested. Refinement was terminated when all parameter shifts were less than 0.075 of their corresponding standard deviations. The final value of R for all 5948 reflections was 0.055 and for R_W, where $R_W = \sum W_F^{1/2}[|F_o| - |F_c|]/\sum W_f^{1/2}|F_o|$ was 0.047. The final positional parameters are given in Table IV.

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Registry No. 2, 78737-62-9; *cis*-2,6-diphenyltetrahydrothiapyran-4-one, 18456-44-5.

Supplementary Material Available: Hydrogen atom parameters, anisotropic thermal parameters, and molecular dimensions of the benzene molecules of solvation (5 pages). Ordering information is given on any current masthead page.

Acid-Catalyzed Rearrangement of [5.*n*.2]Propella-ε-lactones

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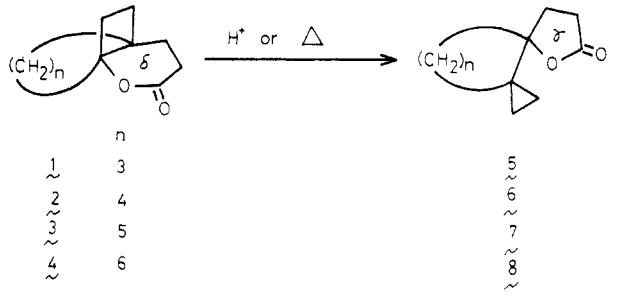
The acid-catalyzed rearrangement of [5.3.2]- and [5.4.2]propella-ε-lactones **9** and **10** in boiling acetic acid takes place readily to afford the 1,2-disubstituted cyclopentene **21** and cyclohexene **26** as the major products, respectively, while such lactone ring cleavage of the [4.3.2]- and [4.4.2]propella-δ-lactones **1** and **2** does not occur at all under similar conditions. The remarkable distinction in reactivity in the acid-catalyzed rearrangement between the ε-lactones and the δ-lactones is attributed to the effect of lactone ring size.

In a continuation of the studies on the transformation of readily available [*n*.3.2]propellanes into other important polycarbocyclic ring systems,[1] we reported the first example of the cyclobutyl–cyclopropylcarbinyl rearrangement of some propella-δ-lactones, **1**–**4**, composed of a cyclobutane ring, a δ-lactone ring, and one five- to eight-membered ring as the third ring, to the corresponding dispiro γ-lactones **5**–**8**.[2] In these reactions, under acidic conditions (in acetic acid at reflux for 72 h)[2a] unlike under thermal conditions,[2b] only [4.4.2]propella-δ-lactone **2** rearranged to give the dispiro γ-lactone **6**. This remarkable distinction of propella-δ-lactones **1**–**4** in reactivity toward acid could be explained on the basis of the steric effect of the third ring. Namely, it was inferred that the steric effect of the third ring reinforced the puckered geometry of the cyclobutane ring in the δ-lactones which was desirable for the rearrangement to the γ-lactones. In particular, this was the case in **2** because of the steric requirement of the cyclohexane ring to adopt the chair conformation.

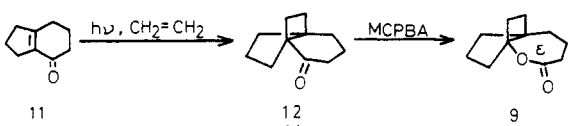


	n	
1	3	5
2	4	6
3	5	7
4	6	8

As an extension of the above reaction, we describe here the acid-catalyzed rearrangement involving the lactone ring cleavage of [5.3.2]- and [5.4.2]propella-ε-lactones **9** and **10**, higher homologues of the δ-lactones **1** and **2**, leading to the 1,2-disubstituted cyclopentene **21** and cyclohexene **26**, respectively. In addition, it is emphasized that the effect of lactone ring size, rather than the steric factor of the third ring, is the dominant factor in the present rearrangement.

Results and Discussion

The ε-lactone **9** was prepared in a manner[2b] similar to that for the δ-lactones: photocycloaddition of bicyclo[4.3.0]non-1(6)-en-2-one (**11**) to ethylene (91%), followed by the Baeyer–Villiger oxidation of the propellanone **12** with *m*-chloroperbenzoic acid (MCPBA) in chloroform.



11 12 9

(1) (a) Sakai, Y.; Toyotani, S.; Tobe, Y.; Odaira, Y. *Tetrahedron Lett.* **1979**, 3855. (b) Tobe, Y.; Hayauchi, Y.; Sakai, Y.; Odaira, Y. *J. Org. Chem.* **1980**, *45*, 637. (c) Sakai, Y.; Tobe, Y.; Odaira, Y. *Chem. Lett.* **1980**, 691. (d) Tobe, Y.; Terashima, K.; Sakai, Y.; Odaira, Y. *J. Am. Chem. Soc.* **1981**, *103*, 2307.

(2) (a) Tobe, Y.; Kakiuchi, K.; Kawakami, Y.; Sakai, Y.; Kimura, K.; Odaira, Y. *Chem. Lett.* **1978**, 1027. (b) Kakiuchi, K.; Tobe, Y.; Odaira, Y. *J. Org. Chem.* **1980**, *45*, 729.

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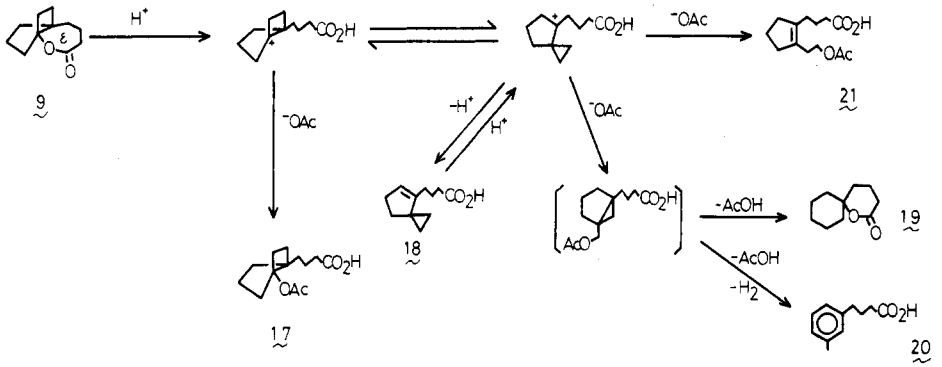
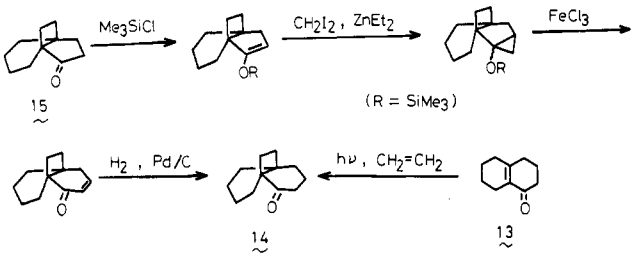
Scheme I

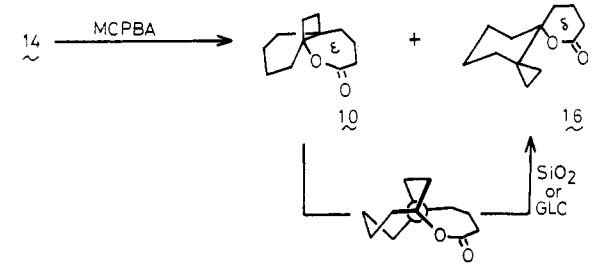


However, in the case of the ε-lactone **10**, the corresponding propellanone **14** was prepared by the ring enlargement[3] of readily available [4.3.2]propellanone (**15**)



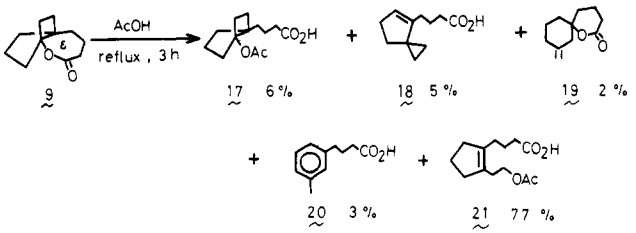
because of the inefficiency of the photocycloaddition of bicyclo[4.4.0]dec-1(6)-en-2-one (**13**) to ethylene (29%). The process leading to **14** is the following: (i) preparation of the trimethylsilyl enol ether of **15** (79%), (ii) cyclopropanation of the enol ether by the Furukawa method (69%),[4] (iii) oxidative cleavage of the siloxycyclopropane with iron(III) chloride (82%),[5] and (iv) catalytic hydrogenation of the [4.4.2]propellenone (84%).

Significantly, the subsequent Baeyer–Villiger oxidation of **14** with MCPBA in chloroform, followed by purification by column chromatography on silica gel,[6] led to the formation of two products, the expected ε-lactone **10** (32%) and the dispiro δ-lactone **16** (52%) which was formed via

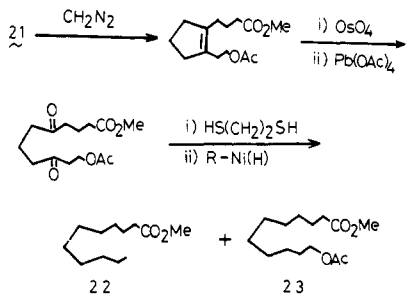


the cyclobutyl–cyclopropylcarbinyl rearrangement of **10** with silica gel catalysis. Moreover, it has been ascertained that **10**, having a cyclohexane ring, rearranges readily under GLC conditions (10% FFAP on Uniport B, 180 °C) or on being allowed to stand for a long time at room temperature (traced by ^{1}H NMR analysis). This should be contrasted with the fact that the ε-lactone **9**, having a cyclopentane ring, was quite stable under the above conditions.[7] Evidently, the facility of the rearrangement of the ε-lactone **10**, in analogy with the δ-lactone **2**,[2b] is due to the steric effect of the cyclohexane ring enforcing the more puckered conformation of the cyclobutane ring which is favorable for the rearrangement.

In order to obtain information on the acid-catalyzed rearrangement of the propella-ε-lactones under conditions similar to those of the case of the propella-δ-lactones, we undertook the reaction of **9** and **10** in boiling acetic acid. When a solution of **9** in acetic acid was heated at reflux for 3 h (after which time the starting lactone was almost consumed), interestingly, the five products **17**–**21**, involving 1,2-disubstituted cyclopentene **21** as the major product (77%), were obtained in 93% combined yield.



The structures of these compounds were determined by spectral and analytical data (for **17**–**19** and **21**) or by comparison with an authentic sample (for **20**). The structure of the major product, **21**, was further confirmed by degradation of **21** to methyl undecanoate (**22**) and methyl 11-acetoxyundecanoate (**23**) as shown. Osmium



tetraoxide oxidation followed by lead tetraacetate oxidation of the methyl ester of **21** and subsequent thioketal reduction of the 1,5-diketone gave two kinds of esters in a ratio of 85:15 which were identical with **22** and **23**, respectively.[8]

For the purpose of elucidating the reaction path, the change of the product distribution during the course of the rearrangement of **9** as well as the product distribution in the reaction of the isolated products such as **17**–**19** and **21**

(3) Hiyama, T.; Nozaki, H. *Yuki Gosei Kagaku Kyokaishi* **1977**, *35*, 979.
(4) Ryu, I.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1977**, 4611.
(5) Ito, Y.; Fujii, S.; Saegusa, T. *J. Org. Chem.* **1976**, *41*, 2073.
(6) IR and ^{1}H NMR spectra of this crude product before purification did not show any signals assigned to a cyclopropane ring.
(7) The δ-lactones **1** and **2** were quite stable under mild conditions such as on silica gel or under GLC conditions as well.
(8) The authentic sample of the latter was prepared by the hydroboration–oxidation of methyl undec-10-enoate followed by the acetylation.

Table I. Acid-Catalyzed Rearrangement of 9, 17-19, and 21

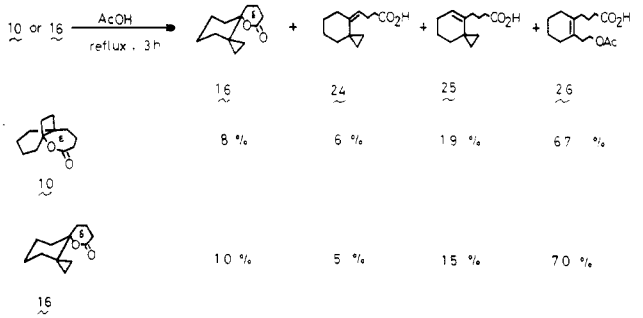
starting material	reaction time	product distribution, %[a] 9	17	18	19	20	21
9[b]	10 min	85	2	8			5
	30 min	54	4	15	3	3	21
	1 h	40	6	13	3	3	35
	3 h	8	6	5	2	3	76
17	3 h		100				
18[b]	3 h		6	13	3	6	72
19	3 h				100		
21	3 h						100

[a] Mole percent of identified products. [b] A small amount of unidentified products was obtained (<4%).

in acetic acid (reflux, 3 h) was determined as summarized in Table I. Judging mainly from the facts that the yield of cyclopentene **21** increased with increasing reaction time and the product distribution obtained from the reaction of **18** after 3 h was similar to that from **9**, it is reasonable to consider that the reaction proceeds according to Scheme I. Namely, the bicyclo[3.2.0]hept-1-yl cation initially formed by ring opening of the ϵ-lactone with acid rearranges to a cyclopropylcarbinyl cation, followed by attack of acetic acid (or acetate anion) on the cyclopropane ring, concerted with ring cleavage and/or rearrangement. Then the major product **21**, which is the most thermodynamically stable one, may be finally formed. The other products, **17**–**19** and **20**, may be derived from the respective cations or may arise by elimination of acetic acid from the intermediate as shown in Scheme I. The present scheme bears a striking resemblance to the reaction scheme via bicyclo[3.2.0]hept-1-yl cation proposed in the solvolysis of bicyclo[3.2.0]hept-1-yl 3,5-dinitrobenzoate by Wiberg et al.[9]

Interestingly, the rearrangement of the ϵ-lactone **9** proceeds smoothly via lactone ring cleavage, though the corresponding δ-lactone **1** was recovered unchanged under similar conditions.[2a] From the above fact, it is obvious that the reactivity of the propellalactones for the rearrangement is governed by the effect of lactone ring size rather than the steric effect of the third ring described above.

Moreover, the treatment of the ϵ-lactone **10** under the above conditions gave a small amount of the dispiro δ-lactone **16** and three kinds of lactone ring-cleaved acids (**24**–**26**) with **26** as the major product (67%).

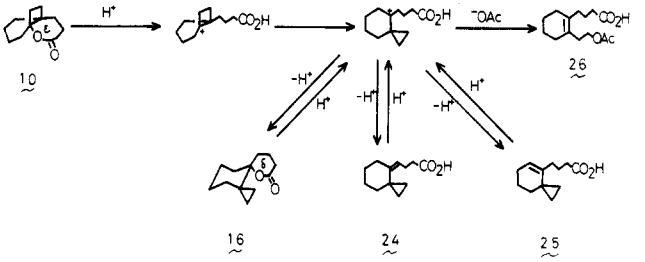


For elucidation of the course of the reaction, the change of the product distribution during the course of the rearrangement of **10** and the product distribution in the reaction of isolated compounds such as **24**–**26** were similarly determined as summarized in Table II. From the fact that the yield of cyclohexene **26** increased with increasing reaction time and the reaction of **16**, **24**, and **25** under similar

Table II. Acid-Catalyzed Rearrangement of 10, 16, and 24-26

starting material	reaction time, h	product distribution, % 16	24	25	26
10	3	8	6	19	67
	72	4	2	2	92
16	3	10	5	15	70
24	3	6	12	24	58
25	3	8	8	24	60
26	3				100

Scheme II



conditions furnished a product distribution similar to that from **10**, the observed products are considered to be derived from the rearrangement through a cyclopropylcarbinyl-type cation as shown in Scheme II.

The facility of the rearrangement of **10** via lactone ring cleavage should be contrasted with the reactivity of the corresponding δ-lactone **2** which only gave the dispiro γ-lactone **6** without any formation of lactone ring-cleavage products.[2a] Furthermore, the acid-catalyzed rearrangement of the dispiro δ-lactone **16** mainly gave ring-cleavage products, while that of the dispiro γ-lactone **6** gave only a little **2**.[10] These results show an additional factor related to lactone ring size in the spiro lactone intermediates (or products). Namely, the product distribution in these propellalactones is presumably governed by the stability (and/or the rate of cyclization from the intermediate carbonium ion) of the rearranged dispiro lactones. For example, in the case of δ-lactone **2**, the lactone ring cleaves to give a carbonium ion, which rearranges and then recloses to give the stable dispiro γ-lactone **6** (five-membered-ring formation). On the other hand, in the case of the ϵ-lactone **10** or **9**, the reclosing from cyclopropylcarbinyl cation intermediates to the dispiro δ-lactone **16** or the hypothetical dispiro δ-lactone may be less favorable (six-membered-ring formation), and the recyclization from them to **10** or **9** seems unlikely to occur (seven-membered-ring formation). As a result, further ring cleavage of the carbonium ion intermediates takes place predominantly.

In conclusion, the two factors governing the skeletal rearrangement of the propellalactones have been elucidated. One is the steric effect of the third ring on the geometry of the cyclobutane ring, and the other is the effect of lactone ring size toward acid-catalyzed cleavage. But the latter is the dominant factor. Finally, the utilization of the 1,2-disubstituted cyclopentene **21** and cyclohexene **26** to synthesize some valuable compounds[11] is now being undertaken.

Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were recorded on a JASCO IR-G spectrometer as liquid films unless otherwise stated. ^{1}H NMR spectra were obtained on a

(9) Wiberg, K. B.; Hiatt, J. E.; Hseih, K. *J. Am. Chem. Soc.* **1970**, *92*, 544.

(10) Unpublished result.

(11) For example, **21** and **26** would be useful intermediates for the synthesis of prostaglandin and thromboxane derivatives, respectively.

JEOL JNM-PS-100 spectrometer, with Me_4Si as an internal standard and CCl_4 as a solvent. Mass spectra were measured with a Hitachi RMU-6E spectrometer. Analytical GLC was carried out on a Hitachi 163 gas chromatograph, and preparative GLC separation was conducted on a Varian Aerograph 920 gas chromatograph.

Bicyclo[4.3.0]non-1(6)-en-2-one (11) and bicyclo[4.4.0]dec-1-(6)-en-2-one (13) were prepared according to the method of Hill and Conley.[12] [4.3.2]Propellanone (15) was prepared as previously described.[13]

[4.3.2]Propellanone (12). A solution of 14.8 g (0.11 mol) of the enone 11 in 270 mL of methylene chloride was irradiated (Pyrex filter) at −70 °C for 25 h while ethylene was bubbled into the solution. After removal of the solvent, the residue was distilled under reduced pressure to give 16.2 g (91%) of the propellanone 12: bp 67–70 °C (3 mm); IR 1680 cm^{-1}; NMR δ 1.18–2.60 (m); mass spectrum, m/e 164 (M^+); semicarbazone, mp 220–221 °C. Anal. Calcd for $C_{12}H_{19}ON_3$: C, 65.12; H, 8.65; N, 18.99. Found: C, 64.88; H, 8.61; N, 19.01.

[4.4.2]Propellanone (14).[14] **(1) By Photocycloaddition.** A solution of 6.4 g (0.043 mol) of the enone 13 was irradiated for 11 h as described for 12. Distillation gave 2.2 g of the propellanone 14 (29%).

(2) By Ring Enlargement of 15. Trimethylsilyl Enol Ether of 15.[15] To a solution of 25.5 g (0.24 mol) of chlorotrimethylsilane and 45.4 g (0.45 mol) of triethylamine in 100 mL of dimethylformamide was added 31.8 g (0.19 mol) of the ketone 15 under a nitrogen atmosphere. The resulting mixture was refluxed with stirring for 42 h (monitored by GLC) and then cooled, diluted with 200 mL of pentane, and washed with three portions of cold saturated sodium hydrogen carbonate ($NaHCO_3$) solution. The aqueous washes were extracted with pentane, and the combined organic layer was washed rapidly in succession with cold 1.5 N HCl and cold saturated $NaHCO_3$ solution. After the mixture was dried over anhydrous sodium sulfate (Na_2SO_4), the solvent was evaporated in vacuo, and the residue was distilled under reduced pressure to yield 36.4 g (79%) of the trimethylsilyl enol ether of 15: bp 79 °C (3 mm); IR 1615, 1230 cm^{-1}; NMR δ 0.18 (s, 9 H), 0.80–2.16 (m, 14 H), 4.43 (t, 1 H); mass spectrum, m/e 236 (M^+). Anal. Calcd for $C_{14}H_{24}OSi$: C, 71.12; H, 10.23. Found: C, 71.17; H, 10.54.

Siloxycyclopropane.[4] To a stirred solution of 36.0 g (0.15 mol) of the above enol ether in 400 mL of hexane was added 37.1 g (30.7 mL, 0.30 mol) of diethylzinc by use of a syringe under a nitrogen atmosphere. Then 56.3 g (0.21 mol) of methylene iodide was added dropwise during about 30 min, and the resulting solution was stirred for 38 h at room temperature. The reaction was quenched by addition of cold ammonium chloride solution, and the solution was washed with saturated $NaHCO_3$ solution and water and dried (Na_2SO_4). After removal of the solvent in vacuo, the residue was distilled under reduced pressure to yield 26.4 g (69%) of siloxycyclopropane: bp 93 °C (3.5 mm); IR 3050, 1220 cm^{-1}; NMR δ 0.12 (s, 9 H), 0.40–0.96 (m, 2 H), 1.00–2.40 (m, 15 H); mass spectrum, m/e 250 (M^+). Anal. Calcd for $C_{15}H_{26}OSi$: C, 71.93; H, 10.46. Found: C, 72.00; H, 10.76.

[4.4.2]Propellenone.[5] To a stirred solution of 48.7 g (0.30 mol) of anhydrous iron(III) chloride in 200 mL of dimethylformamide was added dropwise a solution of 26.0 g (0.10 mol) of the above siloxycyclopropane and 8.1 mL (0.10 mol) of pyridine in 200 mL of dimethylformamide over 3.5 h at 0–10 °C under a nitrogen atmosphere. The resulting brown solution was stirred at room temperature for 1 h and then poured into cold 1 N HCl, and the mixture was extracted with chloroform. The organic layer was washed with 1 N HCl and water and dried (Na_2SO_4). After removal of the solvent in vacuo, the residue was distilled under reduced pressure to yield 15.2 g (82%) of [4.4.2]propellenone: bp 109 °C (5 mm); IR 3050, 1640, 770 cm^{-1}; NMR δ 0.90–2.60 (m, 14 H), 6.00 (dt, 1 H), 6.72 (m, 1 H); mass spectrum, m/e 176 (M^+). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.41; H, 9.00.

[4.4.2]Propellanone (14). A 15.0-g (0.085 mol) sample of the above propellenone was hydrogenated in 150 mL of methanol in the presence of 5% palladized carbon (catalytic amount) at room temperature under an atmospheric pressure of hydrogen. Filtration, concentration of the filtrate in vacuo, and subsequent chromatography of the residue on silica gel gave 12.8 g (84%) of 14. The GLC retention time and IR spectra were identical with those of the ketone which was prepared by the photocycloaddition.

[5.3.2]Propella-ε-lactone (9). A solution of 8.2 g (0.05 mol) of the ketone 12 and 2.5-fold excess of MCPBA in 350 mL of chloroform was stirred at room temperature for 6 days. The solution was washed with saturated sodium sulfite solution, saturated $NaHCO_3$ solution, and water. After the mixture was dried (Na_2SO_4), the solvent was removed in vacuo, and the residue was chromatographed on silica gel. Elution with 20% ether–petroleum ether gave 8.6 g (96%) of the ε-lactone 9 as a white solid: mp 60–61 °C (recrystallized from petroleum ether); IR (KBr) 1700 cm^{-1}; NMR δ 1.24–2.16 (m, 14 H), 2.24–2.60 (m, 2 H); mass spectrum, m/e 180 (M^+). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.33; H, 9.17.

[5.4.2]Propella-ε-lactone (10) and 5-Oxadispiro[2.0.5.4]-tridecan-6-one (16). Ketone 14 (5.8 g, 0.033 mol) was oxidized as described for 9. After the usual workup, the crude product was chromatographed on silica gel (20% ether–petroleum ether) to yield 2.0 g (32%) of the ε-lactone 10 and 3.3 g (52%) of the δ-lactone 16.

10: mp 34.5–35.5 °C; IR (KBr) 1700 cm^{-1}; NMR δ 0.90–2.54 (m); mass spectrum, m/e 194 (M^+). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.21; H, 9.42.

16: IR 3050, 1720 cm^{-1}; NMR δ 0.15–0.60 (m, 3 H), 0.90–1.20 (m, 2 H), 1.30–2.12 (m, 11 H), 2.18–2.60 (m, 2 H); mass spectrum, m/e 194 (M^+). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.89; H, 9.41.

Acid-Catalyzed Rearrangement of ε-Lactone 9. A solution of 135 mg (0.75 mmol) of the ε-lactone 9 in 5 mL of acetic acid was heated at reflux for 3 h. After removal of the solvent in vacuo, the residue was analyzed by GLC (3 mm × 1 m column, 10% FFAP) with octacosane as an internal standard. Five products, 4-(5-acetoxybicyclo[3.2.0]heptyl)butyric acid (17, 6%), 4-(4-spiro[2.4]hept-4-enyl)butyric acid (18, 5%), 8-methylene-1-oxaspiro[5.5]undecan-2-one (19, 2%), *m*-tolylbutyric acid (20, 3%), and 4-[2-(2-acetoxyethyl)cyclopent-1-enyl]butyric acid (21, 77%), were obtained (conversion 93%). The product distribution was recorded at appropriate intervals, and the results are summarized in Table I. The products were separated by column chromatography on silica gel and purified by preparative GLC.

17: IR 3500–2500, 1720, 1690, 1230 cm^{-1}; NMR δ 1.12–1.90 (m, 10 H), 1.92 (s, 3 H), 1.96–2.60 (m, 6 H), 11.50 (br s, 1 H); mass spectrum, m/e 180 ($M^+ - 60$). The methyl ester of 17 was prepared by the treatment with ethereal diazomethane: IR 1720, 1240, 1160 cm^{-1}; NMR δ 1.00–1.88 (m, 9 H), 1.92 (s, 3 H), 1.94–2.64 (m, 7 H), 3.64 (s, 3 H); mass spectrum, m/e 194 ($M^+ - 60$). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.11; H, 8.62.

18: IR 3500–2500, 1690, 1650, 870 cm^{-1}; NMR δ 0.32–0.76 (m, 4 H), 1.40–2.00 (m, 6 H), 2.20–2.56 (m, 4 H), 5.36 (m, 1 H),[16] 11.84 (br s, 1 H); mass spectrum, m/e 180 (M^+). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.29; H, 8.97.

19: IR 3050, 1720, 1645, 890 cm^{-1}; NMR δ 1.98–2.60 (m, 14 H), 4.67 (s, 1 H), 4.73 (s, 1 H); mass spectrum, m/e 180 (M^+). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.23; H, 9.00.

20: IR 3500–2500, 1690, 1600, 770, 690 cm^{-1}; NMR δ 1.60–2.76 (m, 9 H), 6.78–7.20 (m, 4 H), 11.56 (br s, 1 H); mass spectrum, m/e 178 (M^+). The spectral data were identical with those of an authentic sample which was prepared according to the literature.[18]

21: IR 3500–2500, 1720, 1690, 1230 cm^{-1}; NMR δ 1.50–1.88 (, 4 H), 1.96 (s, 3 H), 2.00–2.48 (m, 10 H), 4.00 (t, 2 H), 10.30 (br

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s, 1 H); mass spectrum, m/e 240 (M^+). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.71; H, 8.59. The methyl ester of **21** was prepared by the treatment with ethereal diazomethane: IR 1725, 1230, 1160 cm^{-1}; NMR δ 1.50–1.88 (m, 4 H), 1.96 (s, 3 H), 2.00–2.48 (m, 10 H), 3.60 (s, 3 H), 4.00 (t, 2 H); mass spectrum, m/e 254 (M^+). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 65.86; H, 8.96.

Acid-Catalyzed Rearrangement of ε-Lactone 10 and δ-Lactone 16. The reaction of 236 mg (1.22 mmol) of **10** or 237 mg (1.22 mmol) of **16** in 5 mL of acetic acid was carried out in a manner similar to that of **9**. After removal of the solvent in vacuo, the residue was chromatographed on silica gel to give the following products. Compound **10** gave, 19 mg (8%) of **16**, 16 mg (6%) of 4-(4-spiro[2.5]octylidene)butyric acid (**24**), 45 mg (19%) of 4-(4-spiro[2.5]oct-4-enyl)butyric acid (**25**), and 215 mg (67%) of 4-[2-(2-acetoxyethyl)cyclohex-1-enyl]butyric acid (**26**). Compound **16** gave, 10 mg (4%) of **24**, 45 mg (14%) of **25**, and 214 mg (69%) of **26**, and 23 mg (10%) of **16** was recovered. The products were purified by preparative GLC. The product distribution was recorded as described above, and the results are summarized in Table II.

24: IR 3500–2500, 1680, 1630, 1250, 890 cm^{-1}; NMR δ 0.28 (t, 2 H), 0.48 (t, 2 H), 1.20–1.88 (m, 6 H), 1.96–2.50 (m, 6 H), 4.98 (t, 1 H), 11.20 (br s, 1 H); mass spectrum, m/e 194 (M^+). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.84; H, 9.38.

25: mp 41.5–42.5 °C (recrystallized from pentane); IR 3500–2500, 1670, 1630, 1250, 870 cm^{-1}; NMR δ 0.35 (t, 2 H), 0.72 (t, 2 H), 1.30–1.84 (m, 8 H), 1.98–2.36 (m, 4 H), 5.36 (t, 1 H), 11.64 (br s, 1 H); mass spectrum, m/e 194 (M^+). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.17; H, 9.35.

26: IR 3500–2500, 1720, 1690, 1220 cm^{-1}; NMR δ 1.40–1.90 (m, 6 H), 1.94 (s, 3 H), 1.96–2.40 (m, 10 H), 3.96 (t, 2 H), 10.36 (br s, 1 H); mass spectrum, m/e 254 (M^+). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.08; H, 8.91. The methyl ester of **26** was prepared by treatment with ethereal diazomethane: IR 1725, 1220, 1150 cm^{-1}; NMR δ 1.42–1.90 (m, 6 H), 1.94 (s, 3 H), 1.98–2.36 (m, 10 H), 3.60 (s, 3 H), 3.96 (t, 2 H); mass spectrum, m/e 268 (M^+). Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.02. Found: C, 67.09; H, 9.22.

Degradation of the Methyl Ester of 21. A solution of 254 mg (1.00 mmol) of the methyl ester of **21** and 256 mg (1.01 mmol) of osmium tetraoxide in 3.9 mL of pyridine was stirred in the dark at room temperature for 67 h. To this solution was added a mixture of 0.46 g of sodium hydrogensulfite, 7.7 mL of water, and 5.1 mL of pyridine. The resulting solution was stirred for an additional 6 h and extracted with chloroform. The organic layer was washed with water, dried over potassium carbonate (K_2CO_3), and concentrated in vacuo. The residue was chromatographed on silica gel (50% ether–petroleum ether) to give 181 mg (63%) of the corresponding diol: IR 3450, 1720, 1220 cm^{-1}; NMR δ 1.10–1.92 (m, 12 H), 1.99 (s, 3 H), 2.31 (t, 2 H), 3.00 (br s, 2 H), 3.63 (s, 3 H), 4.20 (t, 2 H); mass spectrum, m/e 256 ($M^+ - 32$).

To a rapidly stirred solution of 113 mg (0.39 mmol) of the above diol in 8 mL of benzene was added 200 mg (0.45 mmol) of lead tetraacetate in 8 mL of benzene. The mixture was stirred for 1 h at room temperature and filtered. The filtrate was dried (K_2CO_3) and concentrated in vacuo to yield a light brown solid. Recrystallization from petroleum ether–acetone gave 83 mg (83%) of the corresponding diketone: mp 57 °C; IR (KBr) 1710, 1690 cm^{-1}; NMR δ 1.20–1.96 (m, 4 H), 1.96 (s, 3 H), 2.12–2.72 (m, 10 H), 3.61 (s, 3 H), 4.22 (t, 2 H); mass spectrum, m/e 226 ($M^+ - 60$). Anal. Calcd for $C_{14}H_{22}O_6$: C, 58.73; H, 7.75. Found: C, 58.50; H, 7.76.

A solution of 139 mg (0.49 mmol) of the above diketone and a small amount of hydroquinone in 0.4 mL of ethylene dithioglycol was added dropwise to 0.3 mL of the cooled boron trifluoride etherate. The resulting solution was stirred at room temperature for 34 h. The reaction was quenched with 10% K_2CO_3 solution, and the mixture was extracted with benzene. The organic layer was washed with brine, dried (Na_2SO_4), and concentrated in vacuo to yield 297 mg of the crude diethylene thioketal (IR 1720, 670 cm^{-1}) which was used directly in the next reaction.

The above thioketal was dissolved in 100 mL of ethanol and heated at reflux for 4 h with about 7 g of Raney nickel (W-4). The mixture was filtered, and the filtrate was concentrated in vacuo to yield 61 mg of a mixture of methyl undecanoate (**22**, 46%) and methyl 11-acetoxyundecanoate (**23**, 8%). Spectral data and GLC retention times of the two products were identical with those of the authentic samples prepared as described below.

Methyl 11-Acetoxyundecanoate (23). To a suspension of 12.0 g (0.061 mol) of methyl undec-10-enoate and 0.69 g (0.020 mol) of sodium borohydride in 30 mL of dry tetrahydrofuran was added 3.1 mL (0.024 mol) of boron trifluoride etherate under a nitrogen atmosphere. The mixture was stirred at room temperature for 1.5 h, water, 6.5 mL of 3 N sodium hydroxide solution, and 6.5 mL of 30% hydrogen peroxide were added successively, and the reaction mixture was left overnight. After suction filtration, the filtrate was extracted with ether. The organic layer was washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was distilled under reduced pressure to give 9.4 g (72%) of methyl 11-hydroxyundecanoate: bp 131–134 °C (2 mm); IR 3400, 1725, 1230 cm^{-1}.

To an ice-cold solution of 134 mg (0.62 mmol) of the above ester in 0.5 mL of pyridine was added 0.1 mL (3.1 mmol) of acetic anhydride. The resulting solution was stirred at room temperature for 1 day and poured into ice–water, and the mixture was extracted with ether. The organic layer was washed successively with dilute HCl, saturated $NaHCO_3$ solution, and brine and then dried (Na_2SO_4). After removal of the solvent in vacuo, 162 mg of **23** was obtained (quantitative) which was purified by preparative GLC: IR 1725, 1220 cm^{-1}; NMR δ 1.14–1.86 (m, 16 H), 1.96 (s, 3 H), 2.21 (t, 2 H), 3.60 (s, 3 H), 3.96 (t, 2 H); mass spectrum, m/e 237 ($M^+ - 31$). Anal. Calcd for $C_{14}H_{26}O_4$: C, 65.08; H, 10.14. Found: C, 64.85; H, 10.24.

Registry No. **9**, 78571-63-8; **10**, 72767-57-8; **11**, 22118-01-0; **12**, 38229-67-3; **12** semicarbazone, 78571-64-9; **13**, 18631-96-4; **14**, 38312-61-7; **15**, 42540-17-0; **15** TMS enol ether, 78571-65-0; **15** siloxy cyclopropane derivative, 78571-66-1; **16**, 72761-00-3; **17**, 78571-67-2; **17** methyl ester, 78571-68-3; **18**, 78591-54-5; **19**, 78571-69-4; **20**, 22156-45-2; **21**, 78571-70-7; **21** methyl ester, 78571-71-8; **21** methyl ester diol, 78571-72-9; **21** methyl ester diketone, 78571-73-0; **21** methyl ester diethylene thioketal, 78571-74-1; **22**, 1731-86-8; **23**, 78571-75-2; **24**, 78571-76-3; **25**, 78571-77-4; **26**, 78571-78-5; **26** methyl ester, 78571-79-6; ethylene, 74-85-1; methyl undec-10-enoate, 111-81-9; methyl 11-hydroxyundecanoate, 24724-07-0; [4.4.2]propellenone, 77827-78-2.