Photochemical Cycloaddition Reactions of α,β-Unsaturated Lactones with Olefins, and Application to Synthesis of Natural Products[1]

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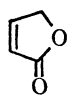
The photochemical cycloaddition reactions of five- and six-membered α,β-unsaturated lactone derivatives with unsaturated substrates (ethylene, acetylene, 1,1-dimethoxyethylene *etc.*) have been studied. The parent α,β-unsaturated lactone (γ-crotonolactone) and the β-,γ-, or δ-alkyl substituted derivatives add to ethylene and acetylene in the acetone solutions and to 1,1-dimethoxyethylene in the benzene solutions in so good yields as to utilize them practically for synthesis. α-Phenyl-γ-crotonolactone and β-phenyl-γ-crotonolactone also add to ethylene and acetylene, whereas, α-methyl, β-hydroxy, and β-methoxy derivatives do not. As the synthetic applications of the reactions, the synthesis of (±)-grandisol has been achieved, and the synthetic approach to (±)-canadensolide has also been described.

Despite many examples of the photochemical cycloaddition reactions of cyclic α,β-unsaturated ketones with a variety of unsaturated substances[2,3] and of the fruitful applications in total syntheses of natural products,[4] the use of α,β-unsaturated lactones such as **1** and **2** has so far been very limited.[5-7] Tada



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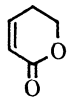

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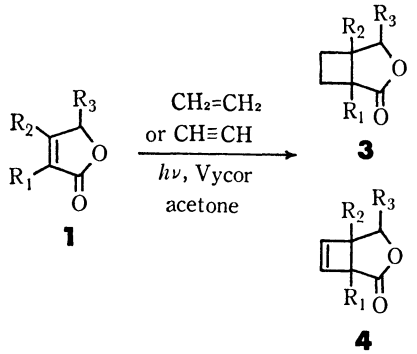
and his co-workers[6] reported, in mechanistic points of view, that γ-crotonolactone (**1**) underwent photocycloaddition reaction with cyclopentene or cyclohexene to give the cycloadduct in 36—42% yield and that the reaction was sensitized by acetone and quenched by 1,3-pentadiene and, therefore, the reaction proceeded through the triplet excited state of **1**. Furthermore, it is one of the most significant findings in their work that 1,1-dimethoxyethylene, which is one of the most reactive olefins in the photocycloaddition of cyclic enones,[2] did not give the cycloadduct with **1**, but quenched the photocycloaddition reaction between **1** and cyclopentene in acetonitrile. As the example of a six-membered α,β-unsaturated lactone, the acetophenone-sensitized cycloaddition of 5,6-dihydro-4-methyl-2*H*-pyran-2-one (**2b**), β-methyl derivative of **2**, to ethylene has been successfully applied to the stereoselective synthesis of (±)-grandisol by Gueldner and his co-workers.[7] We have simultaneously and independently investigated the photochemical cycloaddition reactions of **1** and the simply substituted derivatives of **1** and **2** with unsaturated substrates, especially ethylene, acetylene, and 1,1-dimethoxyethylene, for the actual synthetic purpose including the synthesis of (±)-grandisol, rather than the mechanistic view points. This work was undertaken with several goals in mind: (1) to clarify and generalize the reaction conditions and the effects of the substituents in both lactone and olefin components, (2) to elucidate the structures, including orientations, of the products obtained, (3) to apply the cycloaddition reaction to the synthesis of natural products, (4) to compare the photochemical reactivities of unsaturated lactones with those of enones.

Results and Discussion

Photochemical results are described first, followed by synthetic applications.

Photochemical Cycloadditions. All of the photochemical reactions described herein were conducted in ordinary solvents and with a 500-W high pressure mercury arc lamp fitted with or without a filter (Vycor or Pyrex cooling jacket of a lamp), in contrast with the peculiar conditions (in acetonitrile, 10-W low pressure mercury arc lamp) employed by Tada, *et al.*[6] Described below are studies on the photochemical cycloaddition reactions of γ-crotonolactone (**1a**) and the following derivatives: β-methyl (**1b**), β-phenyl (**1c**), α-methyl (**1d**), α-phenyl (**1e**), and γ-methyl (**1f**), and 5,6-dihydro-6-methyl-2*H*-pyran-2-one, parasorbic acid (**2a**).



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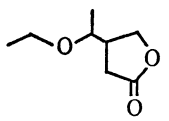
a : $R_1=R_2=R_3=H$
b : $R_1=R_3=H$, $R_2=Me$
c : $R_1=R_3=H$, $R_2=Ph$
d : $R_1=Me$, $R_2=R_3=H$ (no reaction)
e : $R_1=Ph$, $R_2=R_3=H$
f : $R_1=R_2=H$, $R_3=Me$

The photocycloaddition of **1a** to ethylene in acetone (Vycor) proceeded readily and cleanly, and afforded the cycloadduct **3a** in high yield (70% at room temperature; >80% at −50 °C). The analytical and spectral data indicate that **3a** is the expected 1 : 1 cycloadduct. Acetone was the best solvent among other solvents examined in the photocycloaddition of **1a** to ethylene and appears to play a role as the sensitizer, as suggested by Tada, *et al.*[6] For example,

the photocycloaddition of **1a** to ethylene in ether or in ether–acetone (fivefold molar excess amount of **1a**) resulted in lowering remarkably the yield of **3a**, 22 and 6%, respectively. In this case, the major product was a mixture of the diastereomers of the ether addition product **5**. This result suggests that the excited species of **1a** abstracts preferentially a hydrogen atom from ether rather than the photocycloaddition to ethylene, being quite different from the feature of the excited species of enones since enones added satisfactorily to ethylene and other olefins by irradiation in ether without the formation of the ether addition product.[8] However, the abstraction of a hydrogen atom from ether was not always the preferential pathway in the photocycloaddition of **1a** in ether; **5** was obtained as the minor component in



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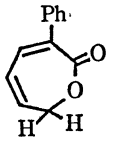
the photocycloaddition with cyclohexene (see below). Propyl bromide–acetone (−50 °C) was also not a suitable solvent system for the photocycloaddition of **1a** to ethylene, giving **3a** in 53% yield. Also, benzene, which is one of the very common solvents for the photocycloaddition of enones,[9] was unsatisfactory for the present reaction due to the relatively low solubility of **1a**: a solution of **1a** in benzene (the same concentration as in acetone) became emulsion by the saturation of ethylene, and in fact, no reaction occurred even in prolonged irradiation.

Similarly, the photocycloaddition of **1b**, **1c**, **1e**, and **1f** to ethylene in acetone afforded products, **3b**, **3c**, **3e**, and **3f** (44, 49, 52, and 35%) whose analytical and spectral data indicated they were the expected cycloadducts. The adduct **3f** and others derived from **1f** were obtained always as a *ca.* 1 : 1 mixture of the stereoisomers. From these experiments, although the reactions proceeded smoothly under the conditions examined (acetone, −50 °C for **1b** and **1f**; room temperature for **1c** and **1e**, Vycor filter for **1b** and **1c**; Pyrex filter for **1e**; no filter for **1f**), it was observed that prolonged irradiation caused to increase the amount of by-products which presumably arose from the participation of acetone, and therefore, in practice for preparation of the adducts it would be better to conduct the photocycloaddition reaction without a filter, resulting in making the reaction much faster. It should be noted that α-methyl derivative **1d**, contrary to the phenyl analog **1e**, did not undergo the photocycloaddition to ethylene, being similar to the observation on the photocycloaddition of 2-methyl-2-cyclohexenone.[2] On the photoeffectiveness of **1e**, the electronic effect of the conjugated phenyl group may play an important role in the reaction.

Contrary to the photochemical unreactivity of 2-cyclohexenone with acetylene (in acetone at −70 °C) observed by Owsley and Bloomfield,[10] we have found that the unsaturated lactones **1a-f** except **1d** underwent actually the photocycloaddition with acetylene under the standard conditions (acetone, −50 °C, Vycor filter for **1a-c**; Pyrex filter for **1e**; no filter for **1f**). The noteworthy features of the reactions are the slowness relative to the cases with ethylene and the formation of a large amount of by-products at the end of the reaction periods. Consequently, for the actual isolation of the desired adducts the progress of the reactions should be carefully followed by glpc or tlc analysis and intermitted at appropriate reaction periods. Thus, the corresponding acetylene adducts **4a**, **4b**, **4c**, **4e**, and **4f** were obtained in 54, 29, 8, 23, and 14% yields, respectively. Again, no reaction was observed in **1d**. The structures of the adducts were established on the basis of analytical and spectral grounds, and among them **4e** was further identified by comparison with the authentic sample obtained from the photocyclization of 3-phenyl-2(7*H*)-oxepinone (**6**).[11] In the case of **1c**, the yield of adduct **4c** was extremely low and the major product (35%) was found to be the dimer **7** which was quantitatively formed by irradiation of **1c** alone. The structure of **7** was assigned on the basis of the analytical and spectral results but the *syn*/*anti* and *cis*/*trans* natures could not be determined.



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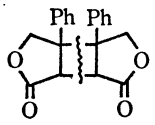

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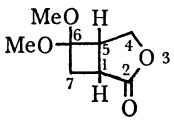
It should be noteworthy that the compound **1a** as well as **1c** effectively adds to 1,1-dimethoxyethylene, contrary to the observation by Tada, *et al.*[6] Thus, irradiation of **1a** or **1c** in the presence of excess 1,1-dimethoxyethylene in the benzene solution without a filter gave the cycloadducts **8** or **9** in 62 or 37% yield, respectively. Acetone was not used as a solvent in these reactions because of the easy formation of the oxetane derivative with 1,1-dimethoxyethylene.[6,12] The presence of excess 1,1-dimethoxyethylene increased the solubility of **1a** in benzene, and now the reaction proceeded smoothly. Furthermore, it was observed that the photoaddition proceeded very slowly by irradiation through a Vycor filter and that a large amount of by-products arising from 1,1-dimethoxyethylene (dimethyl succinate *etc.*) were produced by prolonged irradiation. For example, the ratio of **1a** and **8** reached to about 7 : 2 after 19 hr irradiation through a Vycor filter and did not change considerably on further irradiation, despite of a remarkable consumption of 1,1-dimethoxyethylene. The product **8** was apparently single, being *cis* fused, and the 6,6-dimethoxy structure follows from 100 MHz NMR coupling multiplicity of the methine proton (H-1) at the ring juncture; that is, the signal of H-1 appears as eight lines with the following coupling constants: J_{1-5}= 8.4, J_{1-7}^{trans}=5.1, J_{1-7}^{cis}=9.0. The coupling patterns of the protons in **9** also support the position of the dimethyl acetal grouping, and furthermore, the orientation of the photoaddition of 1,1-dimethoxyethylene was confirmed by chemical transformation of another adduct **24** described in the later section. Hence,



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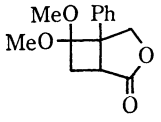

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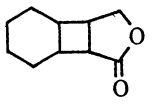
the orientational mode of the photocycloaddition of α,β-unsaturated lactones to 1,1-dimethoxyethylene is apparently the same as the case of cyclic enones.[2,8a] Interestingly, **1e**, which added effectively to ethylene and acetylene as mentioned above, was found to be photochemically unreactive to 1,1-dimethoxyethylene.

In order to gain more informations on the effect of an olefin-solvent combination in these photochemical processes, the reaction of cyclohexene with **1a** was performed in an ether solution. The reaction proceeded well to afford the expected product **10**[6] in 72% yield. This product appears to be a mixture of stereoisomers; however, the aspect of stereochemistry was not investigated further. In this case the by-product **5** was a minor component in a yield of less than 10%.



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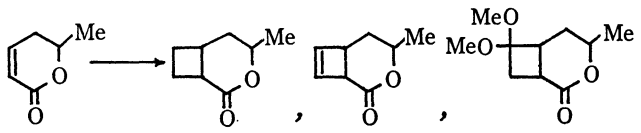
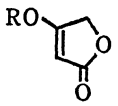
Furthermore, parasorbic acid (**2a**) was selected for study as an example of a six-membered α,β-unsaturated lactone. The photocycloadditions of **2a** to ethylene and acetylene in acetone and to 1,1-dimethoxyethylene in ether equally proceeded readily and gave the adducts, **11** (70%), **12** (66%), and **13** (64%), each of which was a mixture of stereoisomers, and the analytical and spectral data were consistent with the assigned structures.



2a **11** **12** **13**

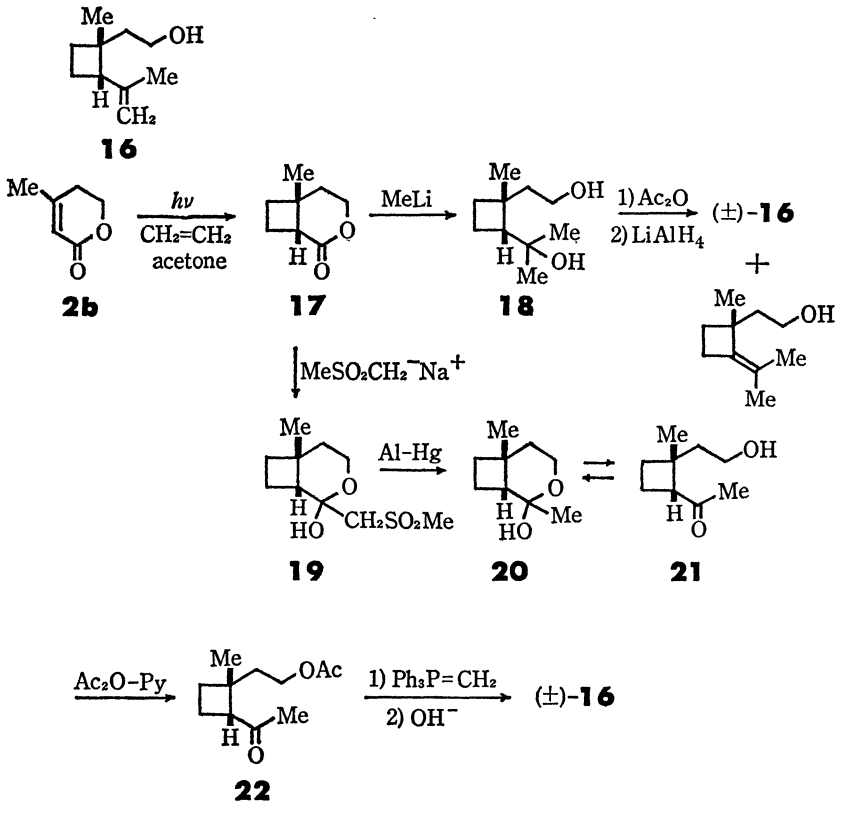
Finally, we also examined the photoreactions using acrylonitrile as an olefinic substrate and tetronic acid as an unsaturated lactonic one. It has been known that acrylonitrile is one of the good olefinic substrates for the photocycloaddition of enones and actually adds to 2-cyclohexenones;[2,8a] however, any of α,β-unsaturated lactones examined in the present work did not give the photocycloadduct with acrylonitrile.

Furthermore, in contrast with the successful photoadditions of 3-hydroxy-[13] and 3-methoxy-[8a] cyclohexenones to olefins, the photoreactions of tetronic acid (**14**) with ethylene or cyclohexene and of the methyl ether **15** with ethylene under the various conditions (solvent, Vycor or no filter *etc.*) did not entirely give the cycloadducts, resulting in recovery of the starting materials **14** and **15** or formation of an intractable mixture.

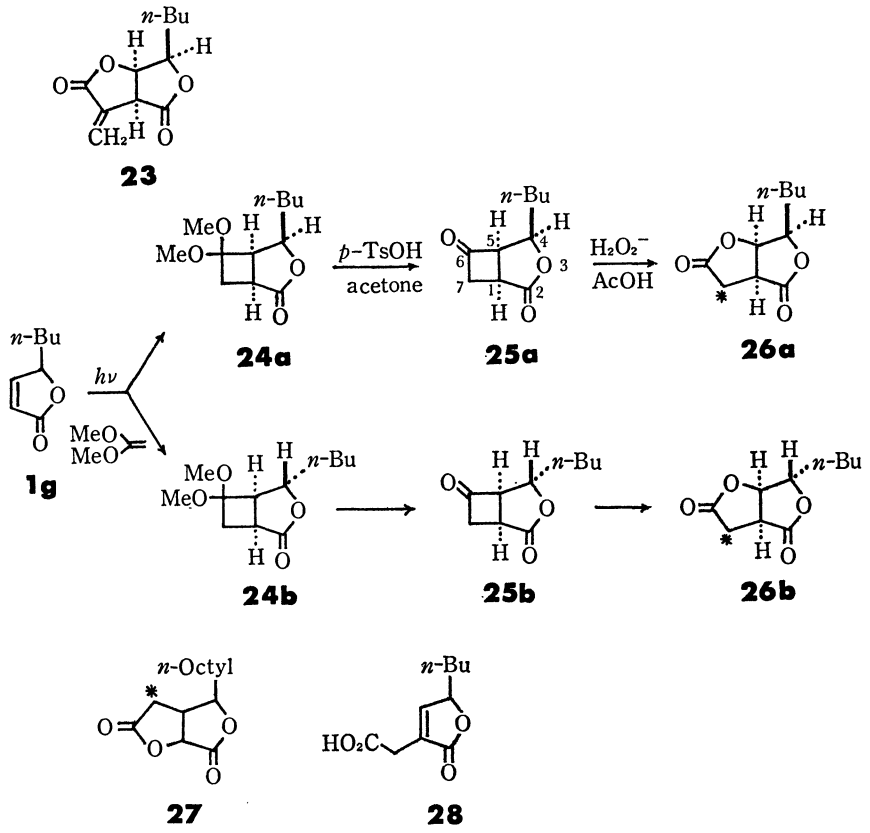


14, R=H
15, R=Me

Any of the mechanistic, sensitized, or competitive studies concerning the feature and reactivity of the



Scheme 1.



Scheme 2.

excited species o. α,β-unsaturated lactones has not been investigated precisely in the present work. However, from the experimental results, it could be pointed out that there are apparently the several different features of the excited species of unsaturated lactones from those of enones; that is, hydrogen abstraction from ether, photoaddition to acetylene, inertness for the photoaddition to acrylonitrile, and unreactive effect of 3-hydroxy and alkoxy groups.

As is clear from the several examples cited above the photocycloaddition reactions of α,β-unsaturated lactones with olefins, especially ethylene, acetylene and 1,1-dimethoxyethylene, should be of considerable utilities for the preparation of a wide variety of four-membered ring fused γ- and δ-lactone derivatives.

Synthetic Applications. (±)-Grandisol. Grandisol (**16**), one of the four components of the male boll weevil sex pheromone,[14] has been previously synthesized in racemic form,[7,9e,14] and additionally, three alternative synthetic courses have very recently been reported.[15] Among these reported synthetic sequences, the photocycloaddition reaction of 5,6-dihydro-4-methyl-2*H*-pyran-2-one (**2b**) with ethylene has been successfully applied as the initial step by Gueldner, *et al.* (**2b**→**17**→**18**→**16** in the scheme 1).[7] In this section we will describe briefly our independent synthetic work of (±)-**16** starting from **2b** and the reaction sequence is outlined in the scheme 1.

Irradiation of a solution of **2b** in acetone at room temperature through a Vycor filter with moderately rapid introduction of ethylene gave a 70% yield of the cycloadduct **17** (the reported conditions:[7] benzene, acetophenone as a sensitizer, a medium-pressure mercury-vapor lamp, no filter, yield of **17**: 56%).

The addition of **17** to excess sodium methylsulfonylcarbanion[16] at 55 °C resulted in the formation of the acetal **19**, mp 103.5—104.5 °C, (75%). For the introduction of one carbon unit the use of sodium methylsulfinylcarbanion[16,17] was unsatisfactory, affording a low yield of non-crystalline product. Reduction of **19** with aluminum amalgam in aqueous tetrahydrofuran gave an equilibrium mixture of the acetal **20** and the methyl ketone **21**, which were apparently separable on silica gel tlc but not obtained in pure form.

Acetylation of the mixture of **20** and **21** with acetic anhydride–pyridine at room temperature afforded in a 40% yield (based on **19**) of the single acetate **22** which is transformed by the Wittig process, methylenetriphenylphosphorane–dimethyl sulfoxide,[18] followed by alkaline hydrolysis to (±)-grandisol (**16**) identical with an authentic sample prepared by Zurflüh, *et al.*[9e]

(±)-Canadensolide. Canadensolide (**23**) is a mould metabolite produced by *Penicillium canadense*[19] and the total synthesis in racemic form and the revision of the stereochemistry has been reported by Yoshikoshi, *et al.*[20] The orientation of the dimethyl acetal grouping in the photocycloadduct **8** from **1a** and 1,1-dimethoxyethylene as mentioned earlier is well suited for the construction of the second lactone ring in the canadensolide bislactone ring system, and hence, the photo-

cycloaddition of γ-butyl-γ-crotonolactone (**1g**) to 1,1-dimethoxyethylene would appear to provide an alternative synthetic route leading to (±)-**23**. This part deals with this synthetic approach to (±)-**23** from **1g** (Scheme 2).

Irradiation of **1g** in the presence of excess 1,1-dimethoxyethylene in benzene gave a mixture of the stereoisomers of the adduct which were easily separated by column chromatography on silica gel into *endo* and *exo* isomers, **24a** and **24b**, in respect of the butyl side chain in 30 and 40% yields, respectively. The orientation of the dimethyl acetal grouping and the configuration of the butyl group were rigorously established on the basis of the NMR coupling pattern of H-5 in the hydrolysis product **25**.

Treatment of each isomer **24a** and **24b** with *p*-toluenesulfonic acid in acetone afforded the corresponding keto lactone **25a** and **25b**. The signals of H-5 in both isomers appear as a doublet of doublets, suggesting the position of the keto group at C-6, with the following coupling constants: $J_{4-5}=7.0$ in **25a** (assignable to *cis* coupling), $J_{4-5}=1.7$ in **25b** (assignable to *trans* coupling) respectively. Thus, the configuration of the butyl group is *endo* in the **a**-series compounds, while *exo* in the **b**-series, as shown in Scheme 2. On treatment with hydrogen peroxide–acetic acid **25a** and **25b** were transformed into the bislactone derivatives **26a** and **26b** which were identified by direct comparison with the authentic samples prepared by Yoshikoshi, *et al.*[20]

Unfortunately, however, in this bislactone ring system the introduction of a carboxylic group (or its equivalent) at the α-methylene position (asterisked) of the newly formed lactone ring failed, in contrast to the successful introduction in the case of the avenaciolide bislactone ring system **27**.[21] All attempts to introduce one carbon unit at the α-methylene position in both **26a** and **26b** under a wide variety of conditions (MMC–DMF–dioxane, *iso*-Pr_2NLi–CO_2–THF, Et_2NH–aq HCHO *etc.*) were unsuccessful; the abstraction of a proton from C-1 occurred exclusively to produce the ring opened product **28**. This problem is still unresolved.

Experimental

All melting points were determined in an oil bath and are uncorrected. Distillation of the liquid products was usually carried out evaporatively using a modified sublimation apparatus and the oil bath temperatures were recorded. IR spectra were taken on a Hitachi EPI-S2 or G2 spectrometer. NMR spectra were obtained on a JEOL Model C-60HL (60 MHz) or PS-100 (100 MHz) instrument using TMS as an internal standard and CCl_4 as the solvent unless otherwise indicated. Reported values are on the cm^{-1} in IR and δ scales in NMR, respectively. Coupling constants are given in Hz. Glpc analyses were performed on a JEOL Model JGC-750 or 1100 instrument using the following columns: A (20% Carbowax 20 M on Chromosorb W, 2 m×3 mm), B (20% Carbowax 20 M on Chromosorb W, 3 m×3 mm), and C (20% SE-30 silicone rubber on Chromosorb W, 2 m×3 mm). Elemental analyses were performed in the microanalytical laboratory of this institute.

General Procedure for Irradiation. The apparatus consisted of an irradiation vessel fitted with a Vycor, Pyrex or quartz (for experiments without a filter) immersion type cooling jacket for a lamp serving a filter as well, a rubber stopple in one side arm, and a gas inlet tube or a three-way stopcock on the other side arm. In the cases of small scale experiments, a quartz reaction tube (3×30 cm) having a glass sponge gas inlet part at the bottom was employed and irradiated externally. The entire apparatus was immersed in a dry-ice—methanol or a running water bath (for room temperature experiments). The gaseous olefinic substrates, ethylene and acetylene, were saturated at appropriate temperatures and continuously bubbled through the solutions as a finely dispersed state throughout irradiation. For the other olefins the irradiations were performed under the nitrogen atmosphere. The solutions were irradiated by a Taika immersion type 500-W high pressure mercury arc lamp and the progress of the reactions was generally monitored by removing aliquots with a syringe and examination by glpc or tlc means. The yields of the photoadducts are based on the starting unsaturated lactones.

*Photoadditions of γ-Crotonolactone (**1a**).* *(a) To Ethylene in Acetone*: A solution of γ-crotonolactone (**1a**)[22] (1.02 g) in freshly distilled acetone (400 ml) was irradiated at −50 °C for 2.5 hr through Vycor with introduction of ethylene. Evaporation of the solvent under reduced pressure and distillation (110—120 °C/15 mmHg) of the residual liquid gave 1.10 g (80%) of the single product, 3-oxabicyclo[3.2.0]-heptan-2-one (**3a**)[23], with a retention time of 24 min on column B (200 °C, He 2.0 kg/cm²). IR (CCl_4) 1780, 1150; NMR 1.90—2.70 (m, 4H), 2.88—3.34 (m, 2H), 4.12 (dd, J=10 and 2, 1H), 4.29 (dd, J=10 and 6, 1H). Found: C, 64.71; H, 7.19%. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19%.

When the reaction was carried out at room temperature, **3a** was isolated in 70% yield.

(b) To Ethylene in Ether: A solution of **1a** (0.94 g) in dry ether (500 ml) was irradiated at room temperature for 2.5 hr through Vycor with introduction of ethylene. Glpc analysis (column A, 180 °C) of the crude photolysate indicated the product contained two components with the retention times of 10.8 min (*ca.* 22% of area) and 18.8 min (*ca.* 54% of area). Pure sample of each component was collected by preparative glpc. The faster moving component was identified to be **3a** and the slower moving one was found to be the ether addition product, β-(1-ethoxyethyl)-γ-butyrolactone (**5**): IR (CCl_4) 1780; NMR around 1.13 (d, J=7, 3H), around 1.16 (t, J=7, 3H) (these are splitted small due to a mixture of diastereomers), 2.20—2.60 (m, 3H), 3.20—3.70 (m, 3H), 4.20 (m, 2H). Found: C, 60.38; H, 8.70%. Calcd for $C_8H_{14}O_3$: C, 60.78; H, 8.92%.

(c) To Acetylene: A solution of **1a** (1.58 g) in acetone (500 ml) was irradiated at −50 °C through Vycor with introduction of acetylene. After 5 hr the amount of by-products gradually increased, presumably arising from photoreaction of acetylene and/or acetone, and therefore, the reaction was stopped after 5 hr irradiation. At this stage the ratio of **1a** (retention time of 2.6 min) and the main product (4.6 min) was about 31% and 54%, in addition to 15% of by-products, respectively, determined from glpc on column C (150 °C, He 1.0 kg/cm²). After removal of the solvent under reduced pressure, the gas-chromatographically homogeneous product, 3-oxabicyclo[3.2.0]hept-6-en-2-one (**4a**), (470 mg, 23%) was collected by column chromatography on silica gel (70 g) using 7 : 3 petroleum ether–ether as eluent. The analytical sample was purified by distillation (110—125 °C/10 mmHg). IR (CCl_4) 3020, 1780, 1160; NMR 3.50—3.70 (m, 2H), 4.20—4.40 (m, 2H), 6.32 (s, 2H). Found: C, 65.79;

H, 5.49%. Calcd for $C_6H_6O_2$: C, 65.44; H, 5.49%.

(d) To Cyclohexene: A solution of **1a** (1.02 g, 12 mmol) and cyclohexene (10.5 g, 116 mmol) in dry ether (500 ml) was irradiated at room temperature for 5 hr through Vycor. Analysis of the crude photolysate by glpc (column C, 190 °C, He 1.5 kg/cm²) indicated the photoproduct consisted of three components eluted at 3.1 min, 5.7 min, and 6.8 min in the area ratio of about 1 : 1.5 : 3, respectively. After removal of the solvent under reduced pressure, the residual liquid was separated into 72 fractions of *ca.* 50 ml portion by chromatography on silica gel (60 g) using initially petroleum ether alone and then a mixture of petroleum ether and ether (gradually increasing the amount of ether, the final ratio of petroleum ether and ether was about 7 : 3) as eluting agent. Fractions 32—39, consisting of the single compoment corresponding to 6.8 min eluate on glpc, were combined and concentrated under reduced pressure to give 302 mg of one stereoisomer of 4-oxatricyclo[5.4.0.$0^{2,6}$]undecan-3-one (**10**). Purified sample by distillation (125—130 °C/6 mmHg) was gradually crystallized on standing, mp 41—45 °C. IR (CCl_4) 1775, 1150; NMR 0.90—3.20 (m, 12H), 4.20—4.40 (m, 2H). Found: C, 72.58; H, 8.75%. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%. Fractions 40—49 amounting 452 mg were found to be a mixture of the 5.7 min and 6.8 min eluates, and the IR and NMR spectra were almost identical with those of the above mentioned pure sample. Therefore, the 5.7 min eluate was another stereoisomer of **10**. Total yield was *ca.* 50%.

The product obtained from the fractions 55—65, which was the 3.1 min eluate, was identified to be **5** (132 mg, 7%).

(e) To 1,1-Dimethoxyethylene: A solution of **1a** (0.84 g, 10 mmol) and freshly distilled 1,1-dimethoxyethylene (8.8 g, 0.1 mol) in dry benzene (50 ml) was irradiated at room temperature for 15 hr without a filter. Evaporation of the solvent under reduced pressure left 2.69 g of oily residue. From the glpc analysis (column A, 230 °C, He 2.3 kg/cm²) the starting material **1a** (retention time of 2.5 min) still remained and the ratio of **1a** and the photoproduct (retention time of 8.8 min) was about 1 : 3. Many other peaks due to by-products (totally comparable area with **1a** and the product) were also observed around 1—3 min and 4—6 min. The crude mixture was chromatographed on silica gel (75 g) using initially hexane and then a mixture of hexane and ether (gradually increasing the amount of ether, the final ratio of hexane and ether was about 7 : 3) as eluting agent to give 435 mg (26% based on **1a** used) of 6,6-dimethoxy-3-oxabicyclo[3.2.0]heptan-2-one (**8**), which was purified by distillation (95 °C/3 mmHg). IR(CCl_4) 2810, 1778; NMR (100 MHz) 2.29 (dd, J=13.0 and 5.1, 1H), 2.50 (ddd, J=13.0, 9.0, and 2.0, 1H), 2.83 (ddd, J=9.0, 8.4, and 5.1, 1H), 3.09 (s, 3H), 3.15 (s, 3H and m, 1H), 4.22 (dd, J=9.3 and 7.8, 1H), 4.48 (dd, J=9.3 and 2.6, 1H). Found: C, 55.79; H, 6.88%. Calcd for $C_8H_{12}O_4$: C, 55.84: H, 7.03%.

Photoadditions of β-Methyl-γ-crotonolactone (1b). (a) To Ethylene: A solution of β-methyl-γ-crotonolactone (**1b**)[24] (250 mg) in freshly distilled acetone (600 ml) was irradiated at −50 °C for 8 hr through Vycor with introduction of ethylene. Evaporation of the solvent under reduced pressure and chromatography of the residual liquid on silica gel (30 g) using 5 : 1 petroleum ether–ether as eluent gave 150 mg (48%) of 5-methyl-3-oxabicyclo[3.2.0]heptan-2-one (**3b**), which was homogeneous on glpc (column A, 200 °C, He 1.6 kg/cm²). Analytical sample was purified by distillation (80—120 °C/12 mmHg). IR (CCl_4) 1780, 1150; NMR 1.35 (s, 3H), 1.70—2.70 (m, 5H), 3.86 and 4.14 (AB type q, J=9.0, 1H each). Found: C, 66.42; H, 7.84%. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99%.

(b) To Acetylene: A solution of **1b** (600 mg) in acetone (800 ml) was irradiated at −50 °C through Vycor with introduction of acetylene. After 9 hr glpc analysis (column A, 200 °C, He 1.5 kg/cm²) indicated the ratio of **1b** (retention time of 6.2 min) and the photoadduct (4.2 min) was about 3 : 1. After an additional 1 hr irradiation the ratio reached to 1 : 1 but the amount of by-products considerably increased. Therefore, for convenience of the isolation of the product, the reaction was intermitted at 9 hr irradiation. Removal of the solvent under reduced pressure and chromatography of the residual liquid (1.1 g) on silica gel (50 g) using 5 : 1 petroleum ether–ether as eluting agent gave 86 mg (29%) of homogeneous 5-methyl-3-oxabicyclo-[3.2.0]hept-6-en-2-one (**4b**). Analytical sample was purified by distillation (80—83 °C/15 mmHg). IR (CCl_4) 1785, 1770, 1160; NMR 1.42 (s, 3H), 3.10 (s, 1H), 3.89 and 4.19 (AB type q, J=9.7, 1H each), 6.27 and 6.38 (AB type q, J=2.8, 1H each). Found: C, 67.56; H, 6.42%. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.50%.

Photoadditions of β-Phenyl-γ-crotonolactone (1c). (a) To Ethylene. A solution of β-phenyl-γ-crotonolactone (**1c**)[25] (500 mg) in acetone (800 ml) was irradiated at room temperature for 3 hr through Vycor with introduction of ethylene. In this case the progress of the reaction was monitored by tlc instead of glpc. Removal of the solvent under reduced pressure and chromatography of the residue (972 mg) on silica gel (50 g) using 4 : 1 petroleum ether–ether as eluent gave 250 mg (50%) of 5-phenyl-3-oxabicyclo[3.2.0]heptan-2-one (**3c**). Analytical sample was purified by distillation (120—140 °C/3 mmHg). IR (CCl_4)1785, 1170; NMR 1.80—2.80 (m, 4H), 3.10—3.40 (m, 1H), 4.05 and 4.40 (AB type q, J=9.0, 1H each), 7.22 (s, 5H). Found: C, 76.42; H, 6.73%. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%.

(b) To Acetylene: A solution of **1c** (500 mg) in acetone (800 ml) was irradiated at −50 °C through Vycor with introduction of acetylene. After 2 hr **1c** was completely consumed. Evaporation of the solvent and chromatography of the residue (806 mg) on silica gel (40 g) using 5 : 1 petroleum ether–ether as eluent gave two products. The faster moving minor product (46 mg, 8%) was purified by distillation (140—150 °C/3 mmHg) and identified to be the expected photoadduct, 5-phenyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (**4c**): IR ($CHCl_3$) 1765, 1180; NMR 3.50 (br. s, 1H), 4.27 and 4.48 (AB type q, J=9.4, 1H each), 6.47 and 6.77 (AB type q, J=2.8, 1H each), 7.30 (s, 5H). Found: C, 77.08; H, 5.41%. Calcd for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41%.

The crystalline major product (173 mg, 35%) isolated from the slower eluted fractions was recrystallized from hexane–chloroform, mp 192—194 °C, and found to be the dimer **7** of the starting lactone **1c**: IR ($CHCl_3$) 1790, 1180; NMR ($CDCl_3$) 3.82 (s), 4.10 (s), 7.00—7.60 (m) with area ratio of 1 : 2 : 5. Found: C, 74.86; H, 5.17%. Calcd for $(C_{10}H_8O_2)_n$: C, 74.99; H, 5.03%.

The almost identical result was obtained when a Pyrex filter instead of a Vycor one was employed. After 4 hr irradiation, the yields of **4c** and the dimer **7** was 8% and 55%, in addition to 10% recovery of **1c**, respectively.

The dimer **7** was quantitatively obtained by irradiation of **1c** in acetone without introduction of acetylene.

(c) To 1,1-Dimethoxyethylene. A solution of **1c** (300 mg, 1.9 mmol) and 1,1-dimethoxyethylene (2.5 g, 28 mmol) in dry benzene was irradiated at room temperature for 21 hr through quartz. After removal of the solvent and excess olefin under reduced pressure, the residue (600 mg) was chromatographed on preparative thin layer of silica gel using 1 : 1 petroleum ether–ether as developing agent to give 172 mg (37%) of 6,6-dimethoxy-5-phenyl-3-oxabicyclo-

[3.2.0]heptan-2-one (**9**). Analytical sample was purified by distillation (110—120 °C/1 mmHg). IR ($CHCl_3$) 2810, 1765; NMR (100 MHz, $CDCl_3$) 2.52 (dd, J=13.0 and 5.0, 1H), 2.87 (dd, J=13.0 and 10.0, 1H), 2.84 (s, 3H), 3.28 (s, 3H), around 3.28 (m, 1H), 4.55 and 5.18 (AB type q, J=9.0, 1H each), 7.20—7.40 (m, 5H). Found: C, 67.43; H, 6.56%. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50%.

*Photoadditions of α-Phenyl-γ-crotonolactone (**1e**).* *(a) To Ethylene*: α-Phenyl-γ-crotonolactone (**1e**) was prepared essentially according to Swain's procedure[26] and the yield was somewhat improved by slightly modified operations. A solution of **1e** (500 mg) in acetone (700 ml) was irradiated at room temperature through Pyrex with introduction of ethylene. After 3.5 hr of the irradiation period, the solvent was removed under reduced pressure and the residue (673 mg) was chromatographed on silica gel (40 g) using 4 : 1 petroleum ether–ether as eluent to yield 305 mg (52%) of 1-phenyl-3-oxabicyclo[3.2.0]heptan-2-one (**3e**), in addition to the recovery of **1e** (100 mg, 20%). Analytical sample was purified by distillation (105—110 °C/2 mmHg). IR ($CHCl_3$) 1765, 1160; NMR ($CDCl_3$) 1.70—2.68 (m, 4H), 3.41 (m, 1H), 4.27 (dd, J=9.8 and 1.5, 1H), 4.49 (dd, J=9.8 and 5.8, 1H), 7.38 (s, 5H). Found: C, 76.66, H, 6.38%. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%.

(b) To Acetylene: A solution of **1e** (500 mg) in acetone (700 ml) was irradiated at −50 °C for 4.5 hr through Pyrex with introduction of acetylene. After removal of the solvent under reduced pressure, the resulting oily residue (814 mg) was chromatographed on silica gel (50 g) using 4 : 1 petroleum ether–ether as eluent to give 131 mg (23%) of 1-phenyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (**4e**). The IR and NMR spectra were identical with those of the authentic specimen[11] in every respect.

*Photoadditions of γ-Methyl-γ-crotonolactone, β-Angelica Lactone (**1f**).* *(a) To Ethylene*: A solution of γ-methyl-γ-crotonolactone (**1f**)[27] (1.0 g) in acetone (700 ml) was irradiated at −50 °C for 2 hr through quartz with introduction of ethylene. Glpc analysis (column A, 210 °C, He 1.4 kg/cm²) of the reaction mixture indicated the photoproduct consisted of two components eluted at 4.2 min and 4.9 min with the area ratio of about 1 : 1. After evaporation of the solvent under reduced pressure, the residual liquid (1.7 g) was chromatographed on silica gel (60 g) using 4 : 1 petrolum ether–ether as eluent. From the rapidly eluted fractions, 266 mg (21%) of *exo*-4-methyl-3-oxabicyclo[3.2.0]heptan-2-one (**3f**), corresponding to the 4.2 min eluate on glpc, was obtained. Analytical sample was purified by distillation (90—100 °C/20 mmHg). IR (CCl_4) 1775, 1155; NMR 1.25 (d, J=6.3, 3H), 1.90—2.60 (m, 4H), 2.65—3.50 (m, 2H), 4.47 (dq, J=6.3 and 1.0, 1H). Found: C, 66.76; H, 8.12%. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99%.

From the slowly eluted fractions, 183 mg (14%) of the *endo*-methyl isomer, corresponding to the 4.9 min eluate on glpc, was isolated. Analytical sample was purified by distillation (90—100 °C/20 mmHg). IR (CCl_4) 1775, 1170; NMR 1.32 (d, J=6.1, 3H), 1.70—2.70 (m, 4H), 2.80—3.30 (m, 2H), 4.56 (dq, J=6.1 and 5.6, 1H). Found: C, 66.75; H, 8.15%. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99%.

(b) To Acetylene: A solution of **1f** (1.5 g) in acetone (800 ml) was irradiated at −50 °C through quartz with introduction of acetylene. At the reaction period of 4.5 hr, the ratio of **1f** and the product to 9 : 11 as determined by glpc on column A (210 °C, He 1.4 kg/cm²) and the product consisted of the *exo*- and *endo*-methyl isomers with the ratio of 6 : 5 (retention times of 3.3 min and 4.1 min, respectively) similar to the case of the ethylene adduct **3f**. At this stage, the reaction was intermitted and the mixture was evaporated *in vacuo*. The residual liquid (2.7 g) was chromatographed on silica gel (60 g) using 9 : 1 petroleum ether–ether as eluent to give the homogeneous *exo*-methyl (134 mg, 7%) and *endo*-methyl (130 mg, 7%) isomers of 4-methyl-3-oxabicyclo[3.2.0]hept-6-en-2-one (**4f**), and the analytical samples were purified by distillation (80—90 °C/20 mmHg). *Exo*-**4f**: IR (CCl_4) 1775, 1170; NMR 1.30 (d, J=6.7, 3H), 3.17 (dd, J=1.7 and 3.5, 1H), 3.61 (d, J=3.5, 1H), 4.50 (dq, J=6.7 and 1.7, 1H), 6.39 (br. s, 2H). Found: C, 67.79; H, 6.65%. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.50%. *Endo*-**4f**: IR (CCl_4) 1770, 1170; NMR 1.38 (d, J=6.2, 3H), 3.20—3.70 (m, 2H), 4.55 (quint, J=6.2 and 6.2, 1H), 6.37 (br. s, 2H). Found: C, 67.27; H, 6.65%.

*Photoaddition of γ-Butyl-γ-crotonolactone (**1g**) to 1,1-Dimethoxyethylene.* A solution of γ-butyl-γ-crotonolactone (**1g**)[27] (1.46 g, 10 mmol) and 1,1-dimethoxyethylene (9.4 g, 107 mmol) in dry benzene (25 ml) was irradiated for 19 hr at room temperature through quartz. The solvent and excess olefin were evaporated under reduced pressure to give 3.5 g of brown liquid which consisted mainly of two components in a ratio of about 1 : 1 as determined by glpc analysis (column B, 218 °C He 2.4 kg/cm²). Chromatography of the residue on silica gel (80 g) using 7 : 3 hexane–ether as eluent gave 650 mg (28%) of *endo*-4-butyl-6,6-dimethoxy-3-oxabicyclo-[3.2.0]heptan-2-one (**24a**) and 900 mg (38%) of the *exo*-butyl isomer (**24b**), in addition to a small amount of the unreacted lactone. The analytical samples were purified by distillation (70—90 °C/3 mmHg). *Endo*-**24a**: IR (CCl_4) 2850, 2820, 1760; NMR (100 MHz) 0.93 (t, J=6.0, 3H), 1.20—1.80 (m, 6H), 2.10—2.50 (m, 2H), 2.70—3.00 (m, 2H), 3.10 (s, 3H), 3.12 (s, 3H), 4.26 (m, 1H). Found: C, 63.26; H, 8.88%. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83%. *Exo*-**24b**: IR (CCl_4) 2850, 2820, 1760; NMR (100 MHz) 0.96 (t, J=6.0, 3H), 1.20—1.80 (m, 6H), 2.20—2.50 (m, 2H), 2.70—2.95 (m, 2H), 3.12 (s, 3H), 3.17 (s, 3H), 4.68 (br. t, J=6.0, 1H). Found: C, 63.26; H, 8.58%.

*Photoadditions of Parasorbic Acid (**2a**).* *(a) To Ethylene*: A solution of parasorbic acid (**2a**)[28] (1.06 g) in acetone (500 ml) was irradiated at room temperature for 3 hr through quartz with introduction of ethylene. Evaporation of the solvent under reduced pressure, followed by chromatography of the residue on silica gel (60 g) using chloroform as eluent gave 260 mg of a mixture of the stereoisomers (at least two isomers) of 4-methyl-3-oxabicyclo[4.2.0]octan-2-one (**11**) as indicated by glpc on column C (170 °C, He 0.65 kg/cm²) Analytical sample was purified by distillation (120—130 °C/10 mmHg). IR (CCl_4) 1740, 1080; NMR 1.29—1.35 (two pairs of doublet, 3H), 1.50—3.20 (m, 8H), 4.00—4.30 (m, 1H). Found: C, 68.97; H, 8.79%. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63%.

(b) To Acetylene: A solution of **2a** (0.5 g) in acetone (250 ml) was irradiated at room temperature for 5 hr through quartz with introduction of acetylene. Analysis of the reaction mixture by glpc (column C, 180 °C, He 1.1 kg/cm²) apparently indicated a single peak due to the photoadduct eluted at 3.5 min with about 66% of area. Spectral sample of the product, 4-methyl-3-oxabicyclo[4.2.0]oct-7-en-2-one (**12**), was collected by preparative glpc using an SE-30 column (3 m×6 mm) at 230 °C. IR (CCl_4) 1740, 1060; NMR 1.29 (d, J=6.0, 3H), 1.60—2.40 (m, 2H), 3.40—3.70 (m, 2H), 4.20—4.40 (m, 1H), 6.00—6.20 (m, 2H).

(c) To 1,1-Dimethoxyethylene: A solution of **2a** (240 mg, 2.1 mmol) and 1,1-dimethoxyethylene (1.15 g, 13.1 mmol) in dry ether (80 ml) was irradiated at room temperature for

10 hr through Vycor. Analysis of the photolysate by glpc (column A, 155 °C, He 1.2 kg/cm²) indicated a main peak eluted at 3.0 min (*ca.* 66% of area) due to the photoproduct, along with the peaks of **2a** and by-products. Spectral sample of the product, 7,7-dimethoxy-4-methyl-3-oxabicyclo-[4.2.0]octan-2-one (**13**), was collected by glpc using a preparative SE-30 column (3 m×6 mm) at 230 °C and then passed through a short column of silica gel with anhydrous ether. IR (CCl_4) 2850, 1740, 1250; NMR 1.34 (d, J= 6.8, 3H), 1.50—3.00 (m, 5H), 3.10 (s, 3H), 3.15 (s, 3H), 3.60—3.80 (m, 1H), 4.20—4.40 (m, 1H).

*Photoaddition of 5,6-Dihydro-4-methyl-2H-pyran-2-one (**2b**) to Ethylene.* A solution of 5,6-dihydro-4-methyl-2*H*-pyran-2-one (**2b**) (344 mg), prepared by dehydration of mevalonic acid lactone with potassium bisulfate, in acetone (600 ml) was irradiated at room temperature for 3 hr through Vycor with introduction of ethylene. At the end of the irradiation period the solvent was removed by distillation under reduced pressure. The residue (770 mg) was chromatographed on preparative layer of silica gel using 1 : 2 petroleum ether–ether as developing agent to give 300 mg (70%) of 6-methyl-3-oxabicyclo[4.2.0]octan-2-one (**17**). Analytical sample was purified by distillation (85—95 °C/4 mmHg). IR (CCl_4) 1740, 1075; NMR (100 MHz) 1.26 (s, 3H), 1.50—3.00 (m, 7H), 4.20—4.60 (m, 2H). Found: C, 68.35; H, 8.45%. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63%.

*2-Hydroxy-6-methyl-2-methylsulfonyl-3-oxabicyclo[4.2.0]octane (**19**).* Sodium methylsulfonyl carbanion was prepared according to the reported manner[16] from sodium hydride (100 mg, 4.2 mmol), dimethylsulfone (495 mg, 4.2 mmol), and dimethyl sulfoxide (3 ml), and diluted with anhydrous tetrahydrofuran (3 ml). Then, a solution of **17** (270 mg, 2.0 mmol) in anhydrous tetrahydrofuran (3 ml) was added at room temperature with stirring and under nitrogen; the mixture turned immediately to deep red, and then heated at 50—60 °C for 1 hr. After cooling, the resulting solution was poured into ice-water, neutralized to pH 4—5, and extracted with chloroform five times. The combined extracts were successively washed with water and saturated salt solution, dried over anhydrous sodium sulfate, and freed from solvent to give 450 mg of crude product. Purification by chromatography on silica gel (15 g) using chloroform afforded 270 mg (76%) of crystalline **19**. Analytical sample was recrystallized from 1 : 1 petroleum ether–ether, mp 103.5—104.5 °C. IR (KBr) 3520, 1315, 1300; NMR ($CDCl_3$) 1.20 (s, 3H), 1.90—2.30 (m, 7H), 2.92 (finely splitted d, J=15.0, 1H), 3.32 (d, J=15.0, 1H), 3.40 (finely splitted s, 3H), 3.65 (ddd, J=11.8, 5.0, and 2.5, 1H), 4.03 (dt, J=11.8, 11.8, and 3.0, 1H). Found: C, 51.62; H, 8.11%. Calcd for $C_{10}H_{18}O_4S$: C, 51.27; H, 7.75%.

*cis-2-(β-Acetoxyethyl)-2-methylcyclobutyl Methyl Ketone (**22**).* To a solution of **19** (770 mg, 3.3 mmol) in 10% aqueous tetrahydrofuran (70 ml) was added aluminum amalgam prepared from 1.0 g of aluminum foil, and the mixture was refluxed for 8 hr. After removal of the insoluble material by filtration, the filtrate was concentrated under reduced pressure and extracted with ether twice. The combined extracts were washed with water and then saturated salt solution, and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 500 mg (96%) of the equilibrium mixture of the methyl ketone **20** and the acetal **21** as indicated by tlc and NMR analyses. The mixture, without further purification, was treated with a mixture of pyridine (3 ml) and acetic anhydride (3 ml) at room temperature overnight. The reaction mixture was poured into ice-water and extracted with ether three times. The combined extracts were washed successively with dilute hydrochloric acid, sodium bicarbonate solution, water, and saturated salt solution, dried over anhydrous sodium sulfate and concentrated. The crude product (500 mg) was purified by passing through a silica gel column (20 g) with 1 : 4 petroleum ether–ether and distilled (100—105 °C/10 mmHg) to give 255 mg (40%) of **22** as a sole product. IR (CCl_4) 1740, 1708, 1235; NMR 1.32 (s, 3H), 1.95 (s, 3H), 2.00 (s, 3H), 2.97 (t, J=7.5, 1H), 1.40—2.40 (m, 6H), 4.00 (t, J=7.5, 2H). Found: C, 66.71; H, 9.47%. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15%.

*cis-2-Isopropenyl-1-methylcyclobutaneethanol = (±)-grandisol (**16**).* The Wittig reagent, methylenetriphenylphosphorane, was prepared in dimethyl sulfoxide as reported in the literature[18] and this solution (1.5 equiv, *ca.* 4 ml) was added dropwise to a solution of **22** (100 mg, 0.5 mmol) in anhydrous tetrahydrofuran (3 ml) at room temperature. The resulting mixture was stirred at room temperature for 3 hr under nitrogen and poured into a separatory funnel containing ice-water. The resulting yellow solution was extracted with petroleum ether three times. The combined extracts were washed successively with 1 : 1 dimethyl sulfoxide–water, water, and then saturated salt solution, dried, and concentrated under reduced pressure to give crude product (125 mg) which consisted of two components, being presumably **16** and the acetate. The mixture was dissolved in methanol (2 ml) containing five drops of 1M sodium hydroxide solution and heated at 60—70 °C for 3 hr. The cooled reaction mixture was diluted with water and extracted with ether three times. Evaporation of the solvent, followed by distillation (100—110 °C/17 mmHg) of the residual liquid gave 67 mg (87%) of (±)—**16**, the IR and NMR spectra of which were completely indistinguishable from those of the authentic (±)-grandisol synthesized through an alternative route.[9e] Found : C, 78.02; H, 11.93%. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76%.

*Hydrolysis of **24a** and **24b**.* A solution of **24a** (400 mg) in acetone (14 ml) containing a catalytic amount of *p*-toluenesulfonic acid was stirred at 60 °C overnight. Usual work-up gave 330 mg of oily product. Chromatography on silica gel (10 g) using 3 : 7 petroleum ether–ether afforded 261 mg (82%) of *endo*-4-butyl-3-oxabicyclo[3.2.0]heptane-2,6-dione (**25a**).

In the same manner *exo*-isomer **25b** was obtained in 94% yield (76 mg) from 100 mg of **24b**. Analytical samples were purified by distillation (110—120 °C/1 mmHg). **25a**: IR (CCl_4) 1790, 1780; NMR 0.95 (t, J=6.0, 3H), 1.20—1.90 (m, 6H) 3.00—3.80 (m, 3H), 4.00 (m, 1H), 4.54 (dq, J= 8.0 and 7.0, 1H). Found: C, 65.62; H, 7.81%. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74%. **25b**: IR (CCl_4) 1790, 1780, 1170; NMR 0.95 (t, J=6.0, 3H), 1.20—1.80 (m, 6H), 3.10—3.80 (m, 4H), 4.58 (dt, J=6.0 and 1.7, 1H). Found: C, 65.66; H, 7.81%.

*Baeyer-Villiger Oxidation of **25a** and **25b**.* To a solution of **25a** (217 mg, 1.19 mmol) in acetic acid (4 ml) was added 30% aqueous hydrogen peroxide (520 mg), and the reaction mixture was allowed to stand at room temperature overnight. The mixture was neutralized with saturated sodium carbonate solution and extracted with ether three times. The combined extracts were washed with water and saturated salt solution and evaporated to dryness to give 216 mg (92%) of crystalline residue. Recrystallization from petroleum ether–ether–chloroform (2 : 2 : 1) gave colorless needles of *endo*-4-butyl-3,6-dioxabicyclo[3.3.0]octane-2,7-dione (**26a**), mp 85.0—85.5 °C:[20] IR (KBr) 1770, 1200, 1150; NMR ($CDCl_3$) 0.96 (t, J=6.5, 3H), 1.20—1.70 (m, 4H), 1.70—2.10 (m, 2H), 2.93 (d, J=6.0, 2H), 3.53 (q, J=6.0, 1H), 4.59 (dt, J=7.0 and 4.0, 1H), 5.10 (dd, J=6.0 and 4.0, 1H). Found: C, 60.26; H, 7.26%. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H,

7.12%.

According to the identical manner using 112 mg of **25b**, crystalline *exo*-isomer **26b** was obtained in 88% yield (106 mg). Recrystallized sample from carbon tetrachloride had mp 85.0—85.5 °C.[20,29] IR (KBr) 1775, 1200; NMR ($CDCl_3$) 0.96 (t, J=6.5, 3H), 1.20—1.90 (m, 6H), 2.94 (d, J=6.2, 2H), 3.47 (q, J=6.4, 1H), 4.70 (t, J=6.5, 1H), 4.88 (d, J=6.4, 1H). Found: C, 60.53; H, 6.77%. The structures of **26a** and **26b** were further confirmed by comparison of the IR and NMR spectra with those of the samples provided by Professor Yoshikoshi.

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