New Method for Derivatization of Squaric Acid to Highly Substituted Cyclobutenones: Lewis Acid-Catalyzed Reaction of Cyclobutene-1,2-dione Monoacetal and Its Vinylog with Unsaturated Organosilanes, and Subsequent Ring Transformation of the Adducts

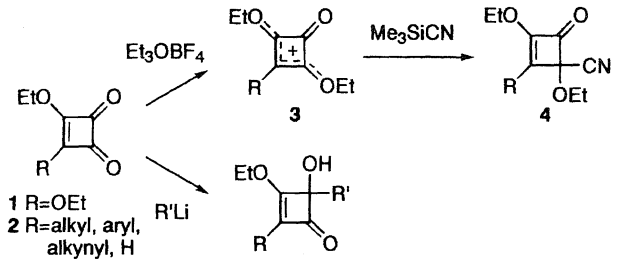
Yoshihiko Yamamoto,# Masatomi Ohno, and Shoji Eguchi*

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464-01

(Received December 4, 1995)

Described herein is a novel method for regio-controlled synthesis of highly substituted cyclobutenones having an unsaturated substituent at 4-position, starting from commercially available squaric acid. Both cyclobutene-1,2-dione monoacetal (4,4-diethoxycyclobutenone) and its vinylog (2,4-diethoxycyclobutenone), which were easily obtained from diethyl squarate, reacted with allylsilanes in the presence of $Et_2O{\cdot}BF_3$ to afford 4-allyl-4-ethoxycyclobutenones having various substituents at 2-position regioselectively. These products were efficiently transformed to highly substituted bicyclo[3.2.0]heptenones by refluxing in xylene. The synthetic utility of this process was demonstrated in the construction of tricyclic ring systems. Further extension of the Lewis acid-catalyzed reaction of the monoacetal using an allenylsilane, a silyl enol ether, and a silyl ketene acetal also afforded the corresponding 4-substituted products. In contrast to the above 4-allylated products, 4-propargylated and 4-acylmethylated products did not undergo an analogous ring transformation under the same conditions.

While squaric acid has unique characteristics[1] and has been applied for advanced materials,[2,3] it has also received much attention from the synthetic point of view as a precursor of substituted cyclobutenones and cyclobutenediones, which can be transformed to important ring systems;[4] e.g. quinone,[5] phenol,[5] cyclopentenedione,[6] butenolide,[7] polyquinane,[8] and various heterocycles.[9] In order to perform such transformations generally and efficiently, selective and viable derivatization of squaric acid is a prerequisite, and therefore, a number of feasible methods were established based on the 1,2-addition of organolithiums[10] and the palladium-catalyzed coupling of organotins.[11] We have developed a $TiCl_4$-catalyzed addition of allylsilane, silyl enol ether, and silyl ketene acetal to squaric acid families leading to various 4-hydroxycyclobutenone derivatives,[12] which were utilized for the novel type of ring transformation to butenolides.[7b] During the course of extensions of this work, we found an interesting triethyloxonium salt-promoted reaction of squaric acid diethyl ester **1** and related monoester **2** with trimethylsilyl cyanide. The cyanide addition was mediated with thermodynamically more favorable ethoxycarbenium ion **3** formed across a β-ethoxy enone moiety to produce *O*-ethyl cyanides **4** with regiochemistry different from that observed in the addition of organolithiums across a β-alkyl (aryl) enone moiety (Scheme 1).[13] In a similar reaction of the diethyl ester **1** with allyltrimethylsilane **5a**, initial mono-allylated

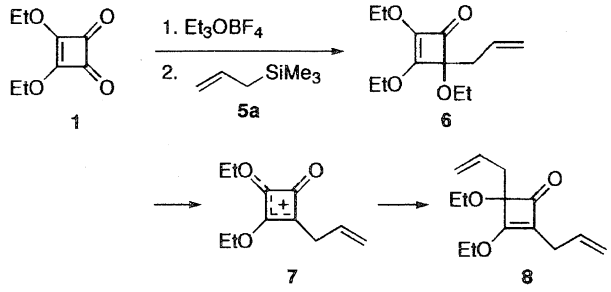


Scheme 1.

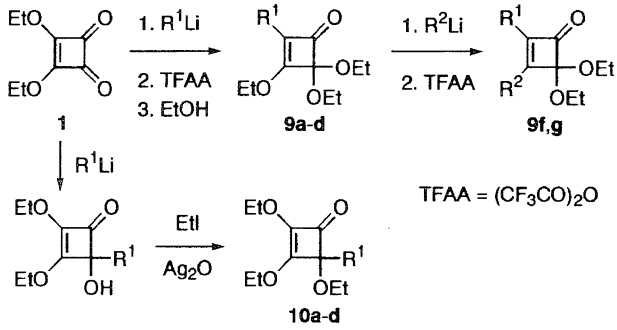
adduct **6** was formed and underwent further allylation under the employed conditions to give bis-allylated adduct **8** via ethoxycarbenium ion intermediate **7** (Scheme 2).[13] From these results, it is envisaged that 4,4-diethoxycyclobutenones (cyclobutene-1,2-dione monoacetal) and synthetically equivalent 2,4-diethoxycyclobutenones (vinylogous acetal) should be promising electrophiles toward unsaturated organosilanes. The required acetal **9** and its vinylog **10** can be conveniently prepared from diethyl squarate **1** according to the known procedure (Scheme 3).[10d]

Recently, Moore et al. reported the thermolysis of 4-allylcyclobutenones to give bicyclo[3.2.0]heptenones via tandem electrocyclic ring-opening and intramolecular [2+2]-cycloaddition of resulted vinylketenes such as **12**→**13**→**14** in Scheme 4.[14] Thus, feasible routes to the 4-allylcyclobutenone having diverse substituents seem to make this transformation more valuable as a powerful means of construc-

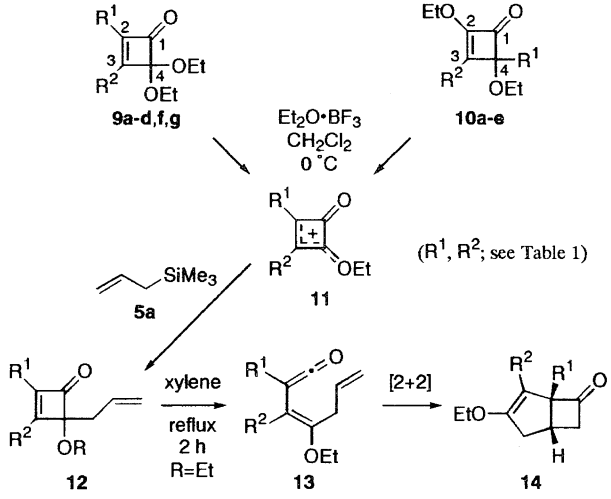
#Research Fellow of the Japan Society for the Promotion of Science.



Scheme 2.



Scheme 3.



Scheme 4.

tion of various bicycloalkanones. However, the reaction of 2-substituted squaric acid ester with allylmagnesium bromide and allyllithium in some cases resulted in low yields.[14] Moreover, the adducts obtained therefrom have a free hydroxyl group at 4-position (e.g., R = H in **12**, Scheme 4), and protection of this group is still better for the thermal ring transformation.[14] In these respects, the alternative synthetic method utilizing the addition of allylsilane via an ethoxycarbenium ion intermediate (e.g. **7**), is expected to solve the problems. In fact, it was communicated by us that 4-allyl-4-ethoxycyclobutenones were obtained in good yields from BF_3-catalyzed reaction of the acetal **9** with allylsilanes, and direct transformation of this protected form to bicyclo[3.2.0]-heptenones was realized in high yield.[15] We now describe the full details of this effective allylation method and applications to syntheses of highly substituted bi- and tricyclic ring systems. The electrophilic reaction using a monoacetal of the cyclobutenedione is also shown to be successful with an allenylsilane, a silyl enol ether, and a silyl ketene acetal.

Results and Discussion

Scheme 4 illustrates the new route to 4-allylcyclobutenones having a variety of substituents at 2-position from the cyclobutene-1,2-dione monoacetal **9** and its vinylog **10**, and the results are summarized in Table 1. The catalytic action of a Lewis acid on **9** produced the key ethoxycarbenium ion intermediate **11**, which reacted with allyltrimethylsilane **5a** regioselectively to afford the desired 4-allyl-4-ethoxycyclobutenone **12**. A typical example is the case of methyl-substituted monoacetal **9a** (Entry a). Thus, a solution of **9a** and **5a** (3 mol amt.) in dry dichloromethane was allowed to react with $Et_2O{\cdot}BF_3$ (1.2 mol amt.) at 0 °C for 1 h and, after standard work-up and chromatographic separation, the expected 4-allyl-4-ethoxycyclobutenone **12a** was obtained in a yield of 79%. The structure was confirmed by comparison with the related known compound, the spectral features of which were in good accordance with those of **12a** (IR, ^{1}H and ^{13}C NMR).[14] The similar reaction of phenyl- and alkynyl-substituted substrate **9b,c** afforded the corresponding products **12b,c** in 72 and 90% yields, respectively (Entries b and c), but the slow reaction of vinyl-substituted substrate **9d** resulted in the formation of the corresponding product **12d** in low yield (Entry d). As expected, the vinylogous acetal **10** was also the other candidate for generation of the common cationic intermediate **11**. Thus, cyclobutenones **10a—d**

Table 1. Synthesis and Thermolysis of 4-Allylcyclobutenones **12a—g**

Entry	R^1	R^2	Starting cyclobutenone		**12** Yield %	**14** Yield %
a	Me	OEt	**9a**	(**10a**)	**12a**, 79[a] (84)[b]	**14a**, 98
b	Ph	OEt	**9b**	(**10b**)	**12b**, 72[a] (75)[b]	**14b**, 73
c	PhC≡C	OEt	**9c**	(**10c**)	**12c**, 90[a] (93)[b]	**14c**, 94
d	H_2C=CH	OEt	**9d**	(**10d**)	**12d**, 15[a] (22)[b]	**14d**, 98
e	BnO_2CCH_2	OEt	**10e**		**12e**, 66[b]	**14e**, 83
f	Me	Ph	**9f**		**12f**, 72[b]	**14f**, 99
g	Ph	Me	**9g**		**12g**, 75[b]	**14g**, 97

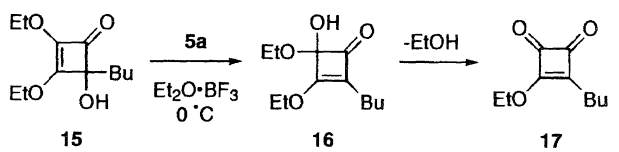
a) Isolated yield from **9**. b) Isolated yield from **10**.

were subjected to the above catalyzed allylation and the same products **12a—d** were obtained in comparable yields (Entries a—d). Notably, the reaction of 4-benzyloxycarbonylmethyl-substituted substrate **10e** was effected under these electrophilic conditions to give **12e** in a yield of 66% (Entry e). Such chemoselective allylation seems to be rather difficult under related nucleophilic conditions. Furthermore, 2,3-alkyl(aryl)-substituted 4-allylcyclobutenones **12f** and **g** were obtained similarly from **9f** and **g** in 72 and 75% yields, respectively (Entries f and g). As a route to such compounds, Moore et al. also reported the 2-step conversion involving addition of an unsaturated organolithium to 2,3-disubstituted cyclobutene-1,2-dione monoacetal and deacetalization.[8f,10d] In our method, acetals **9f,g** were allylated directly in one step.

The above procedure (**10**→**12**) might be more practical if a 1,2-addition product of **1** (e.g. vinylogous hemiacetal **15**) could be used straightforwardly without alkyl-protection for the present allylation. However, $Et_2O{\cdot}BF_3$-catalysis of the hydroxy-form **15** induced elimination of EtOH from the rearranged hemiacetal **16** prior to the desired allylation, leading to the exclusive formation of 4-butyl-3-ethoxy-3-cyclobutene-1,2-dione **17** (Scheme 5). Such a conversion under acidic conditions was exploited in the synthesis of mycotoxin moniliformin derivatives.[10a,10b]

The obtained 4-allylcyclobutenones **12a—g** can be transformed into bicyclo[3.2.0]heptenones via an unsaturated ketene intermediate (i.e. **13**) as described above. Thermal rearrangement of an alcohol form (i.e. **12**, R=H) for this purpose may lead to unsatisfactory results.[14] Advantageously, the hydroxyl group was here already protected by an ethyl group, and therefore, **12a—g** were converted directly and cleanly into bicyclo[3.2.0]heptenones **14a—g** in high yields by refluxing in xylene for 2 h (Scheme 4, Table 1). The structures of these products were elucidated by IR, MS, ^{1}H NMR, and ^{13}C NMR spectral data. The ^{1}H and ^{13}C NMR spectra were especially informative; bicyclic ring protons were indicated with reasonable ABX coupling patterns; chemical shifts for the change of two side chain carbons from sp^2 to sp^3 were also observed.

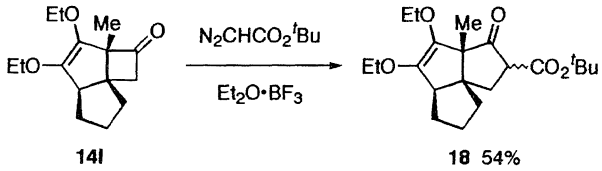
It is well known that allylsilanes react regioselectively (at γ to the silyl group) with electrophiles.[16] Therefore, the above reaction sequence using variously substituted allylsilanes provides a method for the regio-controlled synthesis of 4-allyl-4-ethoxycyclobutenones and, in turn, of highly substituted bicyclo[3.2.0]heptenones. This was exemplified by using the cyclobutene-1,2-dione monoacetal **9a**. Thus, methallylsilane **5b** reacted with **9a** under similar catalytic conditions for 5 h to give **12h** in 72% yield. Ester-functionalized allylsilane **5c** afforded cyclobutenyl-enoate **12i** efficiently. The similar reactions of γ-substituted allylsilanes



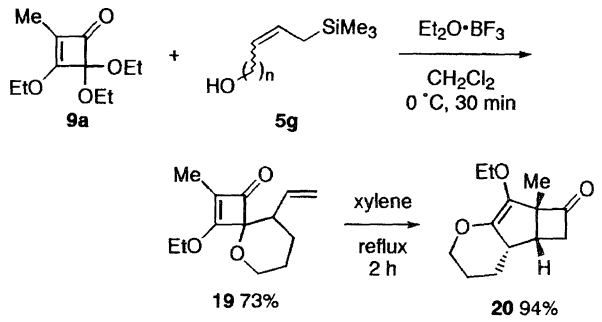
Scheme 5.

such as cinnamylsilane **5d** and prenylsilane **5e** furnished the corresponding products **12j**, **k** in 60 and 50% yields, respectively. The 4-allylcyclobutenones **12h—k** obtained here could be also transformed to highly substituted bicyclo[3.2.0]heptenones **14h—k** in the same manner as above. These results are summarized in Table 2. The structures were likewise confirmed by spectral means; in the case of **14j**, the stereochemistry was assigned as *exo*-configuration (vide infra).

Furthermore, the synthetic potential of the present method was demonstrated by the construction of tricyclic ring systems. An angular triquinane skeleton[17] was constructed efficiently by utilizing our route via electrophilic allylation and thermal ring expansion; thermolysis of 2-methylenecyclopentyl-substituted cyclobutenone **12l**,[18] which was readily prepared from the acetal **9a** and a cyclic allylsilane **5f**, afforded tricyclo[5.3.0.$0^{1,4}$]decenone **14l** in 94% yield (Entry e in Table 2). Ring enlargement of cyclobutanone in the tricyclic system was then carried out by employing *t*-butyl diazoacetate with a $Et_2O{\cdot}BF_3$ catalyst[19] to give a triquinane derivative **18** in 54% yield as a selectively rearranged product (Scheme 6). When the reported spiro-annulation of an ω-hydroxy-substituted allylsilane with an acetal[20] was combined with our method, oxaspiro[3.5]nonenone **19** could be produced from acetal **9a** and an appropriate allylsilane **5g** in 73% yield.[20] Then, thermolysis converted **19** cleanly into oxatricyclo[5.4.0.$0^{2,5}$]undecenone **20** as a single diastereomer in 94% yield (Scheme 7). These tricyclic compounds were characterized by spectral information, in which the stereochemistry of **20** was found to be different from that of phenyl-substituted bicyclic compound **14j**. The ^{1}H NMR spectrum of **20** showed that the coupling constant between the allylic proton H_a and the bridgehead proton H_b was 7.4 Hz, whereas the corresponding coupling between H_a and H_b of **14j** was not observed because H_a and H_b were orthogonal in the case of the *exo* orientation of a C_4-substituent (Fig. 1). Therefore, the stereochemistry of C_4 in **14j** and of C_1 in **20** was determined

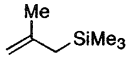
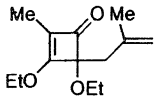
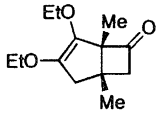
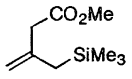
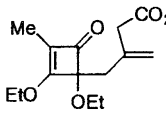
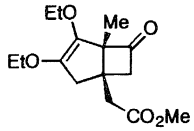
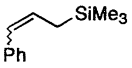
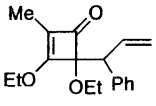
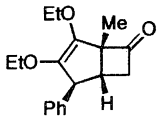
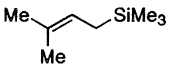
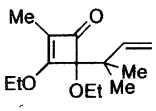
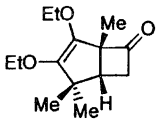
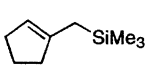
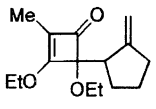
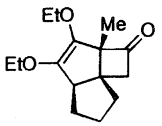


Scheme 6.

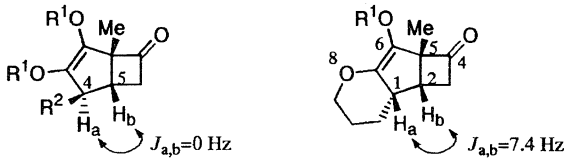


Scheme 7.

Table 2. Synthesis and Thermolysis of 4-Allylcyclobutenones **12h—l**

Entry[a]	Allylsilane		Reaction time/h	4-Allylcyclobutenone[b] (Yield/%)		Bicycloheptenone[c] (Yield/%)	
a		**5b**	5		**12h** (72)		**14h** (94)
b		**5c**	5		**12i** (82)		**14i** (99)
c		**5d**	5		**12j** (60)		**14j** (100)
d		**5e**	5		**12k** (50)		**14k** (57)
e		**5f**	7		**12l** (64)		**14l** (94)

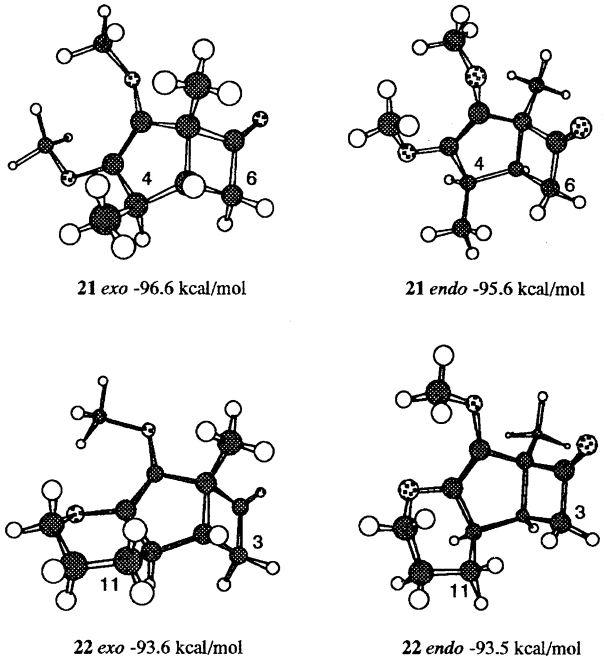
a) The acetal **9a** was used as a substrate throughout Entries a—e. b) Products of the $Et_2O{\cdot}BF_3$-catalyzed reaction at 0 °C for a period indicated. c) Products of the thermal reaction at reflux temperature of xylene for 2 h.



14j *exo* (R^1=Et,R^2=Ph)
21 R^1=R^2=Me

20 *endo* (R^1=Et)
22 R^1=Me

Fig. 1.



21 *exo* -96.6 kcal/mol

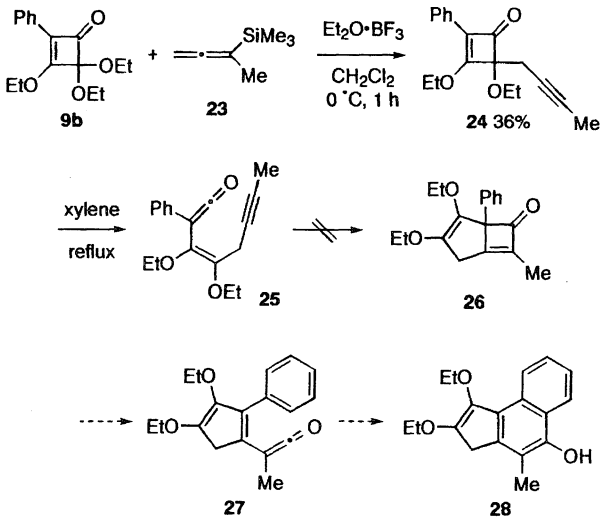
21 *endo* -95.6 kcal/mol

22 *exo* -93.6 kcal/mol

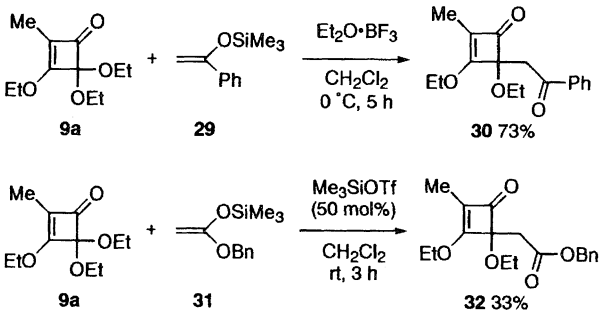
22 *endo* -93.5 kcal/mol

Fig. 2.

to be the *exo*- and *endo*-configurations, respectively. Moore reported the preferential formation of the *exo* isomers in the related rearrangement of 4-(1-methyl-2-propenyl)- and 4-(1-phenyl-2-propenyl)-2,3,4-trimethoxy-2-cyclobutenones.[14] In order to find the origin of the different stereoselectivity in these systems, RHF/PM3 calculations[21] were performed for 2,3-dimethoxy-1,4-dimethylbicyclo[3.2.0]hept-2-en-7-one **21** and 6-methoxy-5-methyl-8-oxatricyclo[5.4.0.$0^{2,5}$]undec-6-en-4-one **22**, as models for simplicity. At first, geometries of both *exo*- and *endo*-isomers of **21** were fully optimized by use of the EF routine in the MOPAC package[22] with the key-word PRECISE, and the heats of formation of both isomers were obtained as shown in Fig. 2. The *exo*-isomer was found to be slightly more favorable in energy (1.0 kcal mol^{-1}) than the *endo*-isomer, and this difference may reflect the predominance of the *exo*-isomer over the *endo*-isomer. In contrast to this bicyclic system, almost the same heats of formation were obtained for both isomers of tricyclic compound **22**. This calculation means that the *exo*-isomer is no longer preferable to the *endo*-isomer, but it does not yet explain the experimental results. At present it is difficult to find out the reason, but a model study for **21** suggested that steric repulsion between the proximate C_4–Me and C_6–H was likely to render the *endo*-transition state disadvantageous. In comparison, such a steric hindrance (C_{11}–CH_2 and C_3–H in the tricyclic **22**) might be slightly decreased at the *endo*-transition state due to a folded oxane structure.



Scheme 8.



Scheme 9.

In continuing the reaction with unsaturated organosilanes, we next attempted the propargylation of the monoacetal using an allenylsilane. Under the same conditions as employed for the above allylation, the desired 4-(2-butynyl)cyclobutenone **24** was obtained from the acetal **9b** and 3-silyl-1,2-butadiene **23** in 21% yield, which was somewhat improved to 36% by the dropwise addition of **23** to the solution of **9b** and $Et_2O{\cdot}BF_3$ in dichloromethane at 0 °C. The thermolysis of **24** might produce a tricyclic phenol **28** via double electrocyclic ring opening/ring reclosure processes as depicted in Scheme 8. However, no sign indicating the conversion of **24** into some products was observed on heating in xylene. This is probably because the intramolecular [2+2] cycloaddition of **25** to a highly strained bicyclo[3.2.0]heptadienone **26** is unlikely.

The present method was then extended to the reaction with a silyl enol ether and a silyl ketene acetal (Scheme 9). The acetal **9a** was reacted with a silyl enol ether **29** derived from acetophenone (3 mol amt.) in the presence of $Et_2O{\cdot}BF_3$ (1.2 mol amt.) at 0 °C for 5 h to afford 4-phenacylcyclobutenone **30** in good yield. On the other hand, the reaction of **9a** with a more reactive silyl ketene acetal **31** produced only a complex reaction mixture under these conditions. Nevertheless, the desired product **32** was obtained in moderate yield, when the reaction was conducted in the presence of 50 mol% of TMSOTf at ambient temperature for 3 h. In the related work, we previously reported Et_3OBF_4-mediated addition of silyl enol ether and silyl ketene acetal to diethyl squarate **1**, leading to 4-acylmethyl-2,3,4-triethoxycyclobutenones.[13] The obtained 4-acylmethylcyclobutenones are considered as an oxa-analog of the 4-allylcyclobutenone. Thus, the thermolysis of **30** was attempted to give a bicyclic β-lactone (or its decarboxylated product) via the similar type of transformation of **12**→**14**; however, **30** remained intact after refluxing in xylene for 1 h.[23]

Conclusions

Regioselective synthesis of 4-allyl-4-ethoxycyclobutenones having alkyl, alkenyl, aryl, and alkynyl substituents at 2-position was achieved by the novel Lewis acid-catalyzed reaction of both 2,4- and 4,4-diethoxycyclobutenones (derivable from diethyl squarate) with a variety of allylsilanes. The products were transformed to the corresponding highly substituted bicyclo[3.2.0]heptenones without appreciable side reactions. This method was successfully applied to synthesis of tricyclic compounds. Further extension to other organosilanes such as allenylsilane, silyl enol ether, and silyl ketene acetal gave 4-propargyl- and 4-acylmethyl-substituted cyclobutenone derivatives. The present electrophilic C–C bond formation on the four-membered ring is of considerable value as a method for regio-controlled synthesis of highly substituted cyclobutenones having an unsaturated substituent at 4-position, which could be more practical than the synthesis under nucleophilic conditions.

Experimental

General. IR spectra were recorded on a JASCO FT/IR 5300 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained with a Varian GEMINI-200 spectrometer at 200 and 50 MHz, respectively, for samples in $CDCl_3$ solution with $SiMe_4$ as an internal standard. Mass spectra were recorded on a JEOL JMS-AX 505 HA mass spectrometer. Flash chromatography was performed with a silica gel column (Fuji–Davison BW-300) eluted with mixed solvents [hexane (H), ethyl acetate (A)]. Microanalyses were performed with a Perkin–Elmer 2400S CHN elemental analyzer. Dichloromethane was dried over $CaCl_2$, distilled, and stored over 4 Å molecular sieves. Xylene was dried over Na, distilled, and stored over Na. Unsaturated organosilanes used here were synthesized according to reported procedures.[24] Squaric acid was supplied by Kyowa Hakko Kogyo Co., Ltd., and diethyl ester **1** as a starting compound was prepared by the azeotropic method.[12]

Typical Procedure for Synthesis of Cyclobutenedione Monoacetals 9a—d. According to the reported procedure,[10d] **9a** was synthesized as follows; to a solution of **1** (510 mg, 3.00 mmol) in dry THF (30 mL) was added methyllithium (3.3 mL, 1 M solution in ether, 1 M = 1 mol dm^{-3}) at −78 °C under a nitrogen atmosphere, and the solution was stirred for 30 min. To this solution was added trifluoroacetic anhydride (0.47 mL, 3.30 mmol). The solution was stirred for 30 min and treated with dry ethanol (12 mL). After stirring for 30 min, the solution was quenched with 10% $NaHCO_3$ (20 mL) and extracted with ether (10 mL×3). The extracts were washed with brine (20 mL), dried (Na_2SO_4), and evaporated to dryness. Flash chromatography of the residue (Elution H–A 10 : 1) gave monoacetal **9a** (792 mg, 74%) as a colorless oil. The other monoacetals **9c—d** were obtained in the same manner with

the corresponding organolithiums.

3,4,4-Triethoxy-2-methyl-2-cyclobutenone (9a). IR (neat) 1767, 1628 cm^{-1}; ^1H NMR δ = 1.24 (6H, t, J = 7.0 Hz), 1.45 (3H, t, J = 7.2 Hz), 1.74 (3H, s), 3.75 and 3.81 (each 2H, dq, J = 9.4, 7.0 Hz), 4.47 (2H, q, J = 7.2 Hz); ^{13}C NMR δ = 6.4, 15.1, 15.4 (2C), 61.5 (2C), 69.0, 112.7, 127.1, 183.7, 193.1; MS (EI) *m/z* (rel intensity) 214 (M^+; 5), 185 (88), 157 (79), 129 (100), 113 (40). Found: C, 61.79; H, 8.34%. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47%.

3,4,4-Triethoxy-2-phenyl-2-cyclobutenone (9b). 63%; oil (Elution H–A 15 : 1); IR (neat) 1757, 1634, 1599 cm^{-1}; ^1H NMR δ = 1.27 (6H, t, J = 7.0 Hz), 1.52 (3H, t, J = 7.0 Hz), 3.78 and 3.89 (each 2H, dq, J = 9.4, 7.0 Hz), 4.63 (2H, q, J = 7.0 Hz), 7.25—7.43 (3H, m), 7.78—7.84 (2H, m); ^{13}C NMR δ = 15.5 (3C), 62.1 (3C), 70.0, 114.9, 127.4 (2C), 128.6, 128.8, 128.9 (2C), 182.2, 191.0; MS (EI) *m/z* (rel intensity) 276 (M^+; 27), 247 (79), 219 (57), 191 (42), 145 (100). Found: C, 69.67; H, 7.18%. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30%.

3,4,4-Triethoxy-2-phenylethynyl-2-cyclobutenone (9c). 23%; oil (Elution H–A 15 : 1); IR (neat) 2209, 1773, 1620, 1593 cm^{-1}; ^1H NMR δ = 1.26 (6H, t, J = 7.0 Hz), 1.56 (3H, t, J = 7.0 Hz), 3.84 (4H, q, J = 7.0 Hz), 4.77 (2H, q, J = 7.0 Hz), 7.30—7.49 (5H, m); ^{13}C NMR δ = 15.1, 15.4 (2C), 61.8 (2C), 71.0, 75.7, 95.6, 111.7, 112.4, 128.8 (2C), 129.4 (2C), 132.1, 184.7, 188.3; MS (EI) *m/z* (rel intensity) 300 (M^+; 75), 271 (78), 243 (57), 215 (71), 187 (100). Found: C, 71.98; H, 6.63%. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%.

2-Ethenyl-3,4,4-triethoxy-2-cyclobutenone (9d). 11%; oil (Elution H–A 5 : 1); IR (neat) 1759, 1642, 1607, 1586 cm^{-1}; ^1H NMR δ = 1.25 (6H, t, J = 7.0 Hz), 1.47 (3H, t, J = 7.0 Hz), 3.76 and 3.83 (each 2H, dq, J = 10.2, 7.0 Hz), 4.51 (2H, q, J = 7.0 Hz), 5.42 (1H, dd, J = 10.6, 2.4 Hz), 5.99 (1H, dd, J = 17.6, 2.4 Hz), 6.19 (1H, dd, J = 17.6, 10.6 Hz); ^{13}C NMR δ = 15.1, 15.4 (2C), 61.7 (2C), 69.7, 113.1, 122.1, 122.4, 127.6, 180.7, 190.6; MS (EI) *m/z* (rel intensity) 226 (M^+; 17), 197 (52), 169 (30), 141 (46), 113 (100). Found: C, 63.92; H, 7.80%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

Synthesis of Cyclobutenedione Monoacetals 9f and g. According to the reported procedure,[10d] **9f** was synthesized as follows; to a solution of **9a** (319 mg, 1.49 mmol) in dry THF (20 mL) was added phenyllithium (4.5 mL, 1 M solution in cyclohexane–ether) at −78 °C under a nitrogen atmosphere, and the solution was stirred for 30 min. To this solution was added trifluoroacetic anhydride (0.32 mL, 2.23 mmol). After stirring for 30 min, the reaction mixture was quenched with 10% $NaHCO_3$ (10 mL) and extracted with ether (10 mL×3). The extracts were washed with brine (20 mL), dried (Na_2SO_4), and evaporated to dryness. Flash chromatography of the residue (Elution H–A 40 : 1) gave monoacetal **9f** (255 mg, 69%) as a colorless oil. Similarly, monoacetal **9g** was obtained from **9b** and methyllithium in 66% yield.

4,4-Diethoxy-2-methyl-3-phenyl-2-cyclobutenone (9f). IR (neat) 1752, 1620, 1574 cm^{-1}; ^1H NMR δ = 1.22 (6H, t, J = 7.0 Hz), 2.10 (3H, s), 3.69 and 3.80 (each 2H, dq, J = 9.2, 7.0 Hz), 7.45—7.53 (3H, m), 7.79—7.86 (2H, m); ^{13}C NMR δ = 9.0, 15.6 (2C), 61.8 (2C), 117.0, 129.1 (2C), 129.5 (2C), 130.9, 131.9, 149.6, 174.9, 197.3; MS (EI) *m/z* (rel intensity) 246 (M^+; 11), 217 (37), 189 (57), 161 (65), 115 (100). Found: C, 73.18; H, 7.33%. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37%.

4,4-Diethoxy-3-methyl-2-phenyl-2-cyclobutenone (9g). Oil (Elution H–A 30 : 1); IR (neat) 1761, 1636, 1597 cm^{-1}; ^1H NMR δ = 1.26 (6H, t, J = 7.0 Hz), 2.49 (3H, s), 3.78 and 3.83 (each 2H, dq, J = 9.2, 7.0 Hz), 7.34—7.48 (3H, m), 7.71—7.77 (2H, m); ^{13}C NMR δ = 13.0, 15.5 (2C), 61.4 (2C), 115.7, 128.2 (2C), 129.1 (2C), 129.4, 130.0, 150.6, 176.3, 193.7; MS (EI) *m/z* (rel intensity) 246 (M^+; 12), 217 (56), 189 (83), 161 (91), 145 (100), 115 (85). Found: C, 73.25; H, 7.27%. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37%.

Typical Procedure for Synthesis of 2,3,4-Triethoxycyclobutenones 10a—d. According to the reported procedure,[14] **10a** was synthesized as follows; a solution of 2,3-diethoxy-4-hydroxy-4-methyl-2-cyclobutenone[7d] (907 mg, 4.87 mmol), iodoethane (3.9 mL, 48.7 mmol) in dry acetonitrile (15 mL) was treated with Ag_2O (4.51 g, 19.5 mmol) and K_2CO_3 (3.37 g, 24.4 mmol) under a nitrogen atmosphere, and the suspension was stirred overnight. Insoluble materials were filtered off and the filtrate was concentrated under reduced pressure. Flash chromatography of the residue (Elution H–A 15 : 1) gave cyclobutenone **10a** (619 mg, 59%) as a colorless oil. In the same manner, **10b—d** were obtained from the corresponding derivatives[7d] of 4-hydroxycyclobutenones. Benzyloxycarbonylmethyl-substituted **10e** was reported in our previous paper.[13]

2,3,4-Triethoxy-4-methyl-2-cyclobutenone (10a). IR (neat) 1771, 1634 cm^{-1}; ^1H NMR δ = 1.20 (3H, t, J = 7.0 Hz), 1.31 (3H, t, J = 7.0 Hz), 1.43 (3H, t, J = 7.0 Hz), 1.47 (3H, s), 3.50 (2H, q, J = 7.0 Hz), 4.28 and 4.33 (each 1H, dq, J = 10.2, 7.0 Hz), 4.45 (2H, q, J = 7.0 Hz); ^{13}C NMR δ = 15.3, 15.5, 15.6, 18.7, 60.1, 66.8, 69.1, 88.1, 132.7, 169.1, 188.3; MS (EI) *m/z* (rel intensity) 214 (M^+; 41), 185 (90), 157 (100), 129 (55), 113 (39). Found: C, 61.86; H, 8.21%. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47%.

2,3,4-Triethoxy-4-phenyl-2-cyclobutenone (10b). 61%; oil (Elution H–A 20 : 1); IR (neat) 1773, 1634 cm^{-1}; ^1H NMR δ = 1.28 (3H, t, J = 7.0 Hz), 1.34 (3H, t, J = 7.0 Hz), 1.38 (3H, t, J = 7.0 Hz), 3.66 (2H, q, J = 7.0 Hz), 4.34 and 4.38 (each 1H, dq, J = 10.2, 7.0 Hz), 4.37 and 4.44 (each 1H, dq, J = 10.2, 7.0 Hz), 7.25—7.41 (3H, m), 7.49—7.56 (2H, m); ^{13}C NMR δ = 15.2, 15.5, 15.6, 61.0, 67.1, 69.4, 92.4, 126.6 (2C), 128.5, 128.7 (2C), 135.0, 137.3, 166.0, 184.7; MS (EI) *m/z* (rel intensity) 276 (M^+; 12), 247 (100), 219 (37), 191 (66), 145 (43). Found: C, 69.76; H, 7.10%. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30%.

2, 3, 4- Triethoxy- 4- phenylethynyl- 2- cyclobutenone (10c). 58%; oil (Elution H–A 20 : 1); IR (neat) 2222, 1779, 1642 cm^{-1}; ^1H NMR δ = 1.27 (3H, t, J = 7.2 Hz), 1.33 (3H, t, J = 7.0 Hz), 1.47 (3H, t, J = 7.0 Hz), 3.87 and 3.92 (each 1H, dq, J = 9.2, 7.0 Hz), 4.34 (2H, q, J = 7.2 Hz), 4.52 and 4.58 (each 1H, dq, J = 10.2, 7.0 Hz), 7.29—7.36 (3H, m), 7.45—7.51 (2H, m); ^{13}C NMR δ = 15.2, 15.6 (2C), 63.0, 67.3, 69.8, 82.3, 83.8, 89.9, 122.3, 128.6 (2C), 129.2, 132.3 (2C), 135.2, 164.5, 180.7; MS (EI) *m/z* (rel intensity) 300 (M^+; 14), 271 (41), 243 (100), 215 (91), 187 (59). Found: C, 71.98; H, 6.63%. Calcd for $C_{18}H_{20}O_4$: C, 71.93; H, 6.76%.

4-Ethenyl-2,3,4-triethoxy-2-cyclobutenone (10d). 44%; oil (Elution H–A 20 : 1); IR (neat) 1773, 1636 cm^{-1}; ^1H NMR δ = 1.24 (3H, t, J = 7.0 Hz), 1.32 (3H, t, J = 7.0 Hz), 1.41 (3H, t, J = 7.0 Hz), 3.60 (2H, q, J = 7.0 Hz), 4.33 (2H, q, J = 7.0 Hz), 4.42 (2H, q, J = 7.0 Hz), 5.34 (1H, dd, J = 10.6, 1.4 Hz), 5.52 (1H, dd, J = 17.4, 1.4 Hz), 5.95 (1H, dd, J = 17.4, 10.6 Hz); ^{13}C NMR δ = 15.3, 15.4, 15.5, 60.6, 67.0, 69.3, 91.8, 118.5, 134.4, 134.6, 166.8, 185.2; MS (EI) *m/z* (rel intensity) 226 (M^+; 56), 197 (23), 169 (35), 141 (98), 113 (100). Found: C, 63.78; H, 7.94%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

Typical Procedure for Synthesis of 4-Allylcyclobutenones 12a—g. To a solution of **9a** (45 mg, 0.21 mmol) and **5a** (72 mg, 0.63 mmol) in dry dichloromethane (2 mL) was added $Et_2O{\cdot}BF_3$ (0.032 mL, 0.25 mmol) at 0 °C under a nitrogen atmosphere. After stirring for 1 h, the reaction mixture was quenched with 10% $NaHCO_3$ (5 mL) and extracted with dichloromethane (5 mL×3). The extracts were dried (Na_2SO_4) and evaporated to dryness. Flash

chromatography of the residue (Elution H–A 5 : 1) gave 4-allylcyclobutenone **12a** (37 mg, 84%) as a colorless oil. The other allylcyclobutenones **12b—g** were obtained according to the same procedure and isolated yields are shown in Table 1.

3,4-Diethoxy-2-methyl-4-(2-propenyl)-2-cyclobutenone (12a). IR (neat) 1761, 1622 cm^{-1}; ^1H NMR δ = 1.20 (3H, t, J = 7.0 Hz), 1.45 (3H, t, J = 7.2 Hz), 1.71 (3H, s), 2.50 and 2.66 (each 1H, ddt, J = 14.2, 7.6, 1.2 Hz), 3.49 and 3.56 (each 1H, dq, J = 8.8, 7.0 Hz), 4.39 and 4.45 (each 1H, dq, J = 10.0, 7.2 Hz), 5.03—5.17 (2H, m), 5.62—5.84 (1H, m); ^{13}C NMR δ = 6.3, 15.3, 15.4, 37.0, 60.7, 68.6, 96.2, 118.7, 123.2, 132.7, 183.5, 193.7; MS (EI) *m/z* (rel intensity) 210 (M^+; 10), 181 (100), 153 (42), 122 (15), 113 (13). Found: C, 68.80; H, 8.38%. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63%.

3,4-Diethoxy-2-phenyl-4-(2-propenyl)-2-cyclobutenone (12b). Oil (Elution H–A 20 : 1); IR (neat) 1755, 1632, 1599 cm^{-1}; ^1H NMR δ = 1.24 (3H, t, J = 7.0 Hz), 1.53 (3H, t, J = 7.0 Hz), 2.61 and 2.88 (each 1H, ddt, J = 14.4, 7.6, 1.2 Hz), 3.58 and 3.68 (each 1H, dq, J = 9.0, 7.0 Hz), 4.50 and 4.57 (each 1H, dq, J = 9.8, 7.0 Hz), 5.05—5.22 (2H, m), 5.78 (1H, m), 7.23—7.41 (3H, m), 7.74—7.80 (2H, m); ^{13}C NMR δ = 15.4, 15.5, 38.3, 61.1, 69.4, 98.3, 119.1, 125.0, 127.3 (2C), 128.4 (2C), 128.8 (2C), 132.3, 182.1, 190.2; MS (EI) *m/z* (rel intensity) 272 (M^+; 46), 243 (100), 215 (28), 145 (91). Found: C, 75.01; H, 7.36%. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40%.

3, 4- Diethoxy- 2- phenylethynyl- 4- (2- propenyl)- 2- cyclobutenone (12c). Oil (Elution H–A 20 : 1); IR (neat) 2209, 1769, 1620, 1593 cm^{-1}; ^1H NMR δ = 1.23 (3H, t, J = 7.0 Hz), 1.55 (3H, t, J = 7.0 Hz), 2.56 and 2.67 (each 1H, ddt, J = 12.0, 5.4, 1.2 Hz), 3.55 and 3.62 (each 1H, q, J = 7.0 Hz), 5.09—5.21 (2H, m), 5.69—5.89 (1H, m), 7.30—7.49 (5H, m); ^{13}C NMR δ = 15.2, 15.4, 36.7, 61.3, 70.7, 93.3, 96.8, 108.3, 119.3, 122.5, 127.3, 128.7 (2C), 129.3, 131.9, 132.0 (2C), 185.8, 190.1; MS (EI) *m/z* (rel intensity) 300 (M^+; 75), 271 (78), 243 (57), 215 (71), 187 (100). Found: C, 71.98; H, 6.63%. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%.

2- Ethenyl- 3, 4- diethoxy- 4- (2- propenyl)- 2- cyclobutenone (12d). Oil (Elution H–A 20 : 1); IR (neat) 1753, 1642, 1582 cm^{-1}; ^1H NMR δ = 1.21 (3H, t, J = 7.0 Hz), 1.47 (3H, t, J = 7.0 Hz), 2.53 and 2.71 (each 1H, ddt, J = 14.4, 7.6, 1.2 Hz), 3.51 and 3.60 (each 1H, dq, J = 9.0, 7.0 Hz), 4.43 and 4.48 (each 1H, dq, J = 10.0, 7.0 Hz), 5.05—5.18 (2H, m), 5.37 (1H, dd, J = 10.6, 2.4 Hz), 5.75 (1H, m), 5.95 (1H, dd, J = 17.6, 2.4 Hz), 6.13 (1H, dd, J = 17.6, 10.6 Hz); ^{13}C NMR δ = 15.1, 15.5, 37.4, 61.0, 69.3, 96.9, 118.9, 121.7, 122.1, 124.4, 132.4, 180.8, 191.2; MS (EI) *m/z* (rel intensity) 222 (M^+; 18), 193 (100), 137 (26), 95 (53), 69 (96). Found: C, 70.33; H, 8.07%. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%.

Benzyl [2,3-Diethoxy-4-oxo-3-(2-propenyl)-1-cyclobutenyl]-acetate (12e). Oil (Elution H–A 8 : 1); IR (neat) 1767, 1738, 1624 cm^{-1}; ^1H NMR δ = 1.15 (3H, t, J = 7.0 Hz), 1.40 (3H, t, J = 7.0 Hz), 2.50 and 2.68 (each 1H, ddt, J = 14.4, 7.6, 1.2 Hz), 3.20 (2H, s), 3.45 and 3.53 (each 1H, dq, J = 9.0, 7.0 Hz), 4.35 and 4.41 (each 1H, dq, J = 9.8, 7.0 Hz), 4.99—5.07 (2H, m), 5.13 (2H, s), 5.71 (1H, m), 7.35 (5H, s); ^{13}C NMR δ = 15.1, 15.3, 27.5, 37.2, 60.9, 67.3, 69.1, 96.9, 118.8, 128.7, 128.8 (3C), 128.9 (2C), 132.4, 135.7, 169.4, 185.3, 192.1; MS (EI) *m/z* (rel intensity) 344 (M^+; 5), 253 (100), 225 (12), 179 (51), 151 (34). Found: C, 69.79; H, 6.98%. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02%.

4-Ethoxy-2-methyl-3-phenyl-4-(2-propenyl)-2-cyclobutenone (12f). Oil (Elution H–A 25 : 1); IR (neat) 1752, 1618, 1572 cm^{-1}; ^1H NMR δ = 1.19 (3H, t, J = 7.0 Hz), 2.07 (3H, s), 2.70 and 2.84 (each 1H, ddt, J = 14.2, 7.4, 1.2 Hz), 3.43 and 3.53 (each 1H, dq, J = 8.8, 7.0 Hz), 4.91—5.04 (2H, m), 5.66 (1H, m), 7.47—7.55 (3H, m), 7.71—7.80 (2H, m); ^{13}C NMR δ = 8.7, 15.5, 37.9, 60.5, 99.2, 118.7, 128.6 (2C), 129.5 (2C), 131.8, 132.0, 132.9, 145.3, 173.0, 197.3; MS (EI) *m/z* (rel intensity) 242 (M^+; 7), 213 (100), 171 (30), 157 (36), 129 (33), 115 (75). Found: C, 79.34; H, 7.45%. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

4-Ethoxy-3-methyl-2-phenyl-4-(2-propenyl)-2-cyclobutenone (12g). Oil (Elution H–A 20 : 1); IR (neat) 1757, 1636, 1597 cm^{-1}; ^1H NMR δ = 1.21 (3H, t, J = 7.0 Hz), 2.43 (3H, s), 2.58 and 2.68 (each 1H, ddt, J = 14.2, 7.2, 1.2 Hz), 3.46 and 3.56 (each 1H, dq, J = 8.8, 7.0 Hz), 5.01—5.18 (2H, m), 5.78 (1H, m), 7.32—7.47 (3H, m), 7.70—7.77 (2H, m); ^{13}C NMR δ = 13.5, 15.6, 37.6, 60.8, 99.2, 118.6, 128.0 (2C), 129.1 (2C), 129.5, 129.6, 132.9, 147.1, 177.0, 195.0; MS (EI) *m/z* (rel intensity) 242 (M^+; 3), 213 (100), 171 (7), 157 (18), 129 (15), 115 (24). Found: C, 79.34; H, 7.46%. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

Synthesis of 4-Allylcyclobutenones 12h—l. 4-Allylcyclobutenones **12h—l** were obtained from **9a** and **5b—f** in the same manner as described for **12a**. Reaction times and isolated yields are compiled in Table 2.

3, 4- Diethoxy- 2- methyl- 4- (2- methyl- 2- propenyl)- 2- cyclobutenone (12h). Oil (Elution H–A 5 : 1); IR (neat) 1761, 1622 cm^{-1}; ^1H NMR δ = 1.20 (3H, t, J = 7.0 Hz), 1.46 (3H, t, J = 7.0 Hz), 1.72 (3H, s), 1.73 (3H, m), 2.47 and 2.62 (each 1H, dd, J = 13.8, 0.8 Hz), 3.47 and 3.55 (each 1H, dq, J = 8.8, 7.0 Hz), 4.48 (2H, q, J = 7.0 Hz), 4.76—4.87 (2H, m); ^{13}C NMR δ = 6.4, 15.2, 15.5, 23.5, 40.8, 60.5, 68.5, 96.3, 115.4, 123.2, 141.0, 183.0, 193.8; MS (EI) *m/z* (rel intensity) (no molecular ion) 195 (73), 167 (100); (CI) *m/z* (rel intensity) 225 (MH^+; 74), 169 (100). Found: C, 69.76; H, 8.84%. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99%.

Methyl 3-[(1,2-Diethoxy-3-methyl-4-oxo-2-cyclobutenyl)-methyl]-3-butenoate (12i). Oil (Elution H–A 4 : 1); IR (neat) 1759, 1740, 1622 cm^{-1}; ^1H NMR δ = 1.18 (3H, t, J = 7.0 Hz), 1.46 (3H, t, J = 7.0 Hz), 1.73 (3H, s), 2.62 and 2.74 (each 1H, dd, J = 14.4, 1.0 Hz), 3.17 (2H, s), 3.46 and 3.53 (each 1H, dq, J = 8.6, 7.0 Hz), 3.68 (3H, s), 4.44 (2H, q, J = 7.0 Hz), 5.00—5.05 (2H, m); ^{13}C NMR δ = 6.6, 15.2, 15.4, 39.3, 41.7, 51.8, 60.6, 68.7, 95.7, 118.6, 123.0, 138.0, 172.5, 183.2, 193.6; MS (EI) *m/z* (rel intensity) 282 (M^+; 13), 254 (11), 221 (85), 193 (100), 165 (69). Found: C, 63.82; H, 7.84%. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85%.

3, 4- Diethoxy- 2- methyl- 4- (1- phenyl- 2- propenyl)- 2- cyclobutenone (12j). Oil (Elution H–A 6 : 1); IR (neat) 1759, 1622 cm^{-1}; ^1H NMR (ca. 1 : 1 diastereomer mixture) δ = 1.19 and 1.13 (each 3/2H, t, J = 7.0 Hz), 1.32 and 1.43 (each 3/2H, t, J = 7.0 Hz), 1.48 and 1.60 (each 3/2H, s), 3.42—3.65 (2H, m), 3.78—3.88 (1H, m), 4.17 and 4.29 (each 1/2H, dq, J = 10.0, 7.0 Hz), 4.35 (1H, q, J = 7.0 Hz), 5.21—5.29 (2H, m), 6.09—6.48 (1H, m), 7.06—7.20 (5H, m); ^{13}C NMR δ = 6.4 and 6.6, 15.1 and 15.3, 15.4 and 15.5, 53.6 and 54.0, 60.9 and 61.0, 68.5 and 68.6, 98.4 and 98.7, 117.4 and 117.6, 123.7 and 124.1, 126.9 and 127.1, 128.3 and 128.4 (each 1C), 129.2 and 129.4 (each 1C), 137.3 and 137.5, 140.2 and 140.3, 181.7 and 181.8, 192.7 and 192.9; MS (EI) *m/z* (rel intensity) 286 (M^+; 5), 258 (99), 229 (33), 183 (100). Found: C, 75.45; H, 7.79%. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74%.

3,4-Diethoxy-2-methyl-4-(1,1-dimethyl-2-propenyl)-2-cyclobutenone (12k). Oil (Elution H–A 6 : 1); IR (neat) 1759, 1622 cm^{-1}; ^1H NMR δ = 1.12 and 1.14 (each 3H, s), 1.19 (3H, t, J = 7.0 Hz), 1.46 (3H, t, J = 7.0 Hz), 1.78 (3H, s), 3.42 and 3.49 (each 1H, dq, J = 9.0, 7.0 Hz), 4.42 (2H, q, J = 7.0 Hz), 4.98 (1H, dd, J = 10.8, 1.4 Hz), 5.02 (1H, dd, J = 17.6, 1.4 Hz), 6.00 (1H, dd, J = 17.6, 10.8 Hz); ^{13}C NMR δ = 6.9, 15.3, 15.4, 22.7, 23.1, 41.2, 60.6, 68.6, 100.2, 112.3, 123.1, 144.8, 183.0, 194.9; MS (EI) *m/z* (rel intensity) 238 (M^+; 6), 223 (57), 210 (46), 167 (91), 139 (100). Found: C, 70.59; H, 9.27%. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30%.

3,4-Diethoxy-2-methyl-4-(2-methylenecyclopentyl)-2-cyclobutenone (12l). Two diastereomers of **12l** were separated by flash chromatography (Elution H–A 10 : 1).

Spectral Data of the First Eluted Diastereomer. 40%; Oil; IR (neat) 1759, 1622 cm^{-1}; ^1H NMR δ = 1.21 (3H, t, J = 7.0 Hz), 1.46 (3H, t, J = 7.0 Hz), 1.73 (3H, s), 1.41—1.98 (4H, m), 2.25 (2H, m), 2.98 (1H, m), 3.48 and 3.55 (each 1H, dq, J = 8.8, 7.0 Hz), 4.44 (2H, q, J = 7.0 Hz), 4.88 and 5.00 (each 1H, m); ^{13}C NMR δ = 6.3, 15.2, 15.4, 24.9, 29.2, 34.7, 46.1, 60.5, 68.3, 98.6, 108.7, 124.0, 152.1, 182.7, 193.6; MS (EI) *m/z* (rel intensity) 250 (M^+; 4), 222 (100), 193 (52), 177 (17), 165 (39). Found: C, 72.04; H, 8.78%. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86%.

Spectral Data of the Second Eluted Diastereomer. 24%; Oil; IR (neat) 1761, 1622 cm^{-1}; ^1H NMR δ = 1.21 (3H, t, J = 7.0 Hz), 1.45 (3H, t, J = 7.0 Hz), 1.75 (3H, s), 1.41—1.98 (4H, m), 2.28 (2H, m), 2.91 (1H, m), 3.50 and 3.57 (each 1H, dq, J = 8.8, 7.0 Hz), 4.44 and 4.45 (each 1H, dq, J = 10.0, 7.0 Hz), 5.00 and 5.04 (each 1H, m); ^{13}C NMR δ = 6.5, 15.1, 15.4, 24.8, 29.2, 34.4, 45.6, 60.5, 68.4, 98.4, 108.8, 123.5, 151.4, 182.3, 194.1; MS (EI) *m/z* (rel intensity) 250 (M^+; 3), 222 (100), 193 (52), 177 (17), 165 (40). Found: C, 72.07; H, 8.76%. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86%.

Typical Procedure for Thermal Rearrangement of 4-Allylcyclobutenones 12a—l. A solution of **12a** (62 mg, 0.29 mmol) in dry xylene (10 mL) was refluxed under a nitrogen atmosphere for 2 h. The solution was cooled to ambient temperature and the solvent was removed under reduced pressure. Flash chromatography of the residue (Elution H–A 10 : 1) gave bicyclo[3.2.0]heptenone **14a** (61 mg, 98%) as a colorless oil. The other bicycloheptenones **14b—l** were obtained according to the same procedure; isolated yields are indicated in Tables 1 and 2.

2,3-Diethoxy-1-methylbicyclo[3.2.0]hept-2-en-7-one (14a). IR (neat) 1771, 1674 cm^{-1}; ^1H NMR δ = 1.21 (3H, t, J = 7.0 Hz), 1.27 (3H, t, J = 7.0 Hz), 1.29 (3H, s), 2.22 (1H, m), 2.29 (1H, d, J = 15.8 Hz), 2.84 (1H, dd, J = 15.8, 8.2 Hz), 2.92 (1H, dd, J = 17.8, 5.8 Hz), 3.22 (1H, dd, J = 17.8, 8.6 Hz), 3.79 and 4.31 (each 1H, dq, J = 9.8, 7.0 Hz), 3.93 and 4.04 (each 1H, dq, J = 9.6, 7.0 Hz); ^{13}C NMR δ = 15.3, 15.4, 15.5, 27.7, 33.5, 51.4, 65.3, 66.6, 73.3, 132.5, 137.2, 210.7; MS (EI) *m/z* (rel intensity) 210 (M^+; 3), 182 (50), 153 (27), 125 (100). Found: C, 68.68; H, 8.50%. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63%.

2,3-Diethoxy-1-phenylbicyclo[3.2.0]hept-2-en-7-one (14b). Oil (Elution H–A 20 : 1); IR (neat) 1771, 1672, 1601 cm^{-1}; ^1H NMR δ = 1.07 (3H, t, J = 7.0 Hz), 1.30 (3H, t, J = 7.0 Hz), 2.40 (1H, d, J = 15.8 Hz), 2.63 (1H, m), 3.01 (1H, dd, J = 15.8, 7.8 Hz), 3.03 (1H, dd, J = 18.2, 5.6 Hz), 3.34 (1H, dd, J = 18.2, 9.2 Hz), 3.72 and 3.89 (each 1H, dq, J = 9.8, 7.0 Hz), 4.01 and 4.11 (each 1H, dq, J = 9.8, 7.0 Hz), 7.20—7.42 (5H, m); ^{13}C NMR δ = 15.3, 15.6, 30.0, 33.7, 51.6, 65.5, 67.0, 80.2, 126.7 (2C), 127.5, 128.8 (2C), 132.6, 138.5, 138.7, 207.4; MS (EI) *m/z* (rel intensity) 272 (M^+; 6), 244 (100), 215 (47), 187 (96), 173 (35). Found: C, 74.95; H, 7.42%. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40%.

2,3-Diethoxy-1-phenylethynylbicyclo[3.2.0]hept-2-en-7-one (14c). Oil (Elution H–A 10 : 1); IR (neat) 2226, 1784, 1674, 1597 cm^{-1}; ^1H NMR δ = 1.27 (3H, t, J = 7.0 Hz), 1.29 (3H, t, J = 7.0 Hz), 2.31 (1H, d, J = 15.6 Hz), 2.75 (1H, m), 2.98 (1H, dd, J = 15.6, 8.0 Hz), 3.07 (1H, dd, J = 18.4, 5.8 Hz), 3.44 (1H, dd, J = 18.4, 9.2 Hz), 3.96 and 4.13 (each 1H, dq, J = 9.8, 7.0 Hz), 4.03 and 4.17 (each 1H, dq, J = 9.8, 7.0 Hz), 7.26—7.47 (5H, m); ^{13}C NMR δ = 15.4, 15.6, 29.6, 33.8, 52.6, 65.6, 67.2, 69.6, 83.9, 88.5, 123.2, 128.5 (2C), 128.6, 129.3, 132.1 (2C), 138.7, 201.5; MS (EI) *m/z* (rel intensity) 296 (M^+; 12), 268 (63), 239 (55), 211 (100), 197 (39), 183 (45). Found: C, 77.03; H, 6.77%. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80%.

1-Ethenyl-2,3-diethoxybicyclo[3.2.0]hept-2-en-7-one (14d). Oil (Elution H–A 20 : 1); IR (neat) 1773, 1672, 1632 cm^{-1}; ^1H NMR δ = 1.20 (3H, t, J = 7.0 Hz), 1.28 (3H, t, J = 7.0 Hz), 2.30 (1H, d, J = 15.8 Hz), 2.49 (1H, m), 2.87 (1H, dd, J = 15.8, 8.2 Hz), 2.92 (1H, dd, J = 18.2, 5.6 Hz), 3.24 (1H, dd, J = 18.2, 9.0 Hz), 3.79 and 4.00 (each 1H, dq, J = 9.6, 7.0 Hz), 4.02 and 4.07 (each 1H, dq, J = 9.8, 7.0 Hz), 5.22 (1H, dd, J = 10.6, 1.4 Hz), 5.35 (1H, dd, J = 17.4, 1.4 Hz), 5.98 (1H, dd, J = 17.4, 10.6 Hz); ^{13}C NMR δ = 15.3, 15.6, 27.7, 33.6, 51.2, 65.4, 66.8, 79.3, 116.9, 131.4, 133.8, 138.2, 207.6; MS (EI) *m/z* (rel intensity) 222 (M^+; 32), 195 (41), 165 (45), 137 (100). Found: C, 70.33; H, 8.07%. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%.

1-(Benzyloxycarbonylmethyl)-2,3-diethoxybicyclo[3.2.0]-hept-2-en-7-one (14e). Oil (Elution H–A 10 : 1); IR (neat) 1777, 1734, 1676 cm^{-1}; ^1H NMR δ = 1.19 (3H, t, J = 7.0 Hz), 1.25 (3H, t, J = 7.0 Hz), 2.26 (1H, d, J = 15.4 Hz), 2.60 (1H, m), 2.66 and 3.07 (each 1H, d, J = 17.6 Hz), 2.75 (1H, dd, J = 15.4, 8.0 Hz), 2.85 (1H, dd, J = 17.8, 5.2 Hz), 3.31 (1H, dd, J = 17.8, 8.8 Hz), 3.83 and 3.97 (each 1H, dq, J = 9.8, 7.0 Hz), 3.86 and 4.01 (each 1H, dd, J = 10.6, 1.4 Hz), 5.10 (2H, s), 7.35 (5H, s); ^{13}C NMR δ = 15.4, 15.5, 25.7, 33.4, 34.7, 52.0, 65.3, 66.8, 67.0, 73.3, 128.7, 128.8 (2C), 128.9 (2C), 130.2, 136.0, 138.3, 171.4, 207.9; MS (EI) *m/z* (rel intensity) 344 (M^+; 8), 316 (100), 302 (58), 225 (19). Found: C, 69.83; H, 6.94%. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02%.

3-Ethoxy-1-methyl-2-phenylbicyclo[3.2.0]hept-2-en-7-one (14f). Oil (Elution H–A 10 : 1); IR (neat) 1767, 1624, 1601 cm^{-1}; ^1H NMR δ = 1.31 (3H, s), 1.34 (3H, t, J = 7.0 Hz), 2.34 (1H, m), 2.67 (1H, dd, J = 17.0, 0.8 Hz), 2.69 (1H, dd, J = 17.6, 6.2 Hz), 3.18 (1H, dd, J = 17.0, 8.0 Hz), 3.27 (1H, dd, J = 17.6, 8.4 Hz), 4.00 and 4.05 (each 1H, dq, J = 9.6, 7.0 Hz), 7.10—7.36 (3H, m), 7.69—7.75 (2H, m); ^{13}C NMR δ = 15.6, 17.5, 29.8, 36.8, 51.1, 65.4, 76.3, 114.0, 126.1, 128.2 (2C), 128.3 (2C), 134.6, 154.1, 211.8; MS (EI) *m/z* (rel intensity) 242 (M^+; 3), 214 (100), 198 (84), 185 (53), 171 (56), 157 (46). Found: C, 79.30; H, 7.50%. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

3-Ethoxy-2-methyl-1-phenylbicyclo[3.2.0]hept-2-en-7-one (14g). Oil (Elution H–A 15 : 1); IR (neat) 1767, 1672, 1601 cm^{-1}; ^1H NMR δ = 1.30 (3H, t, J = 7.0 Hz), 1.44 (3H, dd, J = 2.2, 1.7 Hz), 2.53 (1H, m), 2.74 (1H, m), 2.89 (1H, dd, J = 17.8, 5.2 Hz), 3.11 (1H, ddq, J = 16.2, 7.4, 2.2 Hz), 3.31 (1H, dd, J = 17.8, 9.2 Hz), 3.93 and 3.96 (each 1H, dq, J = 9.8, 7.0 Hz), 7.18—7.37 (5H, m); ^{13}C NMR δ = 8.8, 15.6, 31.9, 36.1, 51.2, 65.0, 83.4, 112.4, 126.4 (2C), 127.2, 128.8 (2C), 139.4, 152.6, 208.0; MS (EI) *m/z* (rel intensity) 242 (M^+; 2), 214 (100), 185 (59), 171 (30), 157 (24). Found: C, 79.30; H, 7.50%. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

2,3-Diethoxy-1,5-dimethylbicyclo[3.2.0]hept-2-en-7-one (14h). Oil (Elution H–A 15 : 1); IR (neat) 1771, 1678 cm^{-1}; ^1H NMR δ = 1.13 (3H, s), 1.16 (3H, s), 1.21 (3H, t, J = 7.0 Hz), 1.27 (3H, t, J = 7.0 Hz), 2.50 (2H, s), 2.75 (1H, d, J = 17.4 Hz), 3.20 (1H, d, J = 17.4 Hz), 3.78 and 3.99 (each 1H, dq, J = 9.8, 7.0 Hz), 3.92 and 4.02 (each 1H, dq, J = 9.8, 7.0 Hz); ^{13}C NMR δ = 11.5, 15.3, 15.5, 20.7, 31.4, 41.2, 58.4, 65.3, 66.5, 73.5, 133.0, 137.1, 211.2; MS (EI) *m/z* (rel intensity) 224 (M^+; 9), 196 (80), 167 (28), 139 (100). Found: C, 69.68; H, 8.92%. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99%.

2,3-Diethoxy-5-(methoxycarbonylmethyl)-1-methylbicyclo-[3.2.0]hept-2-en-7-one (14i). Oil (Elution H–A 10 : 1); IR (neat) 1773, 1738, 1680 cm^{-1}; ^1H NMR δ = 1.16 (3H, s), 1.21 (3H, t, J = 7.0 Hz), 1.27 (3H, t, J = 7.0 Hz), 2.48 (2H, s), 2.66 (2H, s), 3.08 and 3.27 (each 1H, d, J = 18.0 Hz), 3.70 (3H, s), 3.83 and

4.01 (each 1H, dq, J = 9.8, 7.0 Hz), 3.90 and 4.01 (each 1H, dq, J = 9.8, 7.0 Hz); ^{13}C NMR δ = 11.4, 15.4, 15.6, 33.1, 39.1, 39.4, 51.9, 57.2, 65.4, 66.8, 74.1, 132.3, 136.8, 172.3, 209.7; MS (EI) m/z (rel intensity) 282 (M^+; 5), 254 (54), 180 (100), 165 (47), 137 (60). Found: C, 63.92; H, 7.74%. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85%.

2,3-Diethoxy-1-methyl-4-phenylbicyclo[3.2.0]hept-2-en-7-one (14j). Oil (Elution H–A 15 : 1); IR (neat) 1773, 1669 cm^{-1}; ^{1}H NMR δ = 1.13 (3H, t, J = 7.0 Hz), 1.27 (3H, t, J = 7.0 Hz), 1.38 (3H, s), 2.12 (1H, dd, J = 8.6, 5.8 Hz), 3.10 (1H, dd, J = 18.0, 5.8 Hz), 3.31 (1H, dd, J = 18.0, 8.6 Hz), 3.69 (1H, s), 3.86 (2H, q, J = 7.0 Hz), 3.91 and 4.08 (each 1H, dq, J = 9.8, 7.0 Hz), 7.17—7.39 (5H, m); ^{13}C NMR δ = 15.5, 16.0, 37.2, 51.5, 53.5, 65.8, 66.8, 72.8, 127.3, 127.6 (2C), 128.9, 129.1 (2C), 135.0, 139.1, 143.8, 209.8; MS (EI) m/z (rel intensity) 286 (M^+; 5), 258 (100), 229 (34), 213 (20), 201 (46). Found: C, 75.53; H, 7.71%. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74%.

2,3-Diethoxy-1,4,4-trimethylbicyclo[3.2.0]hept-2-en-7-one (14k). Oil (Elution H–A 15 : 1); IR (neat) 1773, 1669 cm^{-1}; ^{1}H NMR δ = 1.05 (3H, s), 1.14 (3H, s), 1.20 (3H, t, J = 7.0 Hz), 1.26 (3H, t, J = 7.0 Hz), 1.33 (3H, s), 2.00 (1H, d, J = 8.4, 6.6 Hz), 2.85 (1H, dd, J = 17.8, 8.4 Hz), 3.21 (1H, dd, J = 17.6, 6.6 Hz), 3.51 and 3.90 (each 1H, dq, J = 9.6, 7.0 Hz), 4.04 and 4.27 (each 1H, dq, J = 9.8, 7.0 Hz); ^{13}C NMR δ = 15.3, 15.6, 16.0, 19.5, 29.8, 40.6, 41.1, 46.1, 66.4, 66.9, 71.9, 131.0, 145.2, 210.7; MS (EI) m/z (rel intensity) 238 (M^+; 12), 210 (100), 195 (70), 181 (57), 167 (44), 153 (68). Found: C, 70.57; H, 9.29%. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30%.

5,6-Diethoxy-4-methyltricyclo[5.3.0.0^{1,4}]dec-5-en-3-one (14l). Oil (Elution H–A 25 : 1); IR (neat) 1773, 1669 cm^{-1}; ^{1}H NMR δ = 1.17 (3H, s), 1.21 (3H, t, J = 7.0 Hz), 1.27 (3H, t, J = 7.0 Hz), 1.35—1.95 (6H, m), 2.86 (1H, dd, J = 9.0, 4.0 Hz), 3.02 (1H, d, J = 18.4 Hz), 3.14 (1H, d, J = 18.4 Hz), 3.76 and 3.99 (each 1H, dq, J = 9.6, 7.0 Hz), 4.02 (2H, q, J = 7.0 Hz); ^{13}C NMR δ = 11.8, 15.3, 15.6, 26.5, 31.0, 33.0, 42.6, 52.0, 54.6, 65.5, 66.6, 72.6, 131.2, 141.4, 211.6; MS (EI) m/z (rel intensity) 250 (M^+; 7), 222 (100), 193 (40), 177 (24), 165 (94). Found: C, 72.02; H, 8.81%. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86%.

Ring Expansion of Tricyclo[5.3.0.0^{1,4}]decenone 14l. To a solution of **14l** (52 mg, 0.21 mmol) and t-butyl diazoacetate (44 mg, 0.31 mmol) in dry dichloromethane (2 ml) was added $Et_2O{\cdot}BF_3$ (0.029 mL, 0.23 mmol) at 0 °C. After stirring for 30 min, the reaction mixture was quenched with 10% $NaHCO_3$ (5 mL) and extracted with dichloromethane (5 mL×3). The extracts were dried (Na_2SO_4), and evaporated to dryness. Flash chromatography of the residue (Elution H–A 20 : 1) gave a triquinane derivative, t-butyl 6,7-diethoxy-5-methyl-4-oxotricyclo[6.3.0.0^{1,5}]undec-6-ene-3-carboxylate **18** (41 mg, 54%) as a colorless oil; IR (neat) 1750, 1723, 1684 cm^{-1}; ^{1}H NMR δ = 1.11 (3H, s), 1.20 (3H, t, J = 7.0 Hz), 1.24 (3H, t, J = 7.0 Hz), 1.35—1.95 (6H, m), 1.48 (9H, S), 2.04 (1H, d, J = 12.8 Hz), 2.05 (1H, d, J = 9.0 Hz), 2.80 (1H, dd, J = 6.0, 4.8 Hz), 3.48 (1H, dd, J = 12.8, 9.0 Hz), 3.75 and 3.93 (each 1H, dq, J = 9.6, 7.0 Hz), 3.92 and 4.00 (each 1H, dq, J = 9.4, 7.0 Hz); ^{13}C NMR δ = 14.2, 15.5, 15.6, 25.1, 28.1, 28.2 (3C), 29.9, 36.5, 36.6, 50.7, 52.1, 53.8, 65.3, 67.4, 81.8, 134.1, 138.3, 169.5, 211.2; MS (EI) m/z (rel intensity) 64 (M^+; 3), 290 (10), 250 (17), 208 (100), 179 (36), 151 (17). Found: C, 69.26; H, 8.79%. Calcd for $C_{21}H_{32}O_5$: C, 69.20; H, 8.85%.

Synthesis of Oxaspiro[3.5]nonenone 19 and Conversion to Oxatricyclo[5.4.0.0^{2,5}]undecenone 20. To a solution of **9a** (62 mg, 0.29 mmol) and **5g** (100 mg, 0.58 mmol) in dry dichloromethane (2 mL) was added $Et_2O{\cdot}BF_3$ (0.044 mL, 0.35 mmol) at 0 °C under a nitrogen atmosphere. After stirring for 0.5 h, the reaction mixture was quenched with 10% $NaHCO_3$ (5 mL) and extracted with dichloromethane (5 mL×3). The extracts were dried (Na_2SO_4), and evaporated to dryness. Flash chromatography of the residue eluted with H–A 8 : 1 and then with H–A 4 : 1 gave the first diastereomer of **19** (12 mg, 19%) followed by the second diastereomer (47 mg, 73%). Thermolysis of **19** was carried out in the similar manner as described for **14** to give **20** in 94% yield.

Spectral Data of the First Eluted Diastereomer of 19. Oil; IR (neat) 1755, 1624 cm^{-1}; ^{1}H NMR δ = 1.43 (3H, t, J = 7.0 Hz), 1.70 (3H, s), 1.59—2.08 (4H, m), 2.55 (1H, m), 3.89—4.17 (2H, m), 4.39 (2H, q, J = 7.0 Hz), 5.02 (1H, ddd, J = 10.2, 1.8, 0.6 Hz), 5.11 (1H, ddd, J = 17.2, 1.8, 1.0 Hz), 5.64 (1H, ddd, J = 17.2, 10.2, 8.6 Hz); ^{13}C NMR δ = 6.6, 15.2, 25.5, 27.5, 43.2, 67.5, 68.4, 94.3, 116.9, 122.9, 138.2, 179.8, 192.3; MS (EI) m/z (rel intensity) 222 (M^+; 85), 194 (97), 165 (100), 149 (19), 137 (29). Found: C, 70.34; H, 8.06%. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%.

Spectral Data of the Second Eluted Diastereomer of 19. Oil; IR (neat) 1765, 1620 cm^{-1}; ^{1}H NMR δ = 1.46 (3H, t, J = 7.0 Hz), 1.62—2.00 (4H, m), 1.76 (3H, s), 2.63 (1H, m), 3.77—4.10 (2H, m), 4.44 (2H, q, J = 7.0 Hz), 4.99—5.17 (2H, m), 5.69 (1H, m); ^{13}C NMR δ = 7.1, 15.2, 24.6, 26.6, 41.0, 66.7, 68.9, 93.8, 116.7, 122.4, 137.5, 182.3, 190.8; MS (EI) m/z (rel intensity) 222 (M^+; 52), 194 (96), 165 (100), 149 (19), 137 (33). Found: C, 70.24; H, 8.16%. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%.

Spectral Data of 6-Ethoxy-5-methyl-8-oxatricyclo[5.4.0.0^{2,5}]-undec-6-en-4-one (20). Oil (Elution H–A 10 : 1); IR (neat) 1775, 1682 cm^{-1}; ^{1}H NMR δ = 1.21 (3H, t, J = 7.0 Hz), 1.28 (3H, s), 1.37—1.92 (4H, m), 2.39 (1H, ddd, J = 8.6, 7.4, 6.6 Hz), 2.84 (1H, m), 2.85 (1H, dd, J = 17.6, 8.6 Hz), 3.29 (1H, dd, J = 17.6, 6.6 Hz), 3.46 (1H, m), 3.99 and 4.06 (each 1H, dq, J = 10.2, 7.0 Hz), 3.89—4.17 (1H, m); ^{13}C NMR δ = 14.6, 15.3, 23.7, 24.7, 33.2, 37.7, 45.0, 66.3, 68.9, 72.1, 133.1, 133.3, 209.3; MS (EI) m/z (rel intensity) 222 (M^+; 17), 194 (100), 165 (91), 151 (30), 137 (39). Found: C, 70.34; H, 8.06%. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%.

Reaction of Cyclobutenedione Monoacetal 9b with Allenylsilane 23. To a solution of **9b** (231 mg, 0.83 mmol) and $Et_2O{\cdot}BF_3$ (0.21 mL, 1.67 mmol) in dry dichloromethane (2 mL) was added dropwise a solution of allenylsilane **23** (316 mg, 2.50 mmol) in dry dichloromethane (2 mL) at 0 °C under a nitrogen atmosphere. After stirring for 1 h, the same work-up as described for **12a** and flash chromatography (Elution H–A 10 : 1) gave 4-(2-butynyl)-3,4-diethoxy-2-phenyl-2-cyclobutenone (**24**) (85 mg, 36%) as a colorless oil; IR (neat) 2238, 1759, 1632, 1599 cm^{-1}; ^{1}H NMR δ = 1.23 (3H, t, J = 7.0 Hz), 1.55 (3H, t, J = 7.0 Hz), 1.66 (3H, t, J = 2.6 Hz), 2.68 and 2.97 (each 1H, dq, J = 17.4, 2.6 Hz), 3.58 and 3.68 (each 1H, dq, J = 9.0, 7.0 Hz), 4.57 (2H, q, J = 7.0 Hz), 7.24—7.43 (3H, m), 7.77—7.83 (2H, m); ^{13}C NMR δ = 3.5, 15.4, 15.5, 24.1, 31.0, 61.6, 69.5, 73.0, 80.4, 98.1, 126.0, 127.4 (2C), 128.4, 128.8 (2C), 181.3, 189.2; MS (EI) m/z (rel intensity) 284 (M^+; 76), 255 (100), 227 (92), 145 (78). Found: C, 76.01; H, 7.11%. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%.

Reaction of Cyclobutenedione Monoacetal 9a with Silyl Enol Ether 29. To a solution of **9a** (162 mg, 0.70 mmol) and **29** (403 mg, 2.10 mmol) in dry dichloromethane (2 mL) was added $Et_2O{\cdot}BF_3$ (0.11 mL, 0.84 mmol) at 0 °C under a nitrogen atmosphere. After stirring for 5 h, the work-up as above and flash chromatography (Elution H–A 4 : 1) gave 3,4-diethoxy-2-methyl-4-phenacyl-2-cyclobutenone (**30**) (159 mg, 73%) as a pale-yellow oil; IR (neat) 1763, 1680, 1622 cm^{-1}; ^{1}H NMR δ = 1.19 (3H, t, J = 7.0 Hz), 1.43 (3H, t, J = 7.0 Hz), 1.69 (3H, s), 3.33 and 3.63 (each 1H, d, J = 15.2 Hz), 3.50 and 3.57 (each 1H, dq, J = 8.8, 7.0 Hz), 4.40 and 4.48

(each 1H, dq, $J=9.8$, 7.0 Hz), 7.40—7.61 (3H, m), 7.94—8.00 (2H, m); ^{13}C NMR $\delta=6.5$, 15.1, 15.3, 40.9, 60.3, 68.8, 94.3, 124.2, 128.8 (2C), 129.0 (2C), 133.6, 137.4, 182.7, 192.0, 197.5; MS (EI) *m/z* (rel intensity) 288 (M^+; 25), 260 (5), 244 (6), 183 (36), 155 (57), 127 (100). Found: C, 70.80; H, 7.00%. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99%.

Reaction of Cyclobutenedione Monoacetal 9a with Silyl Ketene Acetal 31. To a solution of **9a** (147 mg, 0.69 mmol) and **31** (458 mg, 2.10 mmol) in dry dichloromethane (2 mL) was added trimethylsilyl triflate (2.3 M in dichloromethane; 0.15 mL, 0.35 mmol) at room temperature under a nitrogen atmosphere. After stirring for 3 h, the same work-up as above and flash chromatography (Elution H–A 4 : 1) gave benzyl (1,2-diethoxy-3-methyl-4-oxo-2-cyclobutenyl)acetate (**32**) (71 mg, 33%) as a pale-yellow oil; IR (neat) 1765, 1738, 1624 cm^{-1}; ^{1}H NMR $\delta=1.18$ (3H, t, $J=7.0$ Hz), 1.39 (3H, t, $J=7.0$ Hz), 1.61 (3H, s), 2.83 and 2.98 (each 1H, d, $J=14.4$ Hz), 3.47 and 3.54 (each 1H, dq, $J=9.0$, 7.0 Hz), 4.32 and 4.39 (each 1H, dq, $J=9.8$, 7.0 Hz), 5.06 and 5.13 (each 1H, d, $J=12.2$ Hz), 7.33—7.36 (5H, m); ^{13}C NMR $\delta=6.4$, 15.0, 15.3, 38.1, 60.6, 66.7, 68.7, 93.8, 124.2, 128.6, 128.7 (2C), 128.8 (2C), 136.0, 169.4, 182.1, 191.4; MS (EI) *m/z* (rel intensity) 318 (M^+; 100), 290 (24), 227 (6), 199 (24), 155 (53). Found: C, 67.92; H, 6.96%. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97%.

One of the authors (Y. Y.) is grateful for Fellowships from the Japan Society for the Promotion of Science for Japanese Junior Scientists. This work was supported by Grants-in-Aid for Developmental Scientific Research No. 07555285 and for Encouragement of Young Scientists No. 70000863 from the Ministry of Education, Science, Sports and Culture.

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