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Ruthenium-Catalyzed Cyclopropanation of Norbornene with Propargyl Alcohol

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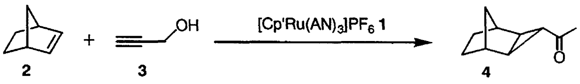
(Received March 31, 1999)

Norbornene as well as its 5,6-disubstituted derivatives and oxa-norbornene undergoes a novel cyclopropanation with propargyl alcohol in methanol containig cationic (η^5-cyclopentadienyl)tris(acetonitrile)ruthenium complexes as catalysts to give *exo*-3-acetyltricyclooctane derivatives. Cyclopentadienylruthenium catalysts having an electron-withdrawing substituent on the Cp ligand exhibited the highest activity and the cyclopropanation proceeded even at −20 °C. On the basis of a deuterium labeling experiment, a reaction mechanism involving a ruthenacycle intermediate is proposed.

There has been an increasing interest in the catalysis promoted by ruthenium complexes in synthetic organic reactions using carbon–carbon unsaturated compounds as a starting substrate.[1] The unique catalysis of ruthenium complexes in such reactions is mainly based on the characteristics of a ruthenium metal which can form a variety of active intermediates such as π-allylruthenium, ruthenium-carbene, and ruthenacycle species. For example, ruthenium complexes such as [$RuH_2(PPh_3)_4$] and [Ru(cod)(cot)] react with allylic esters and carbonates to afford π-allylruthenium species which undergo subsequent reactions with a variety of nucleophiles and electrophiles.[2] Ruthenium-carbene complexes,[3,4] which are formed from the reactions of several ruthenium complexes with olefins, acetylenes, and diazo compounds, effectively catalyze ring opening metathesis polymerization,[5] ring closing metathesis reaction,[6] and cyclopropanation.[7] Ruthenacycle species have been demonstrated to be a key intermediate in carbon–carbon bond formation reactions of acetylenes with olefins.[8] Recently we have shown that cationic (η^5-cyclopentadienyl)tris(acetonitrile)ruthenium complexes **1** can catalyze a novel cyclopropanation of norbornene with propargyl alcohol (Eq. 1) and have already communicated a preliminary result.[9] This Ru(II) mediated catalysis provides the first example of cyclopropanation of olefins in which the methylene moiety comes from propargyl alcohol, although metal-catalyzed cyclopropanation of olefins by diazo compounds and ketone carbonates have been well documented already.[10,11] Here we wish to report the full details of the novel cyclopropanation of norbornene derivatives as well as the reaction mechanism.



(1)

Results and Discussion

Recently we have reported the synthesis of planar-chiral cyclopentadienyl-ruthenium complexes which contain unsymmetrical trisubstituted cyclopentadienyl ligands having an electron-withdrawing group,[12] although most of the known cyclopentadienyl-ruthenium complexes contain non-substituted or electron-donating alkyl-substituted cyclopentadienyl ligands.[13] To determine the reactivity of our alkoxycarbonyl-substituted cyclopentadienylruthenium complexes towards unsaturated compounds, we examined reactions of several alkenes and alkynes with the cyclopentadienylruthenium complexes. We found that the reaction of norbornene **2a** with propargyl alcohol (2-propyn-1-ol) **3** in the presence of a catalytic amount of [(η^5-1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)tris(acetonitrile)ruthenium][hexafluorophosphate] **1a** in methanol at room temperature afforded an unprecedented product, *exo*-3-acetyltricyclo[$3.2.1.0^{2,4}$]octane **4a**, which is a coupled product of one molecule each of **2a** and **3**, in an excellent yield. The structure of the product was determined by spectral analyses including NMR and mass spectra, and finally by an X-ray crystallographic analysis of its hydrazone derivative.[9] It should be noted that the acetylmethylene moiety in **4** was derived from propargyl alcohol with rearrangement.

The present novel cyclopropanation of norbornene proceeds smoothly in the presence of (η^5-trisubstituted cyclopentadienyl)ruthenium complexes **1a**—**d** and (η^5-ethoxycarbonylcyclopentadienyl)ruthenium **1e** as catalysts (Fig. 1). However an (η^5-pentamethylcyclopentadienyl)ruthenium analog, **1g**, was not active for the cyclopropanation although a non-substituted cyclopentadienylruthenium complex, **1f**, showed a low activity (Table 1), suggesting that the ruthenium complexes containing an electron-withdrawing group on the cyclopentadienyl ligand exhibit a higher activity in the cyclopropanation reaction. Other than **1**, ruthenium complexes such as [$CpRuCl(PPh_3)_2$], [CpRuCl(COD)], and [$RuCl_2(PPh_3)_4$] did not show any activity towards the cyclopropanation.

Solvents used in the present system strongly affect the

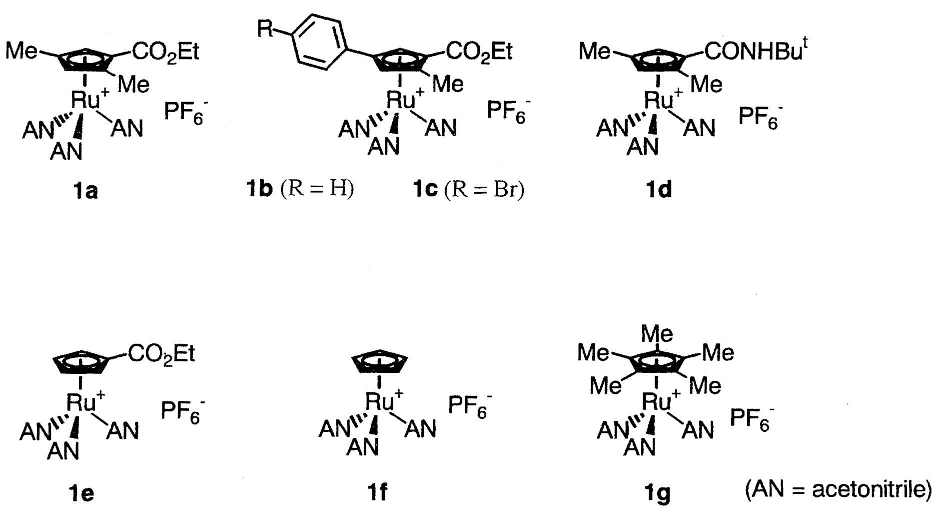


Fig. 1.

Table 1. Comparison of Catalytic Activity in Ethanol[a)]

Run	Ru cat.	Conv.[b)] %	Yield[b)] %
1	**1a**	78	77
2	**1b**	50	47
3	**1c**	77	72
4	**1d**	79	76
5	**1e**	44	40
6	**1f**	30	24
7	**1g**	0	0

a) Reaction conditions: norbornene, 5 mmol; propargyl alcohol, 5.5 mmol; ethanol, 10 ml; catalyst, 1 mol%; Reaction time, 3h. b) Yields are based on norbornene and determined by gas chromatography.

Table 2. Effects of Solvent and Temperature[a)]

Run	Solvent	Temp °C	Yield[b)] %
8	MeOH	R.T.	99
9		0	99
10		−20	31
11		−40	Trace
12	EtOH	0	77
13	*n*-PrOH	0	44
14	*i*-PrOH	0	19
15	EtOH+H_2O	0	9
16	MeCN+MeOH	0	46
17	Acetone+MeOH	0	80
18	AcOEt+MeOH	0	99
19	CH_2Cl_2+MeOH	0	92
20	Et_2O+MeOH	0	93
21	Benzene+MeOH	0	98

a) Reaction conditions: norbornen, 5 mmol; propargyl alcohol, 5.5 mmol; catalyst **1a**, 1 mol%; solvent, 10 ml; reaction time, 3h. b) Yields are based on norbornene and determined by gas chromatography.

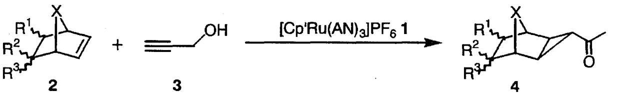
Table 3. Cyclopropanation of Norbornene Derivatives[a)]

Run	Substrate	Catalyst **1a** mol%	Yield[b)] %
22	**2a**	1	99
23	**2b**	5	84
24	**2c**	3	88
25	**2d**	5	89
26	**2e**	2	91
27	**2f**	1	98

a) Reaction conditions: substrate, 5 mmol; propargyl alcohol, 5.5 mmol; methanol, 10 ml; temperature, 0 °C; reaction time, 3h. b) Yields are based on substrates and determined by gas chromatography.

cyclopropanation reaction (Table 2). Thus, the reaction proceeds smoothly in alcohols such as methanol and ethanol, and the relative rate of the reaction decreases in the order: MeOH>EtOH>*n*-PrOH>*i*-PrOH. However almost no reaction occurred in benzene, dichloromethane, tetrahydrofuran (THF), or ether. In a mixed solvent containing alcohols, for example, a 1 : 1 mixture of methanol and diethyl ether, the cyclopropanation reaction took place, implying that the protic solvents play an important role in the cyclopropanation. In methanol the reaction takes place even at −20 °C, and proceeds smoothly above 0 °C.

Then, we have examined applications of the present cyclopropanation to norbornene derivatives and found that 5-mono-, 5,5-di-, and 5,6-disubstituted 2-norbornenes **2** undergo cyclopropanation with propargyl alcohol **3** to give the corresponding acetyltricyclooctane derivatives in high yields (Eq. 2). The reactivity depends on the substituents of the substrates (see Table 3). *exo*-5-Acetyl-2-norbornene showed almost the same reactivity as norbornene, whereas 5-cyano- and 5,6-bis(methoxycarbonyl)-2-norbornene reacted slowly with **3**. All of norbornene derivatives **2a**—**e** gave single isomers **4a**—**e** which have been identified by spectral analyses including ^{1}H and ^{13}C NMR spectroscopies with H–H and C–H cosy, and H–H noesy techniques. For example, **4e**, which is the product from the reaction of 5,6-bis(methoxycarbonyl)-2-norbornene **2e** with **3**, has been identified as follows. The mass spectrum of **4e** exhibited a molecular ion peak, which corresponds to the sum of one molecule each of **2e** and **3**. The presence of two kinds of carbonyl groups was observed at 1688 and 1732 cm^{-1} in the IR spectrum. The $^{13}\mathrm{C}$ NMR spectrum showed two signals due to carbonyl carbons at 206 and 171 ppm attributable to carbonyl groups of ketones and esters respectively. Two signals due to tertiary carbons appeared at 24.0 and 23.2 ppm which were assigned to a cyclopropane ring based on the C–H coupling constants: $J_{\mathrm{C2-H}} = J_{\mathrm{C4-H}} = 184$ and $J_{\mathrm{C3-H}} = 166$ Hz.[14] In addition the $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra taken with H–H and C–H cosy techniques suggested **4e** to be a cyclopropanation product of **2e**, 3-acetyl-6,7-bis(methoxycarbonyl)tricyclo[3.2.1.0^{2,4}]octane. Fortunately we could obtain a good single crystal of **4e**. The X-ray crystallographic analysis has established the structure of **4e** to be 3-*exo*-acetyl-6,7-*endo*-bis(methoxycarbonyl)tricyclo[3.2.1.0^{2,4}]octane, which has the same stereochemistry as cyclopropanation product **4a**[9] from norbornene (Fig. 2). 5,6-Bis(methoxycarbonyl)bicylo[2.2.2]-2-octene did not undergo the cyclopropanation, while 7-oxa-5,6-bis(methoxycarbonyl)-2-norbornene **2f** reacted smoothly with **3** to give two stereo isomers with a ratio of 1 : 6 in an almost quantitative yield. Both of the isomers were isolated by fractional recrystallization, and the major isomer, **4f-1**, has been identified as an *exo*-acetyl isomer having the same stereo structure as that of **4a**, whereas the minor product, **4f-2**, has been found to be an *endo*-isomer whose structure has been established by an X-ray crystallographic analysis (Fig. 3). The formation of the *endo*-isomer from the 7-oxanorbornene derivative provides useful information about the reaction mechanism of the present novel cyclopropanation (vide infra).



2 3 4

a: X=CH$_2$; R^1=R^2=R^3=H
b: X=CH$_2$; R^1=COMe, R^2=R^3=H
c: X=CH$_2$; R^1=CN, R^2=R^3=H
d: X=CH$_2$; R^1=H, R^2=R^3=CH$_2$OH
e: X=CH$_2$; R^1= R^2=CO$_2$Me, R^3=H
f: X=O; R^1= R^2=CO$_2$Me, R^3=H (2)

In contrast with norbornene, norbornadiene (NBD) did not undergo the cyclopropanation with propargyl alcohol **3**. Moreover, the presence of norbornadiene in the system inhibited the reaction of norbornene with **3**. Addition of even small amounts of norbornadiene to the system quenched completely the cyclopropanation of norbornene. A stoichiometric reaction of **1a** with norbornadiene in methanol at room temperature afforded a norbornadiene-coordinated ruthenium complex, [Cp′Ru(NBD)(CH$_3$CN)][PF$_6$] **5** in a good yield.[15] The formation of **5** was confirmed by the NMR spectrum in the quenched reaction mixture (Fig. 4). These results suggest that a ruthenium species, which possesses at least two vacant coordination sites like [Cp′Ru(CH$_3$CN)], is an active intermediate of the cyclopropanation reaction.

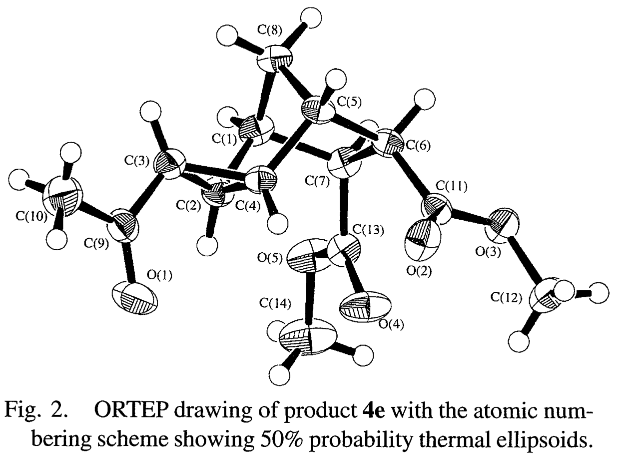


Fig. 2. ORTEP drawing of product **4e** with the atomic numbering scheme showing 50% probability thermal ellipsoids.

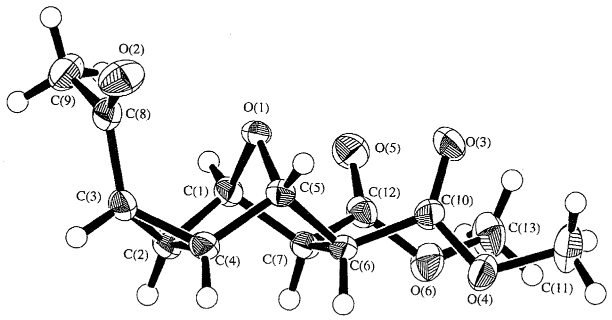
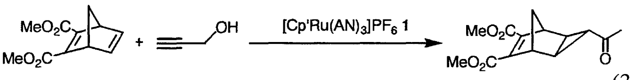
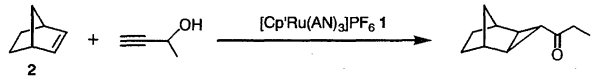


Fig. 3. ORTEP drawing of product **4f-2** with the atomic numbering scheme showing 50% probability thermal ellipsoids.



6 3 7 (3)

On the other hand, 2,3-bis(methoxycarbonyl)-2,5-norbornadiene **6** reacted with **3** by the catalysis of **1a** to give a cyclopropanation product, **7**, in 60% yield (Eq. 3). In this case **6** probably behaves as a norbornene derivative, because one of the two double bonds bears electron-withdrawing groups, resulting in a weak interaction of the ruthenium catalyst.



2 (4)

In order to obtain information on the rearrangement of propargyl alcohol **3** in the reaction, we have tried the cyclopropanation of norbornene with some alkynols other than **3** (see Table 4). 3-Butyn-2-ol slowly reacted with norbornene (Eq. 4). 2-Methyl-3-butyn-2-ol and 2-butyn-1-ol did not react with norbornene at room temperature for 3 h, indicating that both a hydrogen and a hydroxylic group at the propargylic position and a terminal acetylenic group in substrates are requisite for the rearrangement of alkynols in cyclopropanation of norbornene. However, the reaction using methyl 2-propynyl ether with no hydroxy group instead of **3** in the presence

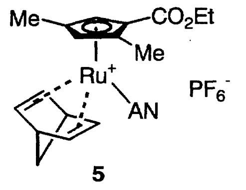


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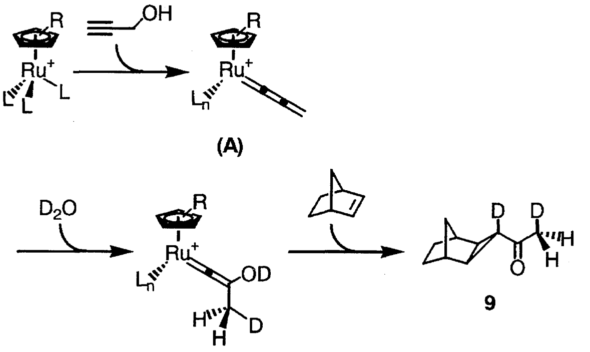
Fig. 4.

Table 4. Cyclopropanation of Norbornene with Alkynol[a)]

Run	Substrate	Yield[b)] / %
28	2-Propyn-1-ol	99
29	3-Butyn-2-ol	31
30	2-Methyl-3-butyn-2-ol	0
31	2-Butyn-1-ol	0
32	3-Butyn-1-ol	0

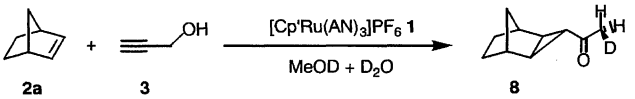
a) Reaction conditions: norbornene, 5 mmol; propargyl alcohol, 5.5 mmol; catalyst **1a**, 1 mol%, solvent, 10 ml; temperature, 0 °C; reaction time 3 h. b) Yields are based on norbornene and determined by gas chromatography.

of a little amount of water similarly gave **4a** in a good yield. These results may also provide valuable information about the reaction mechanism of the present cyclopropanation of norbornene.



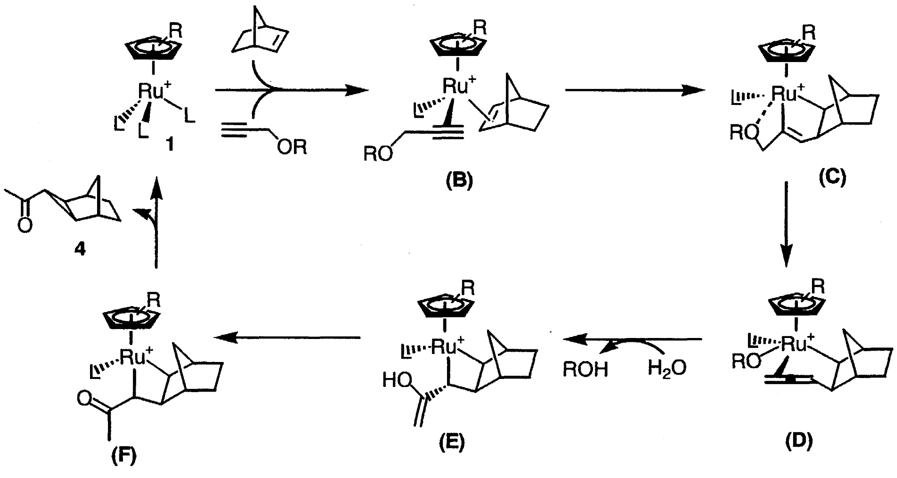
(5)

Since there have been many reports[3,16] on the reactions of ruthenium complexes with propargyl alcohol **3** and its derivatives giving ruthenium-allenylidene complexes, a ruthenium-allenylidene species (**A**) is one of possible active key intermediates in the present cyclopropanation reaction (Eq. 5). The formation of cyclopropanation product **4** may be interpreted by the successive reactions of **A** with norbornene and water. As another possible mechanism, we may postulate a ruthenacycle intermediate on the basis of the study by Trost and his co-workers on a ruthenium-catalyzed C–C bond formation from the reaction of allylic alcohols with alkynes giving γ,δ-unsaturated ketones.[8a] A proposed mechanism involving such a ruthenacyclopentene key intermediate (**C**) is illustrated in Scheme 1. The catalytic cycle may be started by the coordination of substrates to an active ruthenium center, which is formed by dissociation of at least two molecules of acetonitrile ligands. Norbornene presumably prefers *exo*-coordination rather than *endo*-one to a cationic metal atom if one considers the theoretical prediction for the electron density of norbornene.[17]



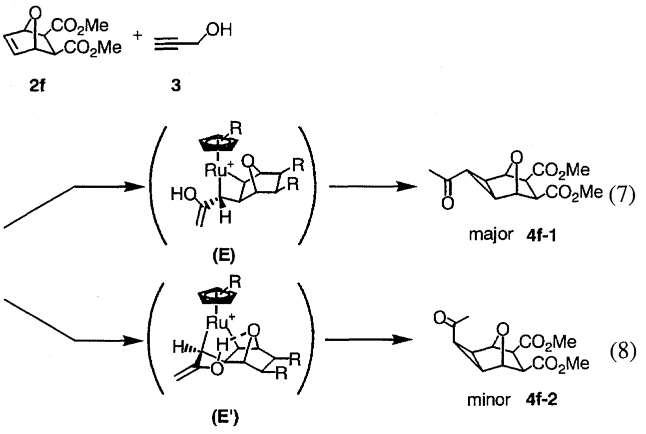
(6)

To establish the roles of methanol and water in the cyclopropanation, we carried out the reaction of **2a** with **3** in MeOD and D_2O (Eq. 6), and obtained mono-deuterated compound **8** as sole product. The mass and NMR spectroscopies of the compound showed that the deuterium atom is located exclusively in the acetyl group of **4a**. Under the same reaction conditions, methyl 2-propynyl ether also afforded **8**. No H–D exchange between **4a** and MeOD or D_2O in the same conditions has been observed. The selective formation of **8** from norbornene in the deuterated medium suggests that the cyclopropanation reaction does not proceed via allenylidene intermediate **A**, because **A** predicts the formation of a *di*-deuterated derivative, **9**. The selective formation of *mono*-deutero **8** may be understood by the mechanism in Scheme 1, in which a π-allene-ruthenium intermediate (**D**) transformed from ruthenacyle **C** picks up one deuterium atom from D_2O or MeOD. The attack of a hydroxyl nucleophile at the β-carbon of π-allene ligands is known for iron complexes.[18] The proposed mechanism may be, therefore, most reasonable to explain the present novel reaction, and is supported by an experimental result obtained from the cyclopropanation of 5,6-bis(methoxycarbonyl)-7-oxa-2-norbornene **2f**. The reaction of **2f** with **3** gave two stereo isomers, **4f-1** and **4f-2**, with a molar ratio of 6 : 1 as already mentioned above. Isomer **4f-1** has an *exo*-3-acetyltricylooctane structure, while **4f-2** is its



Scheme 1. A proposed mechanism of cyclopropanation of norbornene (R = H or Me).

endo-isomer. The former has the same stereochemistry, *exo*, as that of the cyclopronation products from **4a**—**e**, and the *exo* stereochemistry of **4** may be understood by considering steric repulsion between the vinyl group and the subsutituents on the cyclopentadienyl ligand in intermediate (**E**). No formation of *endo*-isomers has been observed in the reaction of **4a**—**e**, suggesting incorporation of the bridge-head oxygen atom in the step constructing the stereochemistry of **4f-2**. An interaction between the bridge-head oxygen and the hydroxy group seems to be most likely, as shown in Eqs. 7 and 8. The overall reaction rearrangement of **3** should be assisted by a proton derived from solvents like methanol.



Conclusion

Cationic (η^5-trisubstituted cyclopentadienyl)tris(acetonitrile)ruthenium complexes catalyze a novel cyclopropanation of norbornene with propargyl alcohol in methanol at room temperature to give *exo*-3-acetyltricyclo[3.2.1.0^{2,4}]octane. Norbornene derivatives such as 5,6-disubstituted norbornenes and 7-oxa-5,6-bis(methoxycarbonyl)-2-norbornene also undergo the novel cyclopropanation with propragyl alcohol. Mechanistic consideration suggests that the reaction proceeds through ruthenacycle and π-allene-ruthenium intermediates with the rearrangement of propargyl alcohol by the assistance of methanol. The present reaction is characterized by the cyclopropanation of the norbornenes with an acetylmethylene species derived from propargyl alcohol.

Experimental

General. All reactions were carried out under an argon atmosphere, but the work-up was performed in air. Melting and decomposition points are corrected. ^{1}H and ^{13}C NMR spectra were measured on JEOL EX-270 (270 MHz), JEOL JNM-LA400 (400 MHz), and JEOL JNM-LA600 (600 MHz) spectrometers. Chemical shifts are given in ppm. IR and mass spectra were taken on a Perkin–Elmer system 2000 FT-IR and a JEOL JMS-600H instrument, respectively. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University. Diethyl ether and THF were distilled over benzophenone ketyl under argon just before use. Dichloromethane was dried over calcium hydride and then distilled. Trisubstituted cyclopentadienes were prepared by the method previously reported.[19] All norbornene derivatives were prepared by a Diels–Alder reaction. Other chemicals available commercially were used without further purification.

Synthesis of 4-(4-Bromophenyl)-1-ethoxycarbonyl-2-methylcyclopentadiene. This compound was prepared by the method reported previously from 4-bromophenacyl bromide. (44% yield) Mp 117.5—118.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 7.48$—7.46 (d, 2H, $J = 8.5$ Hz, C_6H_4), 7.42—7.40 (d, 2H, $J = 8.5$ Hz, C_6H_4), 4.28—4.23 (q, 2H, $J = 7.1$ Hz, CH_2CH_3), 3.68 (s, 2H, CH_2), 2.39 (s, 3H, CH), 1.36—1.33 (t, 3H, $J = 7.1$ Hz, CH_2CH_3). IR (KBr) 1682 cm^{-1}(C=O). MS (FAB) *m/z* 307. Found: C, 58.43; H, 4.71; Br, 25.89%. Calcd for $C_{15}H_{15}BrO_2$: C, 58.65; H, 4.92; Br, 26.01%.

Synthesis of [(η^6-benzene)(η^5-1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)ruthenium] Hexafluorophosphate (10a).[20] To a solution of sodium hydride (60% in oil, 0.88 g, 22 mmol) in THF (10 ml) was added a THF (20 ml) solution of 1-ethoxycarbonyl-2,4-dimethylcyclopentadiene (3.32 g, 20 mmol) at 0 °C. The reaction mixture was stirred for 1 h at room temperature. This solution was added dropwise to an aqueous solution of thallium(I) sulfate (5.0 g, 9.5 mmol), and the mixture was stirred overnight at room temperature to give a pale brown precipitate, which was collected and washed with ether several times. The resulting solid was dried in vacuo and then dissolved in acetonitrile. To this solution was added (η^6-benzene)ruthenium dichloride dimer, [(η^6-C_6H_6)$RuCl_2$]$_2$, (5.0 g, 10 mmol). The reaction mixture was stirred overnight at room temperature and then filtered through Celite. The filtrate was concentrated and to the residual oil was added an aqueous solution of ammonium hexafluorophosphate (6.54 g, 40 mmol). The aqueous solution was extracted with dichloromethane (200 ml×3) and the combined extracts were dried over $MgSO_4$, and filtered. After removal of the solvent under reduced pressure, the residual oil was placed on a column of alumina and eluted with acetone. The acetone solution was evaporated, and the residue was purified by recrystallization from ethanol to give 6.22 g (67% yield) of ruthenium complex **1a** as pale yellow needles. Mp 178.0—178.5 °C. ^{1}H NMR (acetone-d_6, 270 MHz) $\delta = 6.53$ (s, 6H, C_6H_6), 5.90 (d, 1H, $J = 1.7$ Hz, CpH), 5.74 (d, 1H, $J = 1.7$ Hz, CpH), 4.32 (dq, 1H, $J = 1.7$, 7.3 Hz, CH_2CH_3), 4.31 (dq, 1H, $J = 1.7$, 7.3 Hz, CH_2CH_3), 2.31 (s, 3H, $CpCH_3$), 2.09 (s, 3H, $CpCH_3$), 1.35 (t, 3H, $J = 7.3$ Hz, CH_2CH_3). IR (KBr) 1712 cm^{-1} (C=O). MS (FAB) *m/z* 345 ($M^+ - PF_6$). Found: C, 39.49; H, 3.84; P, 6.20; F, 23.21%. Calcd for $C_{16}H_{19}F_6O_2PRu$: C, 39.27; H, 3.91; P, 6.33; F, 23.29%.

Synthesis of [(η^6-Benzene)(η^5-1-ethoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)ruthenium] Hexafluorophosphate (10b). This complex was prepared by the same method as that for **10a** using 1-ethoxycarbonyl-2-methyl-4-phenyl cyclopentadiene (66% yield). Mp 145.0—146.0 °C. ^{1}H NMR (acetone-d_6, 270 MHz) $\delta = 7.74$—7.69 (m, 2H, Ph), 7.45—7.42 (m, 2H, Ph), 6.51 (d, 1H, $J = 1.7$ Hz, CpH), 6.39 (d, 1H, $J = 1.7$ Hz, CpH), 6.28 (s, 6H, C_6H_6), 4.90 (dq, 1H, $J = 2.3$, 7.3 Hz, CH_2CH_3), 4.89 (dq, 1H, $J = 2.3$, 7.3 Hz, CH_2CH_3), 2.43 (s, 3H, $CpCH_3$), 1.39 (t, 3H, $J = 7.08$ Hz, CH_2CH_3). IR (KBr) 1725 cm^{-1}(C=O). MS (FAB) *m/z* 407 ($M^+ - PF_6$). Found: C, 45.79; H, 3.82; P, 5.63; F, 20.57%. Calcd for $C_{21}H_{21}F_6O_2PRu$: C, 45.74; H, 3.84; P, 5.62; F, 20.67%.

Synthesis of [(η^6-Benzene)(η^5-4-(4-bromophenyl)-1-ethoxycarbonyl-2-methylcyclopentadienyl)ruthenium] Hexafluorophosphate (10c). This complex was prepared by the same method as that for **10a** using 4-(4-bromophenyl)-1-ethoxycarbonyl-2-methylcyclopentadiene (58% yield). Mp 239.0—239.5 °C. ^{1}H NMR (acetone-d_6, 400 MHz) $\delta = 7.69$—7.66 (d, 2H, $J = 8.54$ Hz, C_6H_4), 7.59—7.57 (d, 2H, $J = 8.54$ Hz, C_6H_4), 6.54 (s, 1H, CpH), 6.04 (s, 1H, CpH), 6.03 (s, 6H, C_6H_6), 4.42—4.30 (m, 2H, CH_2CH_3), 2.42 (s, 3H, $CpCH_3$), 1.39—1.36 (t, 3H, $J = 7.08$ Hz, CH_2CH_3). IR (KBr) 1722 cm^{-1}(C=O). MS (FAB) *m/z* 485

(M^+-PF_6). Found: C, 40.05; H, 3.27; P, 4.80; F, 17.87; Br, 12.69%. Calcd for $C_{21}H_{20}BrF_6O_2PRu$: C, 40.02; H, 3.20; P, 4.91; F, 18.08; Br, 12.68%.

Synthesis of [(η^6-Benzene)(η^5-1-*N*-*t*-butylcarbamoyl-2,4-dimethylcyclopentadienyl)ruthenium] Hexafluorophosphate (10d). To a solution of **10a** (0.98, 2 mmol) in acetonitrile (50 ml) was added K_2CO_3 (5% in water, 50 ml) and the mixture was refluxed for 3 h. This solution was neutralized by 6 M HCl (1 M = 1 mol dm^{-3}). The solvent was evaporated under reduced pressure and the residue was dissolved in acetonitrile. This solution was dried over $MgSO_4$ and filtered. After removal of the solvent, the residue was washed with dichlorometane several times. To the suspension of the resulting solid in dichloromethane (10 ml) were added oxalyl chloride (1 ml) and DMF (a catalytic amount) with stirring in the dark at room temperature. After 2 h, the solvent was evaporated under reduced pressure, and the residue was dissolved in acetonitrile (10 ml). This solution was added to an acetonitrile solution (20 ml) containing *t*-butylamine (3 ml) and 4-dimethylaminopyridine (5 mg). The reaction mixture was stirred for 3 h and the precipitate formed was removed by filtration. The filtrate was concentrated under reduced pressure. The residual oil was placed on a column of alumina and eluted with acetone. The acetone solution was evaporated, and then the resulting solid was purified by recrystallization from ethanol to give 0.78 g (76% yield) of ruthenium complex **10d** as pale yellow needles. Mp 202.0—202.5 °C. ^{1}H NMR (acetone-d_6, 400 MHz) $\delta = 6.99$ (br, 1H, NH), 6.26 (s, 6H, C_6H_6), 5.88 (s, 1H, CpH), 5.60 (s, 1H, CpH), 2.26 (s, 3H, $CpCH_3$), 1.39 (s, 9H, *t*-Bu). IR (KBr) 3426 (NH), 1662 cm^{-1}(C=O). MS (FAB) *m/z* 372 (M^+-PF_6). Found: C, 42.05; H, 4.43; N, 2.76; P, 5.87; F, 22.18%. Calcd for $C_{18}H_{24}F_6NOPRu$: C, 41.86; H, 4.68; N, 2.71; P, 6.00; F, 22.07%.

Synthesis of [Tris(acetonitrile)(η^5-1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)ruthenium] Hexafluorophosphate (1a). Ruthenium complex **10a** (0.98 g, 2 mmol) was dissolved in acetonitrile (100 ml) under an argon atmosphere and the solution was irradiated with ultraviolet light for 18 h.[21] Removal of the solvent under reduced pressure gave 1.07 g (99% yield) of ruthenium complex **1a** as an orange powder. Mp 98.0—102.0 °C (decomp). ^{1}H NMR (acetone-d_6, 270 MHz) $\delta = 4.66$ (s, 1H, CpH), 4.22 (dq, 1H, $J = 3.0$, 7.3 Hz, CH_2CH_3), 4.19 (dq, 1H, $J = 3.0$, 7.3 Hz, CH_2CH_3), 2.55 (s, 9H, CH_3CN), 1.97 (s, 3H, $CpCH_3$), 1.77 (s, 3H, $CpCH_3$), 1.30 (t, 3H, $J = 7.3$ Hz, CH_2CH_3). IR (KBr) 1708 cm^{-1} (C=O). Found: C, 35.77 H, 4.12; N, 7.71; P, 5.77; F, 21.22%. Calcd for $C_{16}H_{22}F_6N_3O_2PRu$: C, 35.96; H, 4.15; N, 7.86; P, 5.80; F, 21.33%.

Synthesis of [Tris(acetonitrile)(η^5-1-ethoxycarbonyl-2-methyl-4-phenylcyclopentadienyl)ruthenium] Hexafluorophosphate (1b). This complex was prepared by the same method as that for **1a** using **10b** (99% yield). Mp 65.0—68.0 °C. ^{1}H NMR (acetone-d_6, 270 MHz) $\delta = 7.59$—7.56 (m, 3H, Ph), 7.41—7.39 (m, 2H, Ph), 5.43 (s, 1H, CpH), 4.85 (s, 1H, CpH), 4.33—4.23 (m, 2H, CH_2CH_3), 2.45 (s, 9H, CH_3CN), 2.10 (s, 3H, $CpCH_3$), 1.35 (t, 3H, $J = 7.3$ Hz, CH_2CH_3). IR (KBr) 1716 cm^{-1} (C=O). Found: C, 42.07; H, 3.85; N, 6.97; P, 5.00; F, 19.01%. Calcd for $C_{21}H_{24}F_6N_3O_2PRu$: C, 42.29; H, 4.06; N, 7.04; P, 5.19; F, 19.11%.

Synthesis of [Tris(acetonitrile)(η^5-4-(4-bromophenyl)-1-ethoxycarbonyl-2-methylcyclopentadienyl)ruthenium] Hexafluorophosphate (1c). This complex was prepared by the same method as that for **1a** using **10c** (99% yield). Mp 138.5—139.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 7.49$—7.46 (d, 2H, $J = 8.54$ Hz, C_6H_4), 7.27—7.25 (d, 2H, $J = 8.54$ Hz, C_6H_4), 5.21 (s, 1H, CpH), 4.51 (s, 1H, CpH), 4.34—4.24 (m, 2H, CH_2CH_3), 2.34 (s, 9H, CH_3CN), 2.17 (s, 3H, $CpCH_3$), 1.37—1.33 (t, 3H, $J = 7.08$ Hz, CH_2CH_3). IR (KBr) 1722 cm^{-1} (C=O). Found: C, 37.08; H, 3.18; N, 6.11; P, 4.55; F, 16.86; Br, 11.77%. Calcd for $C_{21}H_{23}BrF_6N_3O_2PRu$: C, 37.35; H, 3.43; N, 6.22; P, 4.59; F, 16.88; Br, 11.83%.

Synthesis of [Tris(acetonitrile)(η^5-1-*N*-*t*-butylcarbamoyl-2,4-dimethylcyclopentadienyl)ruthenium] Hexafluorophosphate (1d). This complex was prepared by the same method as that for **1a** using **10d** (99% yield). Mp 66.0—70.0 °C (decomp). ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 5.57$ (s, 1H, NH), 4.24 (s, 1H, CpH), 3.83 (s, 1H, CpH), 2.42 (s, 9H, CH_3CN), 1.95 (s, 3H, $CpCH_3$), 1.71 (s, 3H, $CpCH_3$), 1.41 (s, 9H, *t*-Bu). IR (KBr) 3428 (NH), 1651 cm^{-1} (C=O). Found: C, 38.31; H, 4.93; N, 10.02; P, 5.73; F, 20.35%. Calcd for $C_{18}H_{27}F_6N_4OPRu$: C, 38.51; H, 4.85; N, 9.98; P, 5.52; F, 20.30%.

Synthesis of [(Acetonitrile)(η^5-1-ethoxycarbonyl-2,4-dimethylcyclopentadienyl)(η^4-norbornadiene)ruthenium] Hexafluorophosphate (5). To a solution of **1a** (0.10 g, 0.20 mmol) in methanol was added an excess of norbornadiene, and the mixture was stirred for 1 h. The solvent was evaporated under reduced pressure. The residue was washed several times with ether and dried in vacuo to give 0.10 g (90% yield) of ruthenium complex **5** as an orange powder. Mp 136.5—139.0 °C (decomp). ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 5.24$ (s, 1H, CpH), 4.88 (m, 1H, C=CH), 4.78 (s, 1H, CpH), 4.75—4.72 (m, 2H, C=CH), 4.62 (m, 1H, C=CH), 4.30—4.27 (m, 2H, CH_2CH_3), 3.78 (d, 2H, $J = 17.32$ Hz, CH), 2.75 (s, 3H, CH_3CN), 2.02 (s, 3H, $CpCH_3$), 1.83 (s, 3H, $CpCH_3$), 1.47 (s, 2H, CH_2), 1.38—1.34 (t, 3H, $J = 7.08$ Hz, CH_2CH_3). IR (KBr) 1716 cm^{-1} (C=O). MS (FAB) *m/z* 400 (M^+-PF_6). Found: C, 41.68; H, 4.34; N, 2.33; P, 5.88; F, 20.98%. Calcd for $C_{19}H_{24}F_6NO_2PRu$: C, 41.92; H, 4.44; N, 2.57; P, 5.69; F, 20.94 %.

General Procedure for Cyclopropanation Reaction: To a solution of norbornene derivatives (5 mmol) in methanol (6 ml) was added ruthenium catalyst **1** (0.05—0.25 mmol), and propargyl alcohol (5.5 mmol) in methanol (4 ml) dropped at 0 °C or room temperature. The reaction mixture was stirred for 3 h. The solvent was evaporated under reduced pressure. The residue was placed on a column of silica gel and eluted with ethyl acetate. The ethyl acetate solution was evaporated and then purification of the residue by recrystallization or distillation with Kugelrohr gave the proposed compounds (Fig. 5).

3-*exo*-Acetyltricyclo[3.2.1.0^{2,4}]octane (4a): Mp 43.0—44.0 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 2.35$ (s, 2H, H^1, H^5), 2.19 (s, 3H, CH_3), 1.89 (t, 1H, $J = 2.4$ Hz, H^3), 1.58—1.44 (m, 2H, H^6, H^7), 1.38 (d, 2H, $J = 2.2$ Hz, H^2, H^4), 1.33—1.27 (m, 2H, $H^{6'}$, $H^{7'}$), 0.95 (dt, 1H, $J = 10.7$, 2.0 Hz, H^8), 0.71 (d, 1H, $J = 10.7$ Hz, $H^{8'}$); ^{13}C NMR ($CDCl_3$, 100 MHz) $\delta = 208.50$ (C=O), 36.04 (C^2, C^4), 30.83 (CH_3), 28.83, 28.81, 28.64 (C^1, C^5, C^6, C^7, C^8), 25.08 (C^3). IR (KBr) 1683 cm^{-1} (C=O). MS (EI, 70 eV) *m/z* 150. Found: C, 80.03; H, 9.20%. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39%

3,6-*exo*-Diacetyltricyclo[3.2.1.0^{2,4}]octane (4b): Bp 128 °C (0.5 mmHg, 1 mmHg = 133.322 Pa). ^{1}H NMR ($CDCl_3$, 400 MHz)

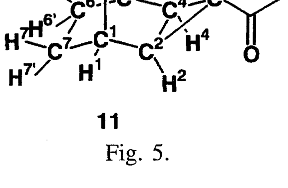


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Fig. 5.

δ = 2.81—2.77 (m, 2H, H^5, H$^{6'}$), 2.44—2.43 (s, 2H, H^1), 2.19 (s, 3H, CH$_3$), 2.15 (s, 3H, CH$_3$), 1.94—1.93 (t, 1H, J = 2.6 Hz, H^3), 1.89—1.85 (m, 1H, H$^{7'}$), 1.60—1.53 (m, 1H, H^7), 1.46—1.43 (m, 1H, H^4), 1.32—1.29 (m, 1H, H^2), 1.15—1.12 (d, 1H, J = 10.7 Hz, H^8), 0.95—0.92 (d, 1H, J = 10.7 Hz, H$^{8'}$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ = 207.52 (C=O), 206.83 (C=O), 54.89 (C^5), 39.25 (C^6), 36.21 (C^1), 30.08 (CH$_3$), 29.88 (C^8), 28.95 (CH$_3$), 28.88 (C^7), 27.37 (C^4), 23.85 (C^3), 23.48 (C^2). IR (KBr) 1698 cm^{-1} (C=O). MS (FAB) *m/z* 192. Found: C, 74.93; H, 8.51%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

3-*exo*-Acetyl-6-cyanotricyclo[3.2.1.0^{2,4}]octane (6-*exo* and 6-*endo* Mixture) (4c): Bp 146 °C (0.5 mmHg). IR (KBr) 2235 (C≡N), 1695 cm^{-1} (C=O). MS (FAB) *m/z* 175. Found: C, 74.93; H, 8.51%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

6-*exo*-Isomer: ^{1}H NMR (CDCl$_3$, 400 MHz) δ = 2.73—2.70 (m, 2H, H^5, H$^{6'}$), 2.54—2.53 (m, 1H, H^1), 2.21 (s, 3H, CH$_3$), 2.03—1.98 (m, 1H, H$^{7'}$), 1.99—1.98 (t, 1H, J = 2.6 Hz, H^3), 1.89—1.88 (m, 1H, H^4), 1.66—1.62 (m, 1H, H^7), 1.57—1.56 (m, 1H, H^2), 1.16—1.13 (d, 1H, J = 12.2 Hz, H^8), 0.82—0.80 (d, 1H, J = 11.7 Hz, H$^{8'}$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ = 206.73 (C=O), 121.52 (C≡N), 39.44 (C^6), 36.04 (C^1), 34.82 (C^7), 30.54 (CH$_3$), 30.10 (C^5), 28.91 (C^8), 26.95 (C^2), 24.23 (C^3), 23.57 (C^4).

6-*endo*-Isomer: ^{1}H NMR (CDCl$_3$, 400 MHz) δ = 2.77 (s, 1H, H$^{6'}$), 2.57 (s, 1H, H^1), 2.49—2.45 (m, 1H, H^5), 2.24 (s, 3H, CH$_3$), 2.01—2.00 (t, 1H, J = 2.2 Hz, H^3), 1.86—1.82 (m, 2H, H^6, H$^{6'}$), 1.41 (d, 2H, J = 1.8 Hz, H^2, H^4), 1.56 (s, 2H, H^8, H$^{8'}$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ = 206.47 (C=O), 121.48 (C≡N), 41.59 (C^6), 35.64 (C^1), 35.41 (C^7), 31.05 (CH$_3$), 29.80 (C^5), 27.69 (C^8), 27.23, 26.45 (C^2, C^4), 24.59 (C^3).

3-*exo*-Acetyl-6,6-bis(hydroxymethyl)tricyclo[3.2.1.0^{2,4}]octane (4d): Bp 138 °C (0.5 mmHg). ^{1}H NMR (CDCl$_3$, 600 MHz) δ = 3.94 (br, 2H, OH), 3.90—3.79 (d, 2H, J = 10.62 Hz, C*H*$_2$OH), 3.64—3.56 (d, 2H, J = 10.99 Hz, C*H*$_2$OH), 2.58 (s, 1H, H^5), 2.38—2.36 (d, 1H, J = 2.20, H^1), 2.23 (s, 3H, CH$_3$), 2.14 (s, 1H, H^3), 1.71—1.70 (d, 1H, J = 6.59 Hz, H^4), 1.43—1.42 (d, 1H, J = 6.59 Hz, H^2), 1.09—1.03 (m, 2H, H$^{7'}$, H^8), 1.01—0.99 (d, 1H, J = 11.73 Hz, H^7), 0.83—0.81 (dd, 1H, J = 2.20, 12.46 Hz, H$^{8'}$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ = 208.90 (C=O), 69.97 (*C*H$_2$OH), 67.79 (*C*H$_2$OH), 49.04 (C^6), 38.02 (C^5), 36.43 (C^1), 35.89 (C^8), 30.93 (CH^3), 28.25 (C^2), 26.80 (C^7), 26.42 (C^3, C^4). IR (KBr) 3419 (OH), 1714 cm^{-1} (C=O). MS (FAB) *m/z* 210. Found: C, 68.31; H, 8.38%. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63%.

3-*exo*-Acetyl-6,7-*endo*-bis(methoxycarbonyl)tricyclo-[3.2.1.0^{2,4}]octane (4e): Mp 146.0—146.5 °C. ^{1}H NMR (CDCl$_3$, 600 MHz) δ = 3.68 (s, 6H, OCH$_3$), 3.05—3.04 (t, 2H, J = 1.5, 1.7 Hz, H$^{6'}$, H^7), 2.77 (s, 2H, H^1, H^5), 2.15 (s, 3H, CH$_3$), 2.01—2.00 (d, 1H, J = 2.6 Hz, H^3), 1.92 (d, 2H, J = 2.2 Hz, H^2, H^4), 1.21—1.19 (m, 1H, H^8), 0.87—0.85 (d, 1H, J = 11.4 Hz, H$^{8'}$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ = 206.51 (C=O), 171.59 (OC=O), 51.14 (OCH$_3$), 47.50 (C^6, C^7), 39.74 (C1, C^5), 29.68 (CH$_3$), 28.89 (C^8), 23.98 (C^3), 23.23 (C^2, C^4). IR (KBr) 1732 (OC=O), 1688 cm^{-1} (C=O). MS (FAB) *m/z* 266. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81; O, 30.04%. Found: C, 63.24; H, 6.90%.

3-*exo*-Acetyl-6,7-*exo*-bis(methoxycarbonyl)-8-oxatricyclo-[3.2.1.0^{2,4}]octane (4f-1): Mp 165.5—166.0 °C. ^{1}H NMR (CDCl$_3$, 600 MHz) δ = 4.78 (s, 2H, H^1, H^5), 3.68 (s, 6H, OCH$_3$), 3.11 (s, 2H, H$^{6'}$, H^7), 2.27 (s, 3H, CH$_3$), 2.14—2.13 (t, 1H, J = 2.6 Hz, H^3), 1.74 (d, 2H, J = 2.2 Hz, H^2, H^4); ^{13}C NMR (CDCl$_3$, 100 MHz) δ = 206.32 (C=O), 170.72 (OC=O), 77.71 (C^1, C^5), 51.71 (C^6, C^7), 31.31 (CH$_3$), 26.73 (C^2, C^4), 23.71 (C^3). IR (KBr) 1738 (OC=O), 1683 cm^{-1} (C=O). MS (FAB) *m/z* 268. Calcd for $C_{13}H_{16}O_6$: C, 58.2; H, 6.01; O, 35.78%. Found: C, 58.36; H, 5.80%.

3-*endo*-Acetyl-6,7-*endo*-bis(methoxycarbonyl)-8-oxatricyclo-[3.2.1.0^{2,4}]octane (4f-2): ^{1}H NMR (CDCl$_3$, 600 MHz) δ = 4.89 (s, 2H, H^1, H^5), 3.68 (s, 6H, OCH$_3$), 3.17 (s, 2H, H^6, H^7), 2.18 (s, 3H, CH$_3$), 1.58—1.57 (t, 1H, J = 7.3 Hz, H^2, H^4), 1.47—1.44 (d, 2H, J = 7.3 Hz, H^3); ^{13}C NMR (CDCl$_3$, 100 MHz) δ = 203.56 (C=O), 170.72 (C≡N), 77.81 (C^1, C^5), 52.04 (C^6, C^7), 29.78 (CH$_3$), 26.20 (C^3), 21.48 (C^2, C^4).

***exo*-3-Acetyl-6,7-bis(methoxycarbonyl)tricyclo[3.2.1.0^{2,4}]-6-octene (7):** Bp 138 °C (0.5 mmHg). ^{1}H NMR (CDCl$_3$, 600 MHz) δ = 3.79 (s, 6H, OCH$_3$), 3.38 (s, 2H, H^1, H^5), 2.97 (t, 1H, J = 2.6 Hz, H^3), 2.22 (s, 3H, CH$_3$), 1.98 (d, 2H, J = 1.8 Hz, H^2, H^4), 1.31 (s, 2H, H^8, H$^{8'}$); ^{13}C NMR (CDCl$_3$, 100 MHz) δ = 203.92 (C=O), 164.50 (OC=O), 149.15 (C^6, C^7), 51.69 (OCH$_3$), 45.51 (C^1, C^5), 39.46 (C^3), 38.14 (C^8), 32.73 (C^2, C^4), 29.95 (CH$_3$). IR (KBr) 1732 (OC=O), 1695 (C=O), 1615 cm^{-1} (C=C). MS (FAB) *m/z* 264. Found: C, 63.36; H, 6.31%. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10%.

Cyclopropanation in MeOD as a Solvent. To a solution of norbornene (0.47 g, 5 mmol) in MeOD (6 ml) and D$_2$O (0.1 ml) was added ruthenium catalyst **1a** (0.05 mmol), and methyl 2-propynyl ether (0.30 g, 5.0 mmol) in MeOD (4 ml) dropped at room temperature. The reaction mixture was stirred for 3 h. The solvent was evaporated under reduced pressure. The residue was placed on a column of silica gel, and eluted with 1/1 hexane/dichloromethane. Removal of the solvent gave 0.50 g (67% yield) of **8** as a colorless solid. ^{1}H NMR (CDCl$_3$, 400 MHz) δ = 2.35 (s, 2H, H^1, H^5), 2.19 (t, 2H, J = 1.6 Hz, CH$_2$D), 1.89 (t, 1H, J = 2.4 Hz, H^3), 1.58—1.44 (m, 2H, H^6, H^7), 1.38 (d, 2H, J = 2.2 Hz, H^2, H^4), 1.33—1.27 (m, 2H, H$^{6'}$, H$^{7'}$), 0.95 (dt, 1H, J = 10.7, 2.0 Hz, H^8), 0.71 (d, 1H, J = 10.7 Hz, H$^{8'}$). MS (EI, 70 eV) *m/z* 151.

X-Ray Diffraction Analysis of 3-*exo*-Acetyl-6,7-*endo*-bis(methoxycarbonyl)tricyclo[3.2.1.0^{2,4}]octane (4e) and 3-*endo*-Acetyl-6,7-*endo*-bis(methoxycarbonyl)-8-oxatricyclo[3.2.1.0^{2,4}]-octane (4f-2). Crystals suitable for X-ray diffraction were mounted on a glass fiber with epoxy resin. All measurements were performed on a Rigaku AFC5R automated four-circles diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71069 Å) at −70 °C in the range of $6° < 2\theta < 55°$ with a scan rate of 16° min^{-1}. Three standard reflections were monitored at every 150 measurements and no damage was observed in all measurements. Intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR 92) and refined by full-matrix least-squares minimizing of $\sum w(|F_o|-|F_c|)^2$. Anisotropic thermal parameters were used for all non-hydrogen atoms and isotropic ones for hydrogen atoms. The final cycles of full matrix least squares refinement were converged. Crystallographic data are as follows.

4e: $C_{14}H_{18}O_5$, MW = 266.29, colorless, monoclinic, $C2/c$ (#15), a = 26.377(2), b = 10.016(3), c = 10.576(3) Å, β = 107.68(1)°, V = 2662(1) Å^3, Z = 8, μ = 1.00 cm^{-1}, R = 0.050 and R_w = 0.076 for 244 parameters against 1949 reflections with $I > 3\sigma(I)$ out of 3050 unique reflections (R_{int} = 0.026), GOF = 0.95.

4f-2: $C_{13}H_{16}O_6$, MW = 268.27, colorless, triclinic, $P1$ (#2), a = 10.967(2), b = 11.750(2), c = 5.4286(6) Å, α = 95.55(1)°, β = 101.03(1)°, γ = 66.44(1)°, V = 629.2(2) Å^3, Z = 2, μ = 1.12 cm^{-1}, R = 0.038, and R_w = 0.053 for 236 parameters against 2253 reflections with $I > 3\sigma(I)$ out of 2877 unique reflections (R_{int} = 0.021), GOF = 1.25.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition numbers 133100—133101, and the final atomic parameters and structure factors have been deposited as Document

No. 72036 at the Office of the Editor of Bull. Chem. Soc. Jpn.

This research was supported partially by COE from the Ministry of Education, Science, Sports and Culture.

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