Rearrangement Approaches to Cyclic Skeletons. X. Pinacol-Type Rearrangement of 2-Substituted 1-Methoxybicyclo[2.2.2]oct-5-en-2-ols into Bicyclo[3.2.1]oct-6-en-2-ones. Remarkable Substituent Effects on Predominant Migration of the Unsaturated Bridge[1)]

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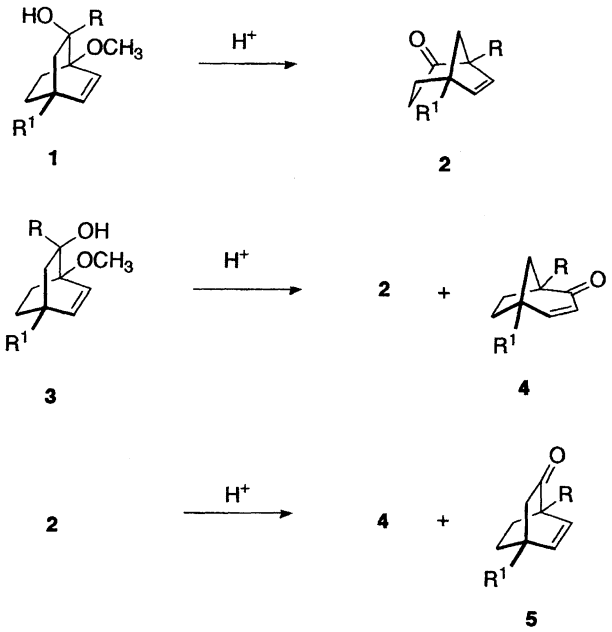
(Received January 9, 1996)

Pinacol-type rearrangement of 2-substituted 1-methoxybicyclo[2.2.2]oct-5-en-*exo*-2-ols (**1**) by treatment with *p*-toluenesulfonic acid in boiling benzene gave bicyclo[3.2.1]oct-6-en-2ones (**2**) and -3en-2-ones (**4**) in a ratio of $\geqq$10 to 1 along with small amounts of dehydration products. Treatment of the endo isomers (**3**) under the same conditions gave **2**, **4**, and the dehydration products. The ratios of **2** to **4**, in this case were within a certain range and were influenced by the substituent at the C-2 position. The ratio of the relative disappearance rate constant of **1** to that of the corresponding **3** was less than 10. This observation suggests that the unsaturated bridge does not offer *remarkable* anchimeric assistance in the reaction of **1**. A similar acid treatment of the dehydration products gave **2** and **4** and their ratio was somewhat affected by the substituent. A mechanism is proposed for the pinacol-type rearrangement.

Since the first report by Rogers and his co-workers,[2)] pinacol-type rearrangement of 2-substituted 1-methoxybicyclo-[2.2.2]oct-5-en-2-ols has been recognized as a practical synthetic method for bicyclo[3.2.1]oct-6-en-2-ones[3)] and has been applied to the syntheses of natural products.[4)] It has already been mentioned that 1) acid treatment of the *exo* alcohols (**1**) gives almost exclusively the unconjugated bicyclo[3.2.1]oct-6-en-2-ones (**2**), 2) while the corresponding *endo* alcohols (**3**) yield predominantly the conjugated ketones (**4**), and 3) in addition, the β,γ-unsaturated ketones **2** are convertible into a mixture of conjugated ketones **4** and the bridgehead substituted bicyclo[2.2.2]oct-5-en-2-ones (**5**) under the same reaction conditions, as shown in Scheme 1.[2)] Then, Monti and his co-workers have also investigated the rearrangement of substrates containing a functional group in the side chain at the C-2 position using *p*-toluenesulfonic acid (TsOH) as an acid catalyst and acetic acid as a solvent.[3)]

In connection with our studies on rearrangement approaches to cyclic skeletons,[1)] we must not skip over the pinacol-type rearrangement of bicyclo[2.2.2]oct-5-en-2-ols.[4d)] We have already reported formal bridgehead substitution of bicyclo[3.2.2]non-6-en-2-ones based on a similar pinacol-type rearrangement[5)] and are interested in the rearrangement of bicyclo[2.2.2]oct-5-en-2-ols as a reaction of *a more rigid bicyclic system* than bicyclo[3.2.2]non-6-en-2-ols. It is sur-



Scheme 1.

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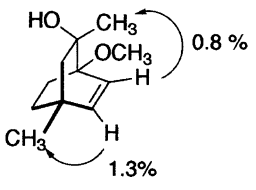
prising that standard values of the formation ratios of **2** to **4** were not listed in the previous reports. The present paper describes a regioselective aspect of the rearrangement of isomeric alcohols **1** and **3** under reaction conditions deemed ineffective on the secondary conversion of ketones **2** into a mixture of ketones **4** and **5** (Scheme 1).

Results and Discussion

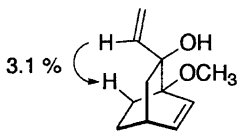
Preparation and Acid Treatment of Alcohols. Alcohols **1** and **3** were derived from the corresponding ketones[6] by treatment with organometallic reagents. Stereochemistries of the alcohols were assigned on the basis of their NMR data including NOE experiments (Fig. 1). Preliminary studies of pinacol rearrangement were carried out using tertiary alcohols **1b** and **3b** with less than 10 mol % of TsOH as an acid catalyst in various solvents at 60—80 °C (bath temperature). When toluene was used as the solvent, **2b**, **4b**, and dehydration products were derived from the alcohols. Not even a detectable amount of ketone **5b**[7] by VPC was formed. This suggests that the primary product **2b** is not transformed into a mixture of **4b** and **5b** under the reaction conditions.

Table 1 shows the product composition of the acid treatment under representative conditions for the pinacol-type rearrangement. From exo alcohols **1**, unconjugated ketones **2** were derived predominantly along with a small portion of conjugated ketones **4**. Regardless of the substituent R, the ratios of **2** to **4** were almost the same ($\geqq$10 : 1). In addition to these ketones, at least one of the predictable dehydration products (**6**—**12**) was detected in each case. Identification of these minor products was carried out by VPC using authentic specimens prepared independently.

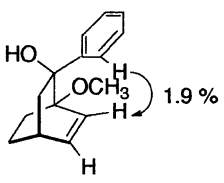
A very similar reaction of the endo alcohols **3** to that of **1** also gave a mixture of the corresponding ketones **2** and **4**, but their ratios were not identical to those derived from the corresponding **1**. Table 1 shows clear substituent effects on the ratios of **2** to **4** derived from **3**. It is noteworthy that the ratio of **2d** to **4d** derived from **3d** is equal to that from



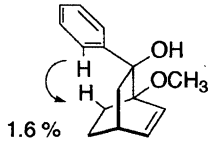
1a



3c

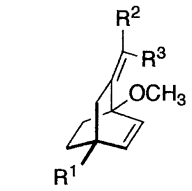


1d



3d

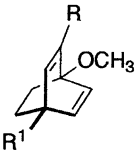
Fig. 1. Key interactions obtained from the NOE difference spectra.



6 R^1= CH_3, R^2= H, R^3= H

7 R^1= H, R^2= *n*-Pr, R^3= H

8 R^1= H, R^2= H, R^3= *n*-Pr



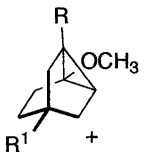
9 R= CH_3, R^1=CH_3

10 R= *n*-Bu, R^1=H

11 R= CH_2=CH, R^1=H

12 R= Ph, R^1=H

Chart 1.



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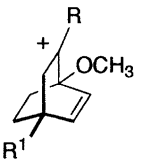

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Chart 2.

1d. Thus, the conclusion mentioned by Rogers and his coworkers[2] previously should be corrected.

Plots of the composition vs. reaction time for benzene solutions of **1** and **3** are shown in Figs. 3, 4, 5, and 6. It is clear that pinacol rearrangements predominate in the acid treatment. The dienes derived by the dehydration disappeared slowly. This suggests the possibility of transformation of the dehydration products into ketones **2** and **4** under these reaction conditions (vide post),[4a] while they are not the intermediates of the pinacol rearrangement.

Monti and his co-workers postulated participation of the double bond to furnish cyclopropylcarbenium intermediate **13** for the rearrangement of their *exo* alcohols (**1**) giving the corresponding unconjugated ketones (**2**) exclusively.[4a] The formation of the conjugated ketones (**4**) from their *endo* alcohols (**3**) predominantly was rationalized by postulating a simultaneous *trans*-antiparallel migration of the saturated bridge in which some crossover occurs to give the unconjugated ketones (**2**).

In contrast to these results, the regioselectivity of the reaction of **3d** is identical to that of **1d** and the ratio of **2c** to **4c** derived from **3c** is nearly equal to that from **1c**. These results suggest that if the substituent (R) stabilizes tertiary cation **14** sufficiently, this cation may become the intermediate and the ratio of **2** to **4** reflects the relative migratory aptitude of the unsaturated bridge vs. that of the saturated bridge of **14**. Conjugated ketones **4** were always derived from *exo* alcohols **1** even though the yields were less than 10%. This suggests that the double bond should participate efficiently not only in simultaneous bridge migration to give **2** but also in accumulation of cation intermediates **14**. The production of **4** from *endo* alcohols **3** may be rationalized by the competition between the concurrent *trans*-antiparallel migration of the saturated bridge[3a] and the rearrangement through tertiary cations **14**. The substituents (R) affect the stepwise process

Table 1. Product Composition Derived from 1-Methoxybicyclo[2.2.2]oct-5-en-2-ols[a)]

Alcohols	R	R^1	Reaction time (h)	Consumption[b)] %	Products[b)] (yiedld/%)			2 : 4	Internal standard[c)]	Yield[d)] %
1a	Me	Me	2.9	95	**2a** (89),	**4a** (3),	**6** (0.2)	97 : 3	A	78
1b	Bu	H	1.2	100	**2b** (90),	**4b** (6),	**7** (<3)	94 : 6	B	94
1c	vinyl	H	0.26	99	**2c** (89),	**4c** (9),	**11** (0.4)	91 : 9	C	82
1d	Ph	H	0.56	100	**2d** (93),	**4d** (5),	**12** (0.8)	95 : 5	D	80
3a	Me	Me	6.0	100	**2a** (32),	**4a** (66),	**6** (0.3)	33 : 67	A	78
3b	Bu	H	5.0	100	**2b** (58),	**4b** (34),	**7** (<5)	63 : 37	B	90
3c	vinyl	H	0.3	100	**2c** (83),	**4c** (13),	**11** (0.8)	87 : 13	C	90
3d	Ph	H	0.3	100	**2d** (90),	**4d** (5),	**12** (4)	95 : 5	D	96

a) A reaction was carried out in a 0.05 M benzene solution containing 10 mol % of TsOH at 80 °C (bath temperature). b) Determined by VPC. c) Used for VPC analyses, A: dodecane; B: hexadecane; C: tetradecane; D: nonadecane. d) A total yield of the products isolated by column chromatography.

considerably rather than the simultaneous process. Figure 2 shows energetic aspects for the reactions of *endo* alcohols **3**. A downward arrow indicates the possibility of stabilization by the substituent R.

The relative disappearance rates estimated from the reactions shown in Figs. 3, 4, 5, and 6 are as follows, **1a**, 2; **1b**, 10; **1c**, 50; **1d**, 20; **3a**, 1; **3c**, 50; and **3d**, 40. The values of k_{rel} (**1**)/k_{rel} (**3**) are in the range of 0.5 to 10. These small differences suggest that the double bond of *exo* alcohols **1** kinetically assists the rearrangement very little under the conditions investigated.

Preparation and Acid Treatment of Dienes. In order to obtain information on the relative migratory aptitude of the unsaturated bridge and that of the saturated one, we focused our attention on acid treatment of the following dienes. Dienes **6**, **7**, and **8** were prepared by a Wittig olefination from the corresponding 1-methoxybicyclo[2.2.2]oct-5-en-2-ones.[3a,6)] Diene **9** was derived by a coupling reaction of the enol trifluoromethanesulfonate of 1-methoxy-4-methylbicyclo[2.2.2]oct-5-en-2-one with $(CH_3)_2CuLi$.[8)] Dienes **10**, **11**, and **12** were obtained by a method similar to that used for preparing **9**.

When one of these dienes was treated under the same conditions used for the rearrangement of the corresponding alcohols, transformation into the ketones was not completed. Upon treatment with TsOH in benzene saturated with water at 80 °C however, each of the dienes was converted into a mixture of the corresponding ketones **2** and **4** as shown in Table 2 and none of alcohols **1** and **3** was detected. Here, reactions of dienes **6**, **7**, **11**, and **12** directly correlate with those of alcohols **1** and **3**. The ratios of **2** to **4** from the dienes are affected by the substituents. Ratios of **2a** to **4a** from dienes **6** and **9** are different. This suggests that the regio- and stereochemistry of the protonation of the double bond may

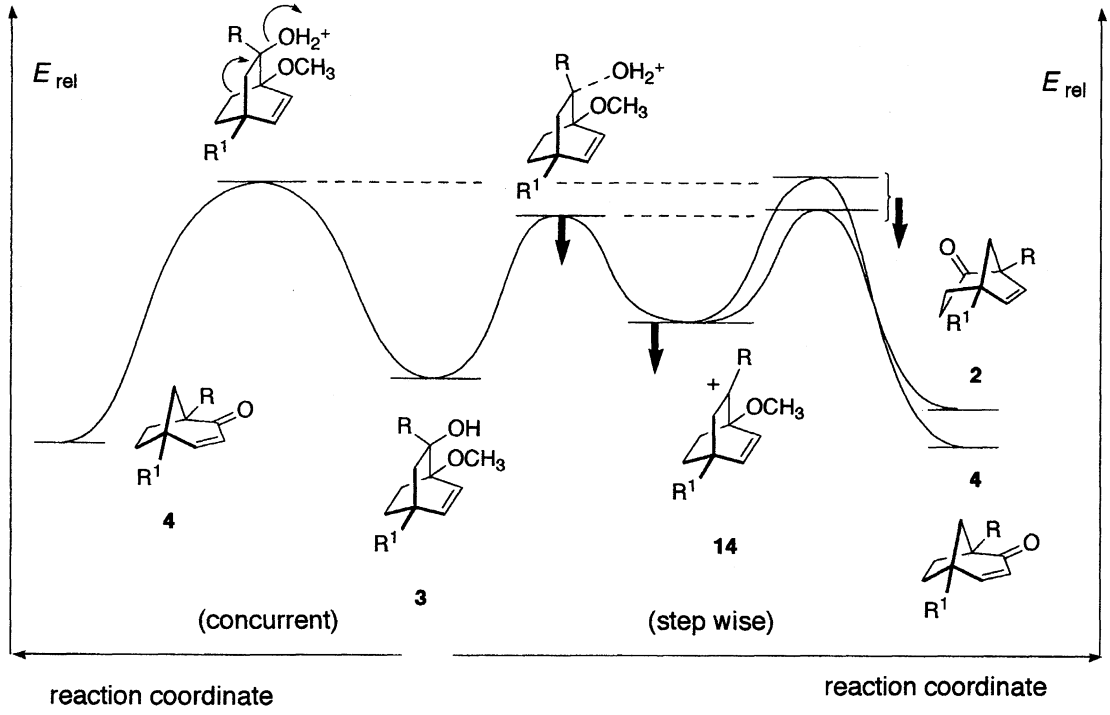

Fig. 2. The changing aspects of the potential energy during the pinacol type rearrangement of the endo alcohols (**3**).

Table 2. Product Composition Derived from 2-Alkylidene-1-methoxybicyclo[2.2.2]oct-5-enes and 1-Methoxybicyclo[2.2.2]-octa-2,5-dienes[a)]

Substrate	Reaction time (h)	Consumption[b)] %	Products[b)] (yield, %)			2 : 4	Internal standard[c)]
6	0.8	99	**2a** (73),	**4a** (20),	**9** (0.3)	78 : 22	A
9	1.4	100	**2a** (54),	**4a** (31)		63 : 37	A
7	8.5	>99	**2b** (77),	**4b** (15)		84 : 16	B
8	4.3	>99	**2b** (71),	**4b** (20),	**7** (0.7)	78 : 22	B
10	1.4	>99	**2b** (62),	**4b** (18),	**7** (12)	77 : 23	B
11	5.5	100	**2c** (44),	**4c** (5)[d)]		90 : 10	C
12	12	87	**2d** (82),	**4d** (5)		95 : 5	D

a) A reaction was carried out in a 0.05 M benzene solution containing 10 mol % of TsOH at 80 °C (bath temperature). b) Determined by VPC. c) Used for VPC analyses, A: dodecane; B: pentadecane; C: tridecane; D: octadecane. d) With an unknown compound (ca. 31%).

partly influence the product composition. In contrast with the outcome, the ratio of **2d** to **4d** from diene **12** is identical with that of alcohols **1d** and **3d**. This suggests that cation **14d** may also be the intermediate in this case. If we postulate that the protonation of the trisubstituted double bond of the dienes occurs from the less hindered side preferentially, formation of **4** may be rationalized by the competition between the concurrent *trans*-antiparallel migration of the saturated bridge and the rearrangement through tertiary cations **14**.

The ratio of **2c** to **4c** derived from **11** is almost equal to that from **1c** and **3c**. This suggests that cation **14c** is acceptably stabilized by the vinyl group, in analogy with the phenyl group of **14d**, and the reaction proceeds mainly through **14c**.

Conclusions

Bicyclo[3.2.1]oct-6-en-2-ones (**2**) and -3-en-2-ones (**4**) were derived in $\geqq$10 to 1 ratios from 2-substituted 1-methoxybicyclo[2.2.2]oct-5-en-*exo*-2-ols (**1**) by treatment with *p*-toluenesulfonic acid in boiling benzene. From the *endo* isomers (**3**), **2** and **4** were also derived under the same con-

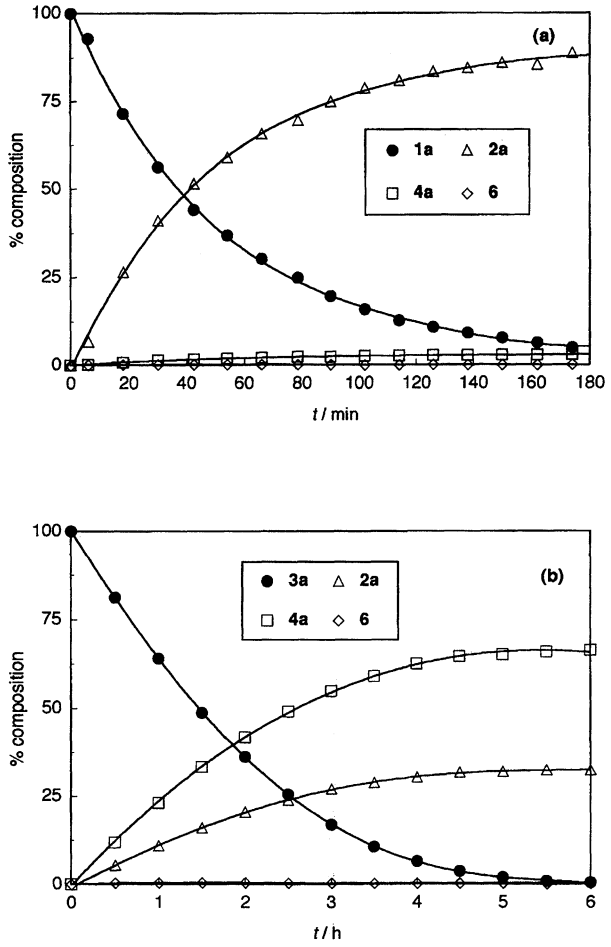

Fig. 3. Conversion of **1a** (a) and **3a** (b) under the conditions listed in Table 1.

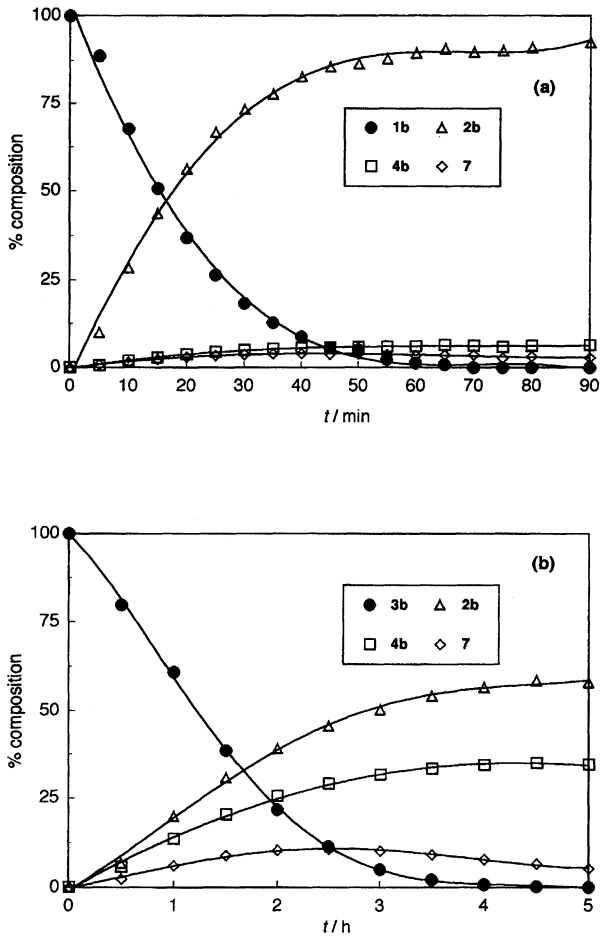

Fig. 4. Conversion of **1b** (a) and **3b** (b) under the conditions listed in Table 1.

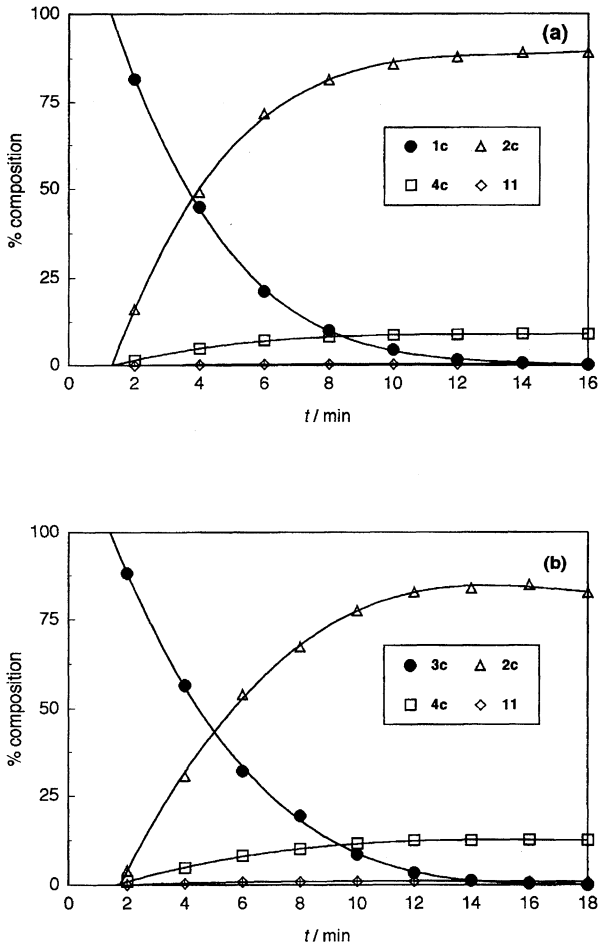

Fig. 5. Conversion of **1c** (a) and **3c** (b) under the conditions listed in Table 1.

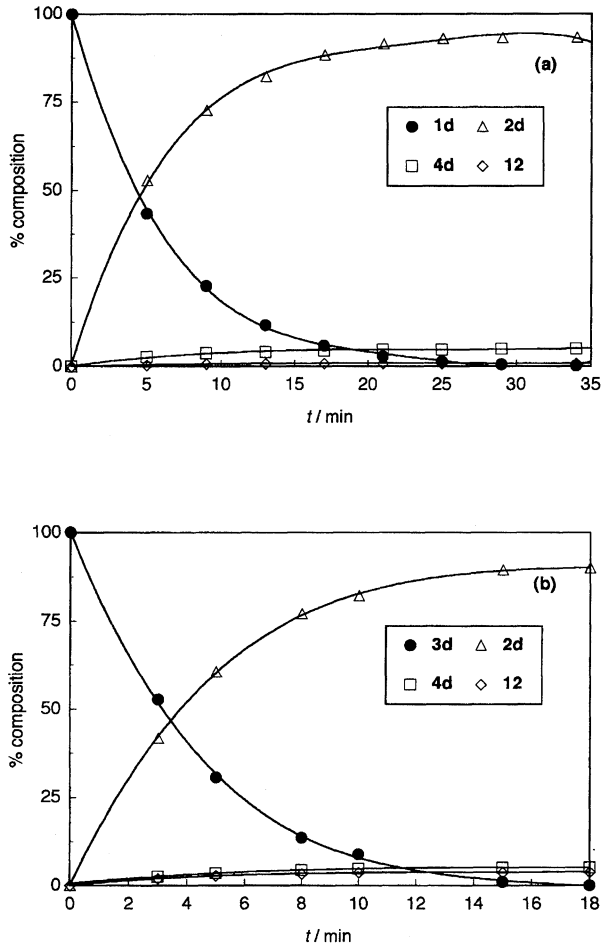

Fig. 6. Conversion of **1d** (a) and **3d** (b) under the conditions listed in Table 1.

ditions, and the ratios of **2** to **4** in this case were influenced by the substituent at the C-2 position. These results indicate that participation of the double bond at the cationic center decreases geometrically according to the structural rigidity of the carbon system.

Experimental

General. The ^{1}H NMR spectra were measured at 300 and 600 MHz in $CDCl_3$ using TMS [$(CH_3)_4Si$] as the internal standard. COSY and NOESY experiments were frequently employed for assigning the stereostructures. THF and diethyl ether were distilled from benzophenone ketyl under argon immediately prior to use. Benzene was distilled from P_2O_5. Dichloromethane was distilled from CaH_2 under argon immediately prior to use. All of the preparative reactions were monitored by analytical TLC using Merck pre-coated silica-gel $60F_{254}$ plates. VPC was carried out by using a fused silica capillary column (Shimadzu CPB1-M-25-025). Column chromatography was performed with Merck silica-gel 60 (70—230 mesh ASTM). Flash chromatography was carried out with Cica–Merck silica-gel 60 (230—400 mesh ASTM). Semi-preparative HPLC was performed using a Merck Hiber prepacked column RT (250×10 mm)

1-Methoxy-*endo*-2,4-dimethylbicyclo[2.2.2]oct-5-en-*exo*-2-ol and Its *endo* Isomer (1a and 3a, Respectively). To a stirred solution of 1-methoxy-4-methylbicyclo[2.2.2]oct-5-en-2-one (1.66 g, 9.97 mmol) in THF (80 cm^3) was added dropwise a solution of 1.09 M methyllithium (11.0 cm^3, 12.0 mmol, 1 M = 1 mol dm^{-3}) in ether at −78 °C under argon. This mixture was stirred for 2.5 h, allowed to warm to room temperature, and stirred for an additional 2 h. The reaction mixture was treated with a saturated aqueous NH_4Cl solution and then extracted with three portions of ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to leave an oil. Chromatography of this oil on silica gel (1st: 126 g; 19 : 6 hexane–ethyl acetate, 2nd: 71 g; 4 : 1 hexane–ethyl acetate) gave **1a** (331 mg, 13.1 mmol, 18%) and **3a** (1.00 g, 1.97 mmol, 55%).

1a: Colorless needles; mp 53.0—54.0 °C; IR (KBr) 3500 cm^{-1} (OH); ^{1}H NMR (300, $CDCl_3$) δ = 6.22 (1H, d, $J_{6,5}$ = 8.7 Hz, H_6), 5.87 (1H, d, $J_{5,6}$ = 8.7 Hz, H_5), 3.37 (3H, s, OCH_3), 2.01 (1H, m, H_{7exo}), 1.99 (1H, broad s, OH), 1.65—1.48 (3H, m), 1.30 (1H, dd, $J_{3endo,3exo}$ = 16.2 and $J_{3endo,8endo}$ = 3.6 Hz, H_{3endo}), 1.26 (1H, m, H_8), 1.13 (3H, s, 2-CH_3), and 1.10 (3H, s, 4-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.6 (C-5), 131.8 (C-6), 82.9 (C-1), 76.7 (C-2), 51.6 (OCH_3), 50.1 (C-3), 34.5 (C-4), 33.2 (C-8), 27.1 (2-CH_3), 24.7 (4-CH_3), and 22.9 (C-7). Found: C, 72.15; H, 10.13%. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95%.

3a: Colorless oil; IR (neat) 3500 cm^{-1} (OH); ^{1}H NMR (300, $CDCl_3$) δ = 6.29 (1H, d, $J_{6,5}$ = 8.7 Hz, H_6), 6.06 (1H, d, $J_{5,6}$ = 8.7 Hz, H_5), 3.42 (3H, s, OCH_3), 2.15 (1H, brond s, OH), 1.67 (1H, ddd, $J_{7endo,7exo}$ = 12.0 and $J_{7endo,8exo}$ = $J_{7endo,8endo}$ = 5.1 Hz, H_{7endo}) 1.59—1.26 (5H, m), 1.32 (3H, s, 2-CH_3), and 1.12 (3H, s, 4-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.7 (C-5), 131.6 (C-6), 82.4 (C-

1), 76.2 (C-2), 52.6 (C-3), 51.6 (OCH_3), 34.5 (C-4), 32.7 (C-8), 25.1 (C-7), 24.54 (2- or 4-CH_3), and 24.47 (4- or 2-CH_3). Found: C, 72.48; H, 10.24%. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95%.

***endo*-2-Butyl-1-methoxybicyclo[2.2.2]oct-5-en-*exo*-2-ol and Its *endo* Isomer (1b and 3b, Respectively).** 1-Methoxy-bicyclo[2.2.2]oct-5-en-2-one (1.52 g, 10.0 mmol) was treated with butylmagnesium bromide, derived from bromobutane (22.0 mmol) and magnesium (20.2 mmol) in THF (100 cm^3), at 0 °C and then at room temperature for 2 h. The alcohols (**1b** and **3b**) were obtained in 54 and 22% yields, respectively.

1b: Colorless needles; mp 31.5—32.5 °C; IR (KBr) 3480 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ = 6.24 (1H, d, $J_{6,5}$ = 8.8 Hz, H_6), 5.87 (1H, d, $J_{5,6}$ = 8.8 and $J_{5,4}$ = 6.2 Hz, H_5), 3.35 (3H, s, OCH_3), 2.49 (1H, m, H_4), 2.01 (1H, ddd, $J_{7exo,7endo}$ = 11.2, $J_{7exo,8exo}$ = 10.4, and $J_{7exo,8endo}$ = 3.8 Hz, H_{7exo}), 1.79 (1H, broad s, OH), 1.74 (1H, m, H_{8exo}),1.70 (1H, m, $H_{1'}$), 1.56 (1H, ddd, $J_{3endo,3exo}$ = 13.2, $J_{3endo,4}$ = 3.2, and $J_{3endo,8endo}$ = 3.2 Hz, H_{3endo}), 1.46 (1H, ddd, $J_{7endo,8endo}$ = 12.2, $J_{7endo,7exo}$ = 11.4, and $J_{7endo,8exo}$ = 4.4 Hz, H_{7endo}), 1.40 (1H, dd, $J_{3exo,3endo}$ = 13.4 and $J_{3exo,4}$ = 2.2 Hz, H_{3exo}), 1.37 (1H, m, H_{8endo}), 1.35 (1H, m, $H_{2'}$) 1.30—1.20 (4H, m), and 0.87 (3H, t, J = 7.2 Hz, $H_{4'}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 133.3 (C-5), 132.8 (C-6), 83.0 (C-1), 78.3 (C-2), 51.5 (OCH_3), 39.5 (C-3), 38.1 (C-1′), 30.5 (C-4), 25.0 (C-8), 24.5 (C-2′), 23.4 (C-3′), 21.9 (C-7), and 14.2 (C-4′). Found: *m/z* 210.1627. Calcd for $C_{13}H_{22}O_2$: M, 210.1620. Found: C, 74.01; H, 10.61%. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54%.

3b: Colorless oil; IR (neat) 3500 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ = 6.32 (2H, m, H_5 and H_6), 3.41 (3H, s, OCH_3), 2.52 (1H, m, H_4), 1.86 (1H, m, $H_{1'}$), 1.84 (1H, m, OH), 1.69 (1H, dd, $J_{3exo,3endo}$ = 13.2 and $J_{3exo,4}$ = 2.4 Hz, H_{3exo}), 1.60—1.50 (4H, m), 1.43—1.27 (5H, m), 1.38 (1H, m, H_{3endo}), and 0.92 (3H, t, J = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 133.4 (C-5), 132.8 (C-6), 82.7 (C-1), 77.4 (C-2), 51.6 (OCH_3), 42.8 (C-3), 36.1 (C-1′), 30.3 (C-4), 26.2 (C-2′), 25.2 (C-8), 23.6 (C-3′), 23.3 (C-7), and 14.2 (C-4′). Found: *m/z* 210.1631. Calcd for $C_{13}H_{22}O_2$: M, 210.1620. Found: C, 74.15; H, 10.72%. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54%.

1-Methoxy-*endo*-2-vinylbicyclo[2.2.2]oct-5-en-*exo*-2-ol and Its *endo* Isomer (1c and 3c, Respectively). 1-Methoxybicyclo-[2.2.2]oct-5-en-2-one (1.27 g, 8.35 mmol) was treated with a 0.92 M THF solution of vinylmagnesium bromide (11.5 mmol) at −78 °C for 1 h and then at 0 °C for 1 h. The alcohols (**1c** and **3c**)were isolated in 40 and 37% yields, respectively.

1c: Colorless oil; IR (neat) 3590 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ = 6.29 (1H, d, $J_{6,5}$ = 8.8 Hz, H_6), 6.25 (1H, d, $J_{5,6}$ = 8.8 and $J_{5,4}$ = 6.2 Hz, H_5), 5.90 (1H, J_{trans} = 17.2 and J_{cis} = 10.6 Hz, $H_{1'}$), 5.21 (1H, J_{trans} = 17.2 and J_{gem} = 1.4 Hz, $H_{2'}$), 5.01 (1H, J_{cis} = 10.6 and J_{gem} = 1.4 Hz, $H_{2'}$), 3.35 (3H, s, OCH_3), 2.54 (1H, m, H_4), 2.23 (1H, broad s, OH), 2.05 (1H, ddd, $J_{7exo,7endo}$ = 11.2, $J_{7exo,8exo}$ = 10.4, and $J_{7exo,8endo}$ = 3.8 Hz, H_{7exo}), 1.81 (1H, dddd, $J_{8exo,8endo}$ = 12.0, $J_{8exo,7exo}$ = 10.4, $J_{8exo,7endo}$ = 4.2 and $J_{8exo,4}$ = 2.4 Hz, H_{8exo}), 1.63 (2H, m, H_3), 1.51 (1H, ddd,$J_{7endo,8endo}$ = 12.4, $J_{7endo,7exo}$ = 11.4, and $J_{7endo,8exo}$ = 4.2 Hz, H_{7endo}), and 1.41 (1H, m, H_{8endo}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 145.1 (C-1′), 134.1 (C-5), 132.2 (C-6), 110.8 (C-2′), 82.8 (C-1), 78.6 (C-2), 51.9 (OCH_3), 41.9 (C-3), 30.3 (C-4), 25.1 (C-8), and 21.8 (C-7). Found: *m/z* 180.1149. Calcd for $C_{11}H_{16}O_2$: M, 180.1150. Found: C, 73.04; H, 8.89%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

3c: Colorless oil; IR (neat) 3595 cm^{-1} (OH); ^1H NMR ($CDCl_3$) δ = 6.36 (1H, d, $J_{5,6}$ = 8.8 and $J_{5,4}$ = 6.2 Hz, H_5), 6.32 (1H, d, $J_{6,5}$ = 8.8 Hz, H_6), 6.12 (1H, J_{trans} = 17.2 and J_{cis} = 10.8 Hz, $H_{1'}$), 5.36 (1H, J_{trans} = 17.2 and J_{gem} = 1.4 Hz, $H_{2'}$), 5.18 (1H, J_{cis} = 10.6 and J_{gem} = 1.4 Hz, $H_{2'}$), 3.39 (3H, s, OCH_3), 2.57 (1H, m, H_4), 2.37 (1H, broad s, OH), 1.86 (1H, dd, $J_{3exo,3endo}$ = 13.6 and $J_{3exo,4}$ = 2.4 Hz, H_{3exo}), 1.61—1.56 (3H, m, H_7 and H_8), 1.50 (1H, ddd, $J_{3endo,3exo}$ = 13.6, $J_{3endo,4}$ = $J_{3endo,8endo}$ = 3.2 Hz, H_{3endo}), and 1.45 (1H, m, H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 141.4 (C-1′), 133.7 (C-5), 132.3 (C-6), 113.2 (C-2′), 82.5 (C-1), 77.8 (C-2), 51.8 (OCH_3), 42.9 (C-3), 30.1 (C-4), 25.2 (C-8), and 23.4 (C-7). Found: C, 73.09; H, 9.14%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%. Found: *m/z* 180.1147. Calcd for $C_{11}H_{16}O_2$: M, 180.1150.

1-Methoxy-*endo*-2-phenylbicyclo[2.2.2]oct-5-en-*exo*-2-ol and Its *endo* Isomer (1d and 3d). 1-Methoxybicyclo[2.2.2]oct-5-en-2-one (972 mg, 6.38 mmol) was treated with a 2.0 M THF solution of phenylmagnesium bromide (0.76 mmol) at −78 °C for 1 h and then at room temperature for 2 h. The alcohols (**1d** and **3d**) were obtained in 62 and 23% yields, respectively.

1d: Colorless needles; mp 46.7—47.5 °C; IR (KBr) 3470 cm^{-1} (OH) ; ^1H NMR ($CDCl_3$) δ = 7.44 (2H, m, $H_{2'}$ and $H_{6'}$), 7.23 (3H, m, $H_{3'}$, $H_{4'}$, $H_{5'}$), 6.35 (2H, m, H_5 and H_6), 3.23 (3H, s, OCH_3), 2.77 (1H, broad s, OH), 2.71 (1H, m, H_4), 2.20 (1H, m, H_{7exo}), 2.12 (1H, ddd, $J_{3endo,3exo}$ = 13.8, $J_{3endo,4}$ = 2.7, and $J_{3endo,8endo}$ = 2.7, H_{3endo}), 1.94 (1H, dd, $J_{3exo,3endo}$ = 13.5 and $J_{3exo,4}$ = 2.7 Hz, H_{3exo}), 1.82 (1H, m, H_{8exo}), and 1.50 (2H, m, H_{7endo} and H_{8endo}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.7 (C-1′), 133.4 (C-5), 132.8 (C-6), 127.2 (C-2′ and -6′), 127.0 (C-3′ and -5′), 126.1 (C-4′), 83.2 (C-1), 79.2 (C-2), 51.8 (OCH_3), 46.1 (C-3), 30.8 (C-4), 24.6 (C-8), and 24.1 (C-7). Found: C, 78.01; H, 7.71%. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%.

3d: Colorless oil; IR (neat) 3560 cm^{-1} (OH) ; ^1H NMR (300, $CDCl_3$) δ = 7.54 (2H, m, $H_{2'}$ and $H_{6'}$), 7.34 (2H, m, $H_{3'}$ and $H_{5'}$), 7.26 (1H, m, $H_{4'}$), 6.47 (1H, dd, $J_{5,6}$ = 8.7 and $J_{5,4}$ = 6.0 Hz, H_5), 6.41 (1H, dd, $J_{6,5}$ = 8.7 Hz, H_6), 3.23 (3H, s, OCH_3), 2.79 (1H, broad s, OH), 2.76 (1H, m, H_4), 2.41 (1H, dd, $J_{3exo,3endo}$ = 14.1 and $J_{3exo,4}$ = 2.4 Hz, H_{3exo}), 1.85 (1H, m, H_{8exo}), 1.78 (1H, ddd, $J_{3endo,3exo}$ = 14.1, $J_{3endo,4}$ = 3.0, and $J_{3endo,8endo}$ = 3.0 Hz, H_{3endo}), 1.58 (1H, m, H_{7endo}), and 1.54—1.47 (2H, m, H_{7exo} and H_{8endo}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 142.7 (C-1′), 134.5 (C-5), 133.2 (C-6), 127.2 (C-2′ and -6′), 127.1 (C-3′ and -5′), 126.5 (C-4′), 82.5 (C-1), 79.7 (C-2), 51.7 (OCH_3), 45.9 (C-3), 30.5 (C-4), 25.6 (C-8), and 23.0 (C-7). Found: *m/z* 230.1318. Calcd for $C_{15}H_{18}O_2$: M, 230.1307. Found: C, 78.20; H, 8.07%. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%.

Pinacol-Type Rearrangement of 2-Substituted 1-Methoxybicyclo[2.2.2]oct-5-en-2-ol (1 and 3). a) A General Procedure for Product Analysis. In a flask equipped with a serum cap and a reflux condenser connected with a three-way stopcock attached to an argon-filled balloon were placed an alcohol **1a** (35.7 mg, 0.196 mmol), dodecane (33.9 mg, 0.199 mmol), *p*-TsOH (3.73 mg, 0.0196 mmol), and dry benzene (9.8 ml). The resulting mixture was heated under reflux in a preheated oil bath at 80 °C. Samples (2.5×10^{-3} cm^3) were withdrawn every 10 min and treated rapidly with ether (0.5 cm^3) and a saturated aqueous $NaHCO_3$ solution (0.25 cm^3). The ether layer was analyzed by VPC. After **1a** was consumed, the remaining reaction mixture was treated with a saturated aqueous $NaHCO_3$ solution and extracted with ether. The combined extracts were washed with saturated brine, dried over $MgSO_4$, and concentrated to afford an oil. The oil was used for NMR analysis.

b) A General Procedure for Preparation. In a flask equipped with a serum cap and a reflux condenser connected with a three-way stopcock attached to an argon-filled balloon were placed an alcohol **3b** (121.5 mg, 0.578 mmol), *p*-TsOH (11.1 mg, 0.0584 mmol), and dry benzene (12 ml). The resulting mixture was heated under reflux in a preheated oil bath at 80 °C for 5 h. This mixture

was allowed to cool to room temperature and stirred with saturated aqueous $NaHCO_3$ solution for 15 min. The organic layer was diluted with ether, separated, washed with brine, and dried over $MgSO_4$. Evaporation of the solvent gave an oil. Chromatography of this oil on silica gel (hexane–ethyl acetate) gave **2b** (55.9 mg, 0.31 mmol, 54%), a mixture of **2b** and **4b** (19.8 mg, 19%), and **4b** (17.4 mg, 0.10 mmol, 17%).

1,5-Dimethylbicyclo[3.2.1]oct-6-en-2-one (2a): Colorless oil; IR (neat) 1650 and 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 5.89 (1H, d, $J_{6,7}$ = 5.7 Hz, H_6), 5.66 (1H, d, $J_{7,6}$ = 5.7 Hz, H_7), 2.66 (1H, ddd, $J_{3endo,3exo}$ = 17.4, $J_{3endo,4endo}$ = 7.2, and $J_{3endo,4exo}$ = 9.0 Hz, H_{3endo}), 2.29 (1H, ddd, $J_{3exo,3endo}$ = 17.4, $J_{3exo,4exo}$ = 7.2, and $J_{3exo,4endo}$ = 1.2 Hz, H_{3exo}), 1.91 (1H, dd, $J_{8exo,8endo}$ = 11.4 and $J_{8exo,4endo}$ = 2.7 Hz, H_{8exo}), 1.80 (1H, d, $J_{8endo,8exo}$ = 11.4 Hz, H_{8endo}), 1.80 (1H, ddd, $J_{4exo,4endo}$ = 12.9, $J_{4exo,3endo}$ = 9.0, and $J_{4exo,3exo}$ = 7.2 Hz, H_{4exo}), 1.70 (1H, dddd, $J_{4endo,4exo}$ = 12.9, $J_{4endo,3endo}$ = 9.6, $J_{4endo,8exo}$ = 2.7, and $J_{4endo,3exo}$ = 1.5 Hz, H_{4endo}), 1.23 (3H, s, 5-CH_3), and 1.13 (3H, s, 1-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 211.7 (C-2), 141.7 (C-6), 136.6 (C-7), 58.7 (C-1), 54.8 (C-8), 45.6 (C-5), 35.0 (C-3), 33.7 (C-4), 24.1 (5-CH_3), and 17.2 (1-CH_3). Found: *m/z* 150.1042 Calcd for $C_{10}H_{14}O$: M, 150.1045. Found: C, 79.93; H, 9.62%. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39%.

1-Butylbicyclo[3.2.1]oct-6-en-2-one (2b): Colorless oil; IR (neat) 1710 and 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 6.13 (1H, dd, $J_{6,7}$ = 5.7 and $J_{6,5}$ = 3.0 Hz, H_6), 5.71 (1H, d, $J_{7,6}$ = 5.7 Hz, H_7), 2.89 (1H, m, H_5), 2.67 (1H, ddd, $J_{3endo,3exo}$ = 17.7, $J_{3endo,4endo}$ = 9.3, and $J_{3endo,4exo}$ = 8.4 Hz, H_{3endo}), 2.29 (1H, ddd, $J_{3exo,3endo}$ = 17.7, $J_{3exo,4exo}$ = 7.8, and $J_{3exo,4endo}$ = 1.2 Hz, H_{3exo}), 2.23 (1H, ddd, $J_{8exo,8endo}$ = 11.1, $J_{8exo,5}$ = 5.4, and $J_{8exo,4endo}$ = 2.7 Hz, H_{8exo}), 1.94 (1H, dddd, $J_{4exo,4endo}$ = 13.2, $J_{4exo,3endo}$ = 8.4, $J_{4exo,3exo}$ = 7.8, and $J_{4exo,5}$ = 3.3 Hz, H_{4exo}), 1.77 (1H, d, $J_{8endo,8exo}$ = 11.1 Hz, H_{8endo}), 1.74 (1H, m, H_{4endo}), 1.64—1.55 (2H, m, $H_{1'}$), 1.32 (2H, m, $H_{3'}$), 1.21 (2H, m, $H_{2'}$), and 0.90 (3H, t, J = 7.2 Hz, $H_{4'}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 210.9 (C-2), 137.1 (C-6), 136.4 (C-7), 61.7 (C-1), 44.8 (C-8), 39.6 (C-5), 35.0 (C-3), 30.1 (C-1′), 26.7 (C-2′), 26.2 (C-4), 23.3 (C-3′), and 13.9 (C-4′). Found: *m/z* 178.1364. Calcd for $C_{12}H_{18}O$: M, 178.1357. Found: C, 80.65; H, 10.20%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

1-Vinylbicyclo[3.2.1]oct-6-en-2-one (2c): Colorless oil; IR (neat) 1703 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 6.33 (1H, dd, J_{trans} = 17.7 and J_{cis} = 10.8 Hz, $H_{1'}$), 6.21 (1H, dd, $J_{6,7}$ = 5.4 and $J_{6,5}$ = 2.7 Hz, H_6), 5.88 (1H, d, $J_{7,6}$ = 5.4 Hz, H_7), 5.19 (1H, dd, J_{cis} = 10.8 and $J_{2',2}$ = 1.5 Hz, $H_{2'}$), 5.12 (1H, dd, J_{trans} = 17.7 and $J_{2',2'}$ = 1.5Hz), 2.98 (1H, m, H_5), 2.74 (1H, ddd, $J_{3endo,3exo}$ = 17.4, $J_{3endo,4endo}$ = 9.0, and $J_{3endo,4exo}$ = 9.0 Hz, H_{3endo}), 2.39—2.30 (2H, m), 2.01 (1H, d, $J_{8endo,8exo}$ = 11.1 Hz, H_{8endo}), 1.97 (1H, dddd, $J_{4exo,4endo}$ = 13.2, $J_{4exo,3endo}$ = 9.0, $J_{4exo,3exo}$ = 7.5, and $J_{4exo,5}$ = 3.3 Hz, H_{4exo}), and 1.79 (1H, ddddd, $J_{4endo,4exo}$ = 13.2, $J_{4endo,3endo}$ = 9.0, $J_{4endo,8exo}$ = 2.7, $J_{4endo,5}$ = 2.7, and $J_{4endo,3exo}$ = 1.5 Hz, H_{4endo}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 209.2 (C-2), 137.3 (C-6), 136.6 (C-1′), 135.0 (C-7), 114.8 (C-2′), 64.3 (C-1), 47.1 (C-8), 37.0 (C-5), 34.7 (C-3), and 26.0 (C-4). Found: *m/z* 148.0894. Calcd for $C_{10}H_{12}O$: M, 148.0888. Found: C, 81.16; H, 8.32%. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16%.

1-Phenylbicyclo[3.2.1]oct-6-en-2en-one (2d): Colorless needles; mp 81.2—82.5 °C; IR (KBr) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.40—7.18 (5H, m), 6.30 (1H, dd, $J_{6,7}$ = 5.7 and $J_{6,5}$ = 2.7 Hz, H_6), 6.25 (1H, d, $J_{7,6}$ = 5.7 and $J_{7,8endo}$ = 0.9 Hz, H_7), 3.05 (1H, m, H_5), 2.86 (1H, ddd, $J_{3endo,3exo}$ = 17.7, $J_{3endo,4endo}$ = 9.3, and $J_{3endo,4exo}$ = 8.4 Hz, H_{3endo}), 2.55 (1H, ddd, $J_{8exo,8endo}$ = 11.1, $J_{8exo,5}$ = 5.7, and $J_{8exo,8endo}$ = 2.7 Hz, H_{8exo}), 2.47 (1H, ddd, $J_{3endo,3endo}$ = 17.7, $J_{3exo,4exo}$ = 7.8, and $J_{3exo,4endo}$ = 1.5 Hz, H_{3exo}), 2.38 (1H, d, $J_{8endo,8exo}$ = 11.1 Hz, H_{8endo}), 2.08 (1H, dddd, $J_{4exo,4endo}$ = 13.2, $J_{4exo,3endo}$ = 8.4, $J_{4exo,3exo}$ = 7.8, and $J_{4exo,5}$ = 3.6 Hz, H_{4exo}), and 1.86 (1H, ddddd, $J_{4endo,4exo}$ = 13.2, $J_{4endo,3endo}$ = 9.3, $J_{4endo,8exo}$ = 2.7, $J_{4endo,5}$ = 2.4, and $J_{4endo,3exo}$ = 1.5 Hz, H_{4endo}); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 208.1 (C-2), 139.2 (C-1′), 137.8 (C-6), 135.1 (C-7), 128.1 (C-2′ and -6′), 127.4 (C-3′ and -5′), 126.8 (C-4′), 66.8 (C-1), 46.8 (C-8), 39.6 (C-5), 35.1 (C-3), and 26.3 (C-4). Found: *m/z* 198.1041. Calcd for $C_{14}H_{14}O$: M, 198.1045. Found: C, 84.61; H, 7.23%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

1,5-Dimethylbicyclo[3.2.1]oct-3-en-2-one (4a): Colorless oil; IR (neat) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 6.96 (1H, d, $J_{4,3}$ = 9.6 and $J_{4,8exo}$ = 2.1 Hz, H_4), 5.85 (1H, d, $J_{3,4}$ = 9.6 Hz, H_3), 1.82—1.62 (5H, m), 1.49 (1H, dd, $J_{8exo,8endo}$ = 11.1 and $J_{8exo,4}$ = 2.1 Hz, H_{8exo}), 1.30 (3H, s, 5-CH_3), and 1.23 (3H, s, 1-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 205.0 (C-2), 160.6 (C-4), 126.2 (C-3), 53.7 (C-8), 53.2 (C-1), 44.4 (C-5), 37.7 (C-6), 33.7 (C-7), 23.8 (5-CH_3), and 20.1 (1-CH_3). Found: *m/z* 150.1046. Calcd for $C_{10}H_{14}O$: M, 150.1045. Found: C, 79.90; H, 9.47%. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39%.

1-Butylbicyclo[3.2.1]oct-3-en-2-one (4b): Colorless oil; IR (neat) 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.23 (1H, ddd, $J_{4,3}$ = 9.4, $J_{4,5}$ = 6.9, and $J_{4,8exo}$ = 1.8 Hz, H_4), 5.86 (1H, d, $J_{3,4}$ = 9.4 Hz, H_3), 2.90 (1H, m, H_5), 2.08—1.97 (2H, m), 1.92 (1H, broad d, $J_{8endo,8exo}$ = 11.4 Hz, H_{8endo}), 1.78 (1H, ddd, $J_{7exo,7endo}$ = 13.2, $J_{7exo,6exo}$ = 10.5, and $J_{7exo,6endo}$ = 2.7 Hz, H_{7exo}), 1.65 (1H, dddd, $J_{6endo,6exo}$ = 12.0, $J_{6endo,7endo}$ = 9.0, $J_{6endo,7exo}$ = 2.7, and $J_{6endo,7exo}$ = 2.4 Hz, H_{6endo}), 1.55 (1H, dddd, $J_{7endo,7exo}$ = 13.2, $J_{7endo,6endo}$ = 9.0, $J_{7endo,6exo}$ = 6.0, and $J_{7endo,8endo}$ = 1.2 Hz, H_{7endo}), 1.51 (1H, ddd, $J_{8exo,8endo}$ = 11.4, $J_{8exo,5}$ = 4.2, and $J_{8exo,4}$ = 1.8 Hz, H_{8exo}), 1.40—1.15 (5H, m), and 0.90 (3H, t, J = 6.9 Hz, $H_{4'}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 204.5 (C-2), 155.9 (C-4), 127.7 (C-3), 56.9(C-1), 43.9 (C-8), 38.1 (C-5), 33.9 (C-1′), 31.2 (C-7), 29.6 (C-6), 27.8 (C-2′), 23.4 (C-3′), and 13.9 (C-4′). Found: *m/z* 178.1367. Calcd for $C_{12}H_{18}O$: M, 178.1357. Found: C, 80.59; H, 10.29%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%.

1-Vinylbicyclo[3.2.1]oct-3-en-2-one (4c): Colorless oil; IR (neat) 1672 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.28 (1H, ddd, $J_{4,3}$ = 9.6, $J_{4,5}$ = 6.9, and $J_{4,8exo}$ = 1.5 Hz, H_4), 6.21 (1H, dd, J_{trans} = 17.7 and J_{cis} = 10.8 Hz, $H_{1'}$), 5.90 (1H, d, $J_{3,4}$ = 9.6 Hz, H_3), 5.17 (1H, dd, J_{cis} = 10.8 and $J_{2',2'}$ = 1.2 Hz, $H_{2'}$), 5.09 (1H, dd, J_{trans} = 17.7 and $J_{2',2'}$ = 1.2 Hz, $H_{2'}$), 2.98 (1H, m, H_5), 2.15—1.92 (3H, m), 1.79 (1H, ddd, J = 11.1, 4.2, and 1.5 Hz), and 1.75—1.67 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 202.7 (C-2), 156.3(C-4), 138.5 (C-1′), 127.2 (C-3), 112.9 (C-2′, 58.9 (C-1), 43.6 (C-8), 37.8 (C-5), 30.7 (C-7 or -6), and 29.7 (C-6 or -7). Found: *m/z* 148.0881. Calcd for $C_{10}H_{12}O$: M, 148.0888. Found: C, 80.81; H, 8.12%. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16%.

1-Phenylbicyclo[3.2.1]oct-3-en-2-one (4d): Colorless needles; mp 51.5—52.5 °C; IR (KBr) 1665 cm^{-1}, ^1H NMR ($CDCl_3$) δ = 7.40—7.23 (6H, m), 5.96 (1H, dd, $J_{3,4}$ = 9.6 Hz, H_3), 3.06 (1H, m, H_5), 2.53 (1H, broad d, $J_{8endo,8exo}$ = 11.1 Hz, H_{8endo}), 2.32 (1H, m), 2.23—2.07 (2H, m), 2.01 (1H, ddd, $J_{8exo,8endo}$ = 11.1, $J_{8exo,5}$ = 4.2 $J_{8exo,4}$ = 1.8 Hz, H_{8exo}), and 1.84 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 202.0 (C-2), 155.9 (C-4), 142.1 (C-1′), 127.8 (C-2′, 3′, 5′, and 6′), 127.2 (C-4′), 126.5 (C-3), 61.4 (C-1), 44.4 (C-8), 37.7 (C-5), 31.8 (C-7), and 29.9 (C-6). Found: *m/z* 198.1044. Calcd for $C_{14}H_{14}O$: M, 198.1045. Found: C, 85.01 ; H, 7.27%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

1-Methoxy-4-methyl-6-methylenebicyclo[2.2.2]oct-2-ene (6). To a stirred mixture consisting of methyltriphenylphosphonium bromide (2.15 g, 6.02 mmol) and dry THF (28 cm^3) was added a solution of potassium *t*-butoxide (628 mg, 5.59 mmol) in THF (10 cm^3)

at room temperature. After 30 min of stirring, to the reaction mixture was added a solution of 1-methoxy-4-methylbicyclo[2.2.2]oct-5-en-2-one (471 mg, 2.84 mg mmol) in THF (6 cm^3). This mixture was stirred for 50 min, treated with water (2 cm^3), and then diluted with ether. The resulting mixture was washed with saturated brine, dried over $MgSO_4$, and concentrated to give an oil. Chromatography of this oil on silica gel (20 : 1 hexane–ether) gave **6** (366 mg, 2.24 mmol, 79%) as a colorless oil; IR (neat) 1648, 880, 695, and 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 6.29 (1H, d, $J_{2,3}$ = 8.7 Hz, H_2), 5.98 (1H, d,$J_{3,2}$ = 8.7 Hz, H_3), 4.98 (1H, ddd, $J_{1's,5endo}$ = 2.4, $J_{1's,5endo}$ = 2.1, and $J_{1's,1'a}$ = 1.8, Hz, $H_{1's}$ (*syn* to the C_1–C_6 bond)), 4.72 (1H, ddd, $J_{1'a,5endo}$ = 2.1, $J_{1'a,5exo}$ = 1.8, and $J_{1'a,1's}$ = 1.8 Hz, $H_{1'a}$ (*anti* to the C_1–C_6 bond)), 3.46 (3H, s, OCH_3), 2.22 (1H, ddd, $J_{5exo,5endo}$ = 15.9, $J_{5exo,1's}$ = 2.1, and $J_{5exo,1'a}$ = 1.8 Hz, H_{5exo}), 2.03 (1H, dddd, $J_{5endo,5exo}$ = 15.9, $J_{5endo,8endo}$ = 3.6, $J_{5endo,1's}$ = 2.4, and $J_{5endo,1'a}$ = 2.1 Hz, H_{5endo}), 1.71 (1H, ddd, $J_{7endo,8endo}$ = 11.7, $J_{7endo,7exo}$ = 11.1, and $J_{7endo,8exo}$ = 4.8 Hz, H_{7endo}), 1.63 (1H, dddd, $J_{7exo,7endo}$ = 11.1, $J_{7exo,8exo}$ = 9.3, $J_{7exo,8endo}$ = 4.2, and $J_{7exo,2}$ = 0.9 Hz, H_{7exo}), 1.53 (1H, ddd, $J_{8exo,8endo}$ = 11.7, $J_{8exo,7exo}$ = 9.3, and $J_{8exo,7endo}$ = 4.8 Hz, H_{8exo}), 1.32 (1H, dddd, $J_{8endo,8exo}$ = 11.7, $J_{8endo,7endo}$ = 11.7, $J_{8endo,7exo}$ = 4.2, and $J_{8endo,5endo}$ = 3.6 Hz, H_{8endo}), and 1.17 (3H, s, 4-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.0 (C-6), 137.9 (C-3), 131.6 (C-2), 102.4 (C-1′), 80.9 (C-1), 50.0 (OCH_3), 42.8 (C-5), 35.1 (C-4), 33.4 (C-8), 31.6 (C-7), and 24.4 (4-CH_3). Found: *m/z* 164.1197. Calcd for $C_{11}H_{16}O$: M, 164.1201. Found: C, 80.33; H, 9.84%. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82%.

6-*E*- and 6-(*Z*)-Butylidene-1-methoxybicyclo[2.2.2]oct-2-enes (7 and 8, Respectively). 1-Methoxybicyclo[2.2.2]oct-5-en-2-one (547 mg, 3.60 mmol) was treated with butylidenetriphenylphosphorane derived from butyltriphenylphosphonium bromide (3.05 g, 7.65 mmol) and potassium *t*-butoxide (809 mg, 7.21 mmol) in THF at room temperature. A very similar procedure to that used for the preparation of **6** gave **7** (203 mg, 1.05 mmol, 29%) and **8** (16.5 mg, 0.0860 mmol, 2%).

7: Colorless oil; IR (neat) 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ =6.34 (1H, d, $J_{2,3}$ = 8.7 Hz, H_2), 6.25 (1H, dd, $J_{3,2}$ = 8.7 and $J_{3,4}$ = 6.8 Hz, H_3), 5.38 (1H, m, $H_{1'}$), 3.46 (3H, s, OCH_3), 2.68 (1H, m, H_4), 2.22 (1H, broad d, J = 15.9 Hz, H_5), 2.01 (1H, broad d, J = 15.9 Hz, H_5), 1.91 (2H, broad dt, J = 7.2 Hz, $H_{2'}$), 1.70—1.41 (4H, m), 1.39 (2H, m, $H_{3'}$), and 1.17 (3H, t, J = 7.2 Hz, $H_{4'}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.2 (C-6), 132.94 (C-3),132.85 (C-2), 117.5 (C-1′), 80.1 (C-1), 51.9 (OCH_3), 32.9 (C-5), 30.8 (C4), 30.6 (C-7), 30.1 (C-2′), 25.6 (C-8), 22.5 (C-3′), and 13.8 (C-4′). Found: *m/z* 192.1505. Calcd for $C_{13}H_{20}O$: M, 192.1514.

8: Colorless oil; IR (neat) 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ =6.34 (1H, d, $J_{2,3}$ = 8.7 Hz, H_2), 6.25 (1H, dd, $J_{3,2}$ = 8.7 and $J_{3,4}$ = 6.3 Hz), 5.10 (1H, m, $H_{1'}$), 3.39 (3H, s, OCH_3), 2.54 (1H, m, H_4), 2.41 (1H, m, $H_{2'}$), 2.33—2.18 (2H, m), 2.09 (1H, m, H_{5endo}), 1.76 (1H, m, H_{7endo}), 1.69—1.54 (2H, m, H_{8exo} and H_{7exo}), 1.41 (1H, m, H_{8endo}), 1.35 (2H, qt, J = 7.5 Hz, $H_{3'}$), and 0.90 (3H, t, J = 7.5 Hz, $H_{4'}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 136.1 (C-6), 133.2 (C-3), 132.9 (C-2), 122.5 (C-1′), 82.6 (C-1), 52.1 (OCH_3), 38.9 (C-5), 31.0 (C-4), 32.0 (C-7), 29.3 (C-2′), 25.0 (C-8), 23.8 (C-3′), and 13.9 (C-4′). Found: *m/z* 192.1514. Calcd for $C_{13}H_{20}O$: M, 192.1514.

1-Methoxy-2,4-dimethylbicyclo[2.2.2]oct-2,5-diene (9). To a solution of lithium diisopropylamide (3.5 mmol) in THF (6 cm^3) was added a solution of 1-methoxy-4-methylbicyclo[2.2.2]oct-5-en-2-one (499 mg, 3.00 mmol) in THF (10 cm^3) at −78 °C. After 2 h stirring, to the reaction mixture was added a solution of 1,1,1-[*N*- phenyl- *N*- (trifluoromethyl)sulfonyl] trifluoromethanesulfonamide[9] (1.14 g, 3.19 mmol) in THF(6 cm^3) at −78 °C. This mixture was allowed to warm to 0 °C and stirred for 9 h. Evaporation of the solvent gave an oil. Chromatography of this oil on silica gel (hexane) gave the corresponding enol trifluoromethanesulfonate (705 mg, 2.35 mmol, 78%). To a solution of $(CH_3)_2CuLi$ (3.2 mmol) in THF (7 cm^3) was added a solution of the enol triflate (389 mg, 1.31 mmol) in THF (6 cm^3) at −15 °C.[10] The mixture was stirred for 6 h and then diluted with hexane. The organic layer was filtered through a Florisil® column and concentrated to give an oil. Chromatography of the oil on silica gel (25 : 1 hexane–ethyl acetate) gave **9** (99.6 mg, 0.606 mmol, 46%) as a colorless oil.

9: Colorless oil; IR (neat) 785 and 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 6.46 (1H, d, $J_{6,5}$ = 7.8 Hz, H_6), 6.03 (1H, d, $J_{5,6}$ = 7.8 Hz, H_5), 5.58 (1H, brad s, H_3), 3.55 (3H, s, OCH_3), 1.82 (3H, d, J = 1.5 Hz, 2-CH_3), 1.64 (1H, ddd, J = 10.2, 7.2, and 5.7 Hz, H_7), 1.44 (3H, s, 4-CH_3), and 1.39—1.23 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 145.0 (C-2), 138.7 (C-5), 133.5 (C-6), 131.6 (C-3), 85.4 (C-1), 53.4 (OCH_3), 41.0 (C-4), 35.0 (C-8), 31.2 (C-7), 22.5 (2-CH_3), and 14.6 (4-CH_3). Found: *m/z* 164.1208. Calcd for $C_{11}H_{16}O$: M, 164.1201.

1-Methoxy-2-butylbicyclo[2.2.2]oct-2,5-diene (10). 1-Methoxybicyclo[2.2.2]oct-5-en-2-one (782 mg, 5.14 mmol) was converted into the enol triflate (1.215 g, 4.27 mmol, 83%) by a method similar to that used for preparing **9**. Treatment of the enol triflate (259 mg, 0.906 mmol) with $(n\text{-}C_4H_9)_2CuLi$ (2.5 mmol) in THF (9 cm^3) below −20 °C for 10 h gave **10** (79.2 mg, 0.410 mmol, 45%).

10: Colorless oil; IR (neat) 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 6.49 (1H, d, $J_{6,5}$ = 7.8 Hz, H_6), 5.79 (1H, dd, $J_{5,6}$ = 7.8 and $J_{5,4}$ = 6.0 Hz, H_5), 5.79 (1H, ddd, $J_{3,4}$ = 6.3, $J_{3,1'}$ = 1.8, and $J_{3,1'}$ = 1.5 Hz, H_3), 3.56 (3H, s, OCH_3), 3.46 (1H, m, H_4), 2.19 (2H, m, $H_{2'}$), 1.65—1.18 (8H, m), and 0.90 (3H, t, J = 7.2 Hz, $H_{4'}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 149.6 (C-2), 134.1 (C-6), 133.5 (C-5), 124.5 (C-3), 85.0 (C-1), 53.0 (OCH_3), 36.4 (C-4), 29.8 (C-8), 28.7 (C-7), 28.2 (C-1′),26.4 (C-2′), 22.5 (C-3′), and 14.0 (C-4′). Found: *m/z* 192.1514. Calcd for $C_{13}H_{20}O$: M, 192.1514.

1-Methoxy-2-vinylbicyclo[2.2.2]oct-2,5-diene (11). Treatment of the enol triflate (1.271 g, 4.47 mmol), employed for preparing **10**, with $(CH_2{=}CH)_2CuMgBr$ (6.0 mmol) in THF (12 cm^3) at −78 °C for 7 h gave **11** (121.7 mg, 0.750 mmol, 17%) as a colorless oil; ^1H NMR ($CDCl_3$) δ = 6.49(1H, dd, $J_{6,5}$ = 7.8, and $J_{6,4}$ = 1.5 Hz, H_6), 6.46 (1H, dd, J = 17.7, 11.1, and 0.9 Hz, $H_{1'}$), 6.31 (1H, dd, $J_{5,6}$ = 7.8 and $J_{5,4}$ = 6.0 Hz, H_5), 6.26(1H, broad d, J = 6.0 Hz, H_3), 5.45 (1H, dd, J = 17.7 and 2.1 Hz, $H_{2'}$), 4.97 (1H, dd, $J_{3,4}$ = 11.1 and 2.1 Hz, $H_{2'}$), 3.55 (3H, s, OCH_3), 3.52 (1H, m, H_4), 1.55 (2H, m), and 1.45—1.39 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 146.5 (C-2), 133.9 (C-6), 132.9 (C-5), 131.2 (C-1′), 128.2 (C-3), 112.6 (C-10), 85.0 (C-1), 53.7 (OCH_3), 36.6 (C-4), 29.7 (C-7 or -8), and 26.1 (C-8 or-7).

1-Methoxy-2-phenylbicyclo[2.2.2]oct-2,5-diene (12). Treatment of the enol triflate (805 mg, 2.83 mmol), employed for preparing **10**, with $(C_6H_5)_2CuLi$ (8.0 mmol) in THF (25 cm^3) at −15 °C for 12 h gave **12** (134 mg, 0.866 mmol, 31%) as a colorless oil; IR (neat) 750 and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 7.44—7.40 (2H, m), 7.32—7.20 (3H, m), 6.56 (1H, dd, $J_{6,5}$ = 7.8 and $J_{6,4}$ = 1.5 Hz, H_6), 6.39 (1H, dd, $J_{5,6}$ = 7.8 and $J_{5,4}$ = 6.0 Hz, H_5), 6.19 (1H, broad d, $J_{3,4}$ = 6.0 Hz, H_3), 3.62 (1H, m, H_4), 3.23 (3H, s, OCH_3), 1.77—1.61 (2H, H_7), and 1.56—1.47 (2H, H_8); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 147.9 (C-2), 139.2 (C-1′), 134.8 (C-6), 133.4 (C-5), 131.3 (C-3), 127.9 (C-3′ and-5′), 126.7 (C-2′ and-4′, 126.4 (C-4′), 85.8 (C-1), 54.0 (OCH_3), 37.1 (C-4), 31.3 (C-7), and 26.2 (C-8). Found: *m/z* 212.1203. Calcd for $C_{15}H_{16}O$: M, 212.1201. Found: C, 84.64; H, 7.74%. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60%.

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