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Regio- and Stereoselectivity of the Intramolecular C–H Insertion by Cyclopropylidenes Bearing a Remote Oxido Substituent

Toshiro HARADA, Yasunari YAMAURA, and Akira OKU*
Department of Chemistry, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606
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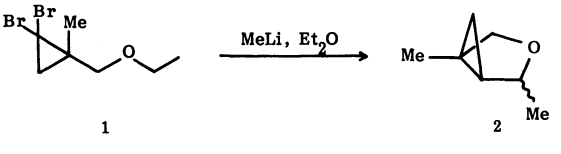
(ω-Oxidoalkyl)cyclopropylidenes generated from (2,2-dibromo-1-methylcyclopropyl)-CH_2-X-$(CH_2)_n$-OH (X=CH_2 or O, n=1, 2) by the reaction with methyllithium underwent a regioselective intramolecular insertion into the C–H bond at the δ position to the carbenic carbon. The activation effect of the oxido substituent on the reactivity of C–H bonds is discussed on the basis of (1) the ratio of the insertion products to the rearrangement product allenyl alcohol, and (2) the endo stereoselectivity of the present insertion reactions.

The intramolecular C–H insertion by carbenes has been utilized as a powerful tool for the construction of highly strained molecules or cage structures which would be otherwise difficult to synthesize.[1] However, due to the lack of regioselectivity, the utilization of carbenic insertion reactions in organic synthesis has been limited only to the cases where the molecular geometry puts a potential insertion site close to the carbenic centers.[2] One of the most promising approaches to the regio-controlled intramolecular insertion in a less stereo-defined system is to activate a specific C–H bond by an adjacent heteroatom, such as oxygen, nitrogen, and sulfur.[3] Recently, we disclosed a novel oxyanionic substituent effect that facilitates the intermolecular insertion by carbenes into the α C–H bond of alkoxides.[4–8] We also showed in the study of ω-oxidoalkyl(phenylthio)carbenes that a regio-controlled intramolecular insertion is made possible by the utilization of the oxyanionic effect.[9,10]

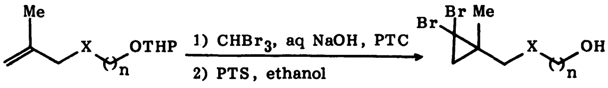
Baird reported a number of substituent effects of oxygen-containing groups on the intramolecular cyclopropylidene insertion reaction.[11] He observed that the treatment of dibromocyclopropane (**1**) with methyllithium gave the regioselective insertion product **2** to the almost complete exclusion of the expected allene derivative 4-ethoxy-3-methyl-1,2-butadiene (Eq. 1).[12] Paquette and Taylor noted, however, that alkoxyl substituents in the norcaranylidene system can either activate or deactivate the adjoining C–H bond toward carbene insertion and that the reactvity depends on the site of the alkoxyl group.[13] In contrast to a number of studies on the effect of neutral oxygen-containing substituents in intramolecular insertion reactions,[3] little is known on the effect of oxyanion. Skattebøl reported an activation effect of oxyanion in his study of the cyclopropylidene bearing an oxido substituent at the β position to the carbenic carbon.[14] The similar effect was also noted recently by Baird et al.[15] In order to investigate the effect of oxido substituents located at more remote positions, we examined the reaction of dibromocyclopropyl alcohols (**6**, **7**, and **8**) with methyllithium.[16]



(1)

Results

Preparations of Dibromocyclopropyl Alcohols. Dibromocyclopropyl alcohols (**6**, **7**, and **8**) were prepared by the reaction of the tetrahydropyranyl ethers (**3**, **4**, and **5**) of the corresponding alkenols with dibromocarbene generated under the phase-transfer conditions (Eq. 2). We also attempted a direct cyclopropanation of 2-(2-methyl-2-propenyloxy)ethanol under similar reaction conditions, but the desired dibromocyclopropyl alcohol **7** was obtained only in 7% yield.

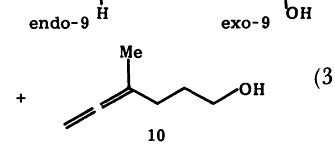


(2)

3; n = 1, X = CH_2
4; n = 2, X = O
5; n = 2, X = CH_2

6; n = 1, X = CH_2
7; n = 2, X = O
8; n = 2, X = CH_2

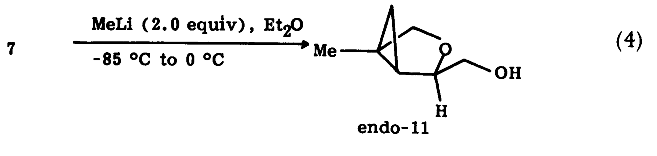
Reaction of Dibromocyclopropyl Alcohols with Methyllithium. The reaction of dibromocyclopropyl alcohol **6** was carried out in ether utilizing 2.0 equiv of methyllithium to give the insertion products (two stereoisomers *endo*-**9** and *exo*-**9**) together with allenyl alcohol **10**[16] in 49% total yield (*endo*-**9**:*exo*-**9**:**10**=44:6:50)(Eq. 3). In order to evaluate the effect of oxido substitution relatively to the effect of alkoxyl substitution, we also performed the reaction of the



(3)

tetrahydropyranyl ether of alcohol **6** under similar reaction conditions. *endo*-**9**, *exo*-**9**, and **10** were obtained in the ratio of 22:18:60 (73% total yield) after the treatment of the reaction mixture with pyridinium *p*-toluenesulfonate (PTS) in ethanol.

In the previous study of ω-oxidoalkyl(phenylthio)-carbenes,[9] we showed that the five- and six-membered ring formation can be achieved by the substitution of an oxido group at the δ and ε position to the carbenic carbon, respectively. We examined the possibility of six-membered ring formation in the reaction of dibromocyclopropyl alcohols **7** and **8** (Eqs. 4 and 5). The reaction of **7** with methyllithium (2.0 equiv) gave exclusively the endo isomer of δ insertion product *endo*-**11** in 54% yield without forming the allene alcohol. On the other hand, the reaction of **8** with methyllithium followed by quenching the reaction mixture with benzoyl chloride gave the endo and exo isomers of insertion product **12** with a low endo selectivity together with the rearrangement product allenyl benzoate **13** (*endo*-**12**:*exo*-**12**:**13**=24:11:65; 59% total yield). Owing to the difficulty in separating the product alcohols, they were isolated and analyzed as benzoate esters in this reaction. In both reactions, the intramolecular insertion proceeded exclusively at the δ position to the carbenic carbon, and six-membered ring formation was not observed.



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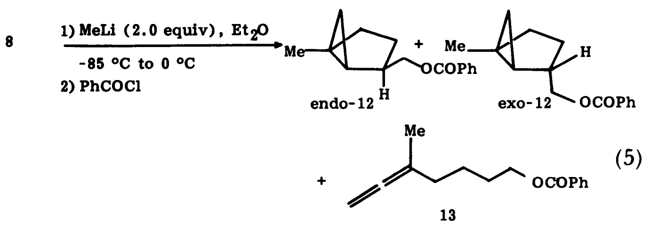
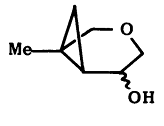


(5)

Determination of the Structure of Insertion Products. The ¹H NMR spectrum of the insertion product obtained in the reaction of **7** (Eq. 4) is consistent with either primary alcohol *endo*-**11** (δ insertion product) or secondary alcohol **14** (ε insertion product). The structure, however, was established unambiguously to be *endo*-5-methyl-3-oxabicyclo-[3.1.0]hexane-2-methanol (*endo*-**11**) by the ¹H NMR analysis of acetyl derivative **15**: The number of proton(s) whose chemical shift was shifted by acetylation to a lower field (δ 3.95 and 4.2) than the corresponding protons of *endo*-**11** was two.



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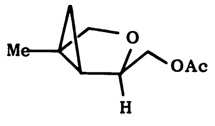

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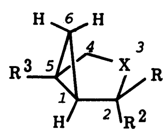


Fig. 1.

Table 1. ¹H NMR Coupling Constants between Protons Attached to C(1) and C(2) of Bicyclo[3.1.0]hex-2-yl Derivatives

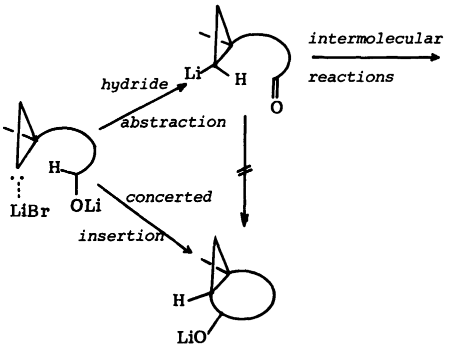
Compound	endo-Isomer J_{12}/Hz	exo-Isomer J_{12}/Hz
9	4.2	<1
11	2.8	—
12	4.6	<1
16	3.0	<1

¹H NMR spectrum of the major insertion product *endo*-**9** obtained in the reaction of dibromocyclopropyl alcohol **6** was identical with that reported previously.[17] In other cases endo and exo stereochemistry of the insertion products was determined by the comparison of ¹H NMR vicinal coupling constants between protons attached to C(1) and C(2) (Fig. 1); J_{12} values for endo isomers range from 2.8 to 4.6 Hz whereas those for the exo isomers are very small (<1 Hz).[17] In Table 1, these coupling constants are summarized together with those reported for the endo and exo isomers of 3-oxabicyclo[3.1.0]hexane-2-methanol (**16**).[18]

Discussion

In a previous study, we clarified that the mechanism of the intermolecular insertion by norcaranylidene into the α C–H bond of alkoxides is different from the concerted insertion which takes place at the C–H bond adjoining to an alkoxyl group,[8] and we proposed the hydride abstraction-recombination mechanism in the reaction of carbenes with alkoxides.[7,8,10] As shown in Scheme 1, if the intramolecular hydride abstraction by the cyclopropylidene proceeds, the intramolecular recombination step becomes unfavorable due to the anti configuration between the generated cyclopropanide anion and the carbonyl-containing side chain: the anion may be consumed by intermolecular reactions. Since the inversion of cyclopropanide anion under the present reaction conditions is unlikely,[19] we conclude that the intramolecular insertion proceeds via a concerted mechanism.

In the reactions of both dibromocyclopropyl



Scheme 1.

alcohol **6** and its tetrahydropyranyl ether with methyllithium, similar ratios of the insertion products to the rearrangement product were observed (Eq. 3). Since the rate of rearrangement to form allenes will not be affected by the oxido group or alkoxyl group located three carbons apart from the cyclopropane ring,[20] these results suggest that the activations by the oxyanion substituent and alkoxyl group are similar in magnitude in the intramolecular insertion by cyclopropylidenes.

It has been known that cyclopropylidenes bearing simple alkyl substituents preferentially undergo the rearrangement to allenes, and when the intramolecular insertion competes with the rearrangement, the insertion generally takes place at the C–H bond β to the carbenoid carbon.[21] Contrastingly, in the present study, the formation of a considerable amount of δ insertion product **12** in the reaction of **8** (Eq. 5) suggests the presence of an activation effect of the adjacent vicinal oxido group which surpasses the other reactions.[22]

It is well-documented in the literature that the cyclopropylidene lithium carbenoids bearing an oxygen-containing substituent at an appropriate position are stabilized by the intramolecular coordination of the oxygen atom with lithium.[23] It has been suggested that the coordination which holds the δ C–H bond in a closer proximity to the carbenic carbon is responsible, at least partly, for the observed efficient insertion of dibromocyclopropyl ether **1** (Eq. 1). As shown in the present study, the reaction of **7** with methyllithium (Eq. 4) which proceeds through the carbenoid intermediate possessing the additional oxido group at the ε position also proceeded efficiently to give *endo*-**11** without forming the allene alcohol. The exclusive formation of the endo isomer can be rationalized by the coordination of two oxygen atoms with lithium on the carbenoid carbon as depicted in Fig. 2. Moreover, the endo selectivity observed in the reaction of dibromocyclopropyl alcohol **6** with methyllithium (product ratio; *endo*-**9**: *exo*-**9**=44:6, Eq. 3) can also be rationalized in terms of the participation of a similar folded conformation of the intermediate carbenoid.

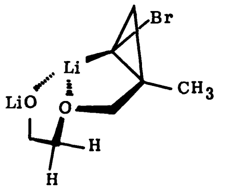


Fig. 2.

Experimental

Infrared spectra were measured on a JASCO IRA-1 grating spectrophotometer, ^{1}H NMR spectra were recorded on a Varian XL-200 (200 MHz) or a Varian T-60A (60 MHz) spectrometer. Mass spectra were measured on a Hitachi M-80 or a Shimazu QP-1000 mass spectrometer. Silica gel (Wakogel C-300) was used as an adsorbent in flash chromatography. GLC analyses were performed utilizing a capillary column (OV-101, 25 m). Analytically pure products were obtained by preparative GLC (5% OV-17 on Chromosorb W, 0.3×200 cm). Ether and dichloromethane were dried over sodium benzophenone ketyl and CaH_2, respectively, and distilled prior to use. An ethereal solution of methyllithium complexed with lithium bromide (ca. 1.4 mol dm^{-3}) was purchased from Aldrich Chemical Co., and used after titration.

2-(4-Methyl-4-pentenyloxy)tetrahydropyran (3). To a stirred suspension of $LiAlH_4$ (30 mmol) in ether (100 ml) was slowly added ethyl 4-methyl-4-pentenoate (1.66 g, 11.7 mmol) at 0 °C, and the mixture was stirred overnight at a room temperature. Ather the addition of 10% aq HCl followed by the extraction with ethyl acetate, the organic layer was washed with aq $NaHCO_3$, dried over sodium sulfate, and concentrated in vacuo to give the crude alcohol. This was dissolved in CH_2Cl_2 (50 ml), and then 3,4-dihydro-2*H*-pyran (2.52 g, 30.0 mmol) and pyridinium *p*-toluenesulfonate (50 mg) were added at a room temperature. After stirring for 14 h, the reaction mixture was concentrated in vacuo, and the residue was purified by flash chromatography (2% ethyl acetate/petroleum ether) to give 1.82 g (9.91 mmol, 85% yield) of **3**: An oil, IR (neat) 1660, 1150, 1130, 1040, and 890 cm^{-1}.

2-[2-(2-Methyl-2-propenyloxy)ethoxy]tetrahydropyran (4). To a stirred solution of 6.6 g of KOH in ethylene glycol (28 ml) was added 9.76 ml (100 mmol) of 3-chloro-2-methylpropene and the mixture was heated at 100 °C for 7 h. After the addition of water followed by the extraction with ether, the organic layer was dried over sodium sulfate and concentrated in vacuo. The crude material was purified by flash chromatography (30% ethyl acetate/petroleum ether) to give 3.96 g (34 mmol, 34% yield) of 2-(2-methyl-2-propenyloxy)ethanol; an oil, ^{1}H NMR (60 MHz, $CDCl_3$) δ=1.77 (3H, br s, CH_3), 2.57 (1H, br s, OH), 3.53 (2H, m, $-CH_2O-$), 3.73 (2H, m, $-CH_2O-$), 3.97 (2H, br s, $=C-CH_2-O$), and 4.97 (2H, m, $CH_2=$).

2-(2-Methyl-2-propenyloxy)ethanol (1.00 g 8.61 mmol) was treated with 3,4-dihydro-2*H*-pyran (1.80 g, 21.5 mmol) and pyridinium *p*-toluenesulfonate (10 mg) in CH_2Cl_2 as described above. A purification by flash chromatography (5% ethyl acetate/petroleum ether) gave **4**: an oil; ^1H NMR (60 MHz, $CDCl_3$) δ=1.2—2.0 (9H, m), 3.4—3.9 (6H, m), 4.65 (1H, m, $-\mathrm{O}\overset{|}{\mathrm{C}}\mathrm{HO}-$), and 4.97 (2H, m, CH_2=).

2-(5-Methyl-5-hexenyloxy)tetrahydropyran (5). To the Grignard reagent prepared by the reaction of 2-(4-chlorobutyloxy)tetrahydropyran (10.4 mmol) and Mg (18 mmol) in THF (10 ml) was slowly added a THF solution (10 ml) of acetaldehyde (440 mg, 10 mmol) at 0 °C, and the mixture was stirred at the same temperature for 1 h. After the addition of aq NH_4Cl followed by the extraction with ethyl acetate, the organic layer was washed with aq $NaHCO_3$, dried over sodium sulfate, and concentrated in vacuo to give the crude alcohol, which was dissolved in 5 ml of CH_2Cl_2. To a stirred suspension of pyridinium chlorochromate (3.23 g, 15 mmol) and sodium acetate (205 mg, 2.5 mmol) in CH_2Cl_2 (20 ml) was added the above solution, and the mixture was stirred at a room temperature for 3 h. After the dilution with ether (200 ml) followed by filtration through a short silica-gel column, the reaction mixture was concentrated to give 1.64 g of the crude ketone, which was used without further purification in the next reaction. To a suspension of methyltriphenylphosphonium bromide (3.93 g, 11.0 mmol) in THF (60 ml) was added *t*-BuOK (1.12 g, 10.0 mmol) at a room temperature. After stirring for 1 h, a THF (2 ml) solution of the crude ketone was added to the resulting orange suspension, and the mixture was stirred for 1 h. After the addition of brine followed by the extraction with ether, the organic layer was dried over sodium sulfate and concentrated in vacuo. The crude material was purified by flash chromatography (5% ethyl acetate/petroleum ether) to give 947 mg (4.78 mmol, 46%) of **5**: an oil; ^1H NMR (60 MHz, $CDCl_3$) δ=0.8—2.4 (15H, m), 3.1—4.2 (4H, m), and 4.59 (1H, m, $-\mathrm{O}\overset{|}{\mathrm{C}}\mathrm{HO}-$); IR (neat) 1660, 1130, 1085, 1040, and 890 cm^{-1}.

General Procedure for the Preparation of Dibromocyclopropyl Alcohols 6, 7, and 8. A mixture of a THP ether (**3**, **4**, or **5**)(2 mmol), bromoform (2.5 mmol), benzyltriethylammonium chloride (20 mg), and 2 ml of 50% aq NaOH was stirred vigorously at a room temperature for 2 d. After the addition of water followed by extraction with CH_2Cl_2, the organic layer was washed with brine, dried over sodium sulfate, and concentrated in vacuo. The resulting mixture was dissolved in 25 ml of ethanol containing 20 mg of pyridinium *p*-toluenesulfonate, and the solution was heated at 60 °C for several hours. After removing ethanol in vacuo at a room temperature, the residue was subjected to flash chromatography (10—20% ethyl acetate/petroleum ether) to give the dibromocyclopropyl alcohol (**6**, **7**, or **8**).

3-(2,2-Dibromo-1-methylcyclopropyl)-1-propanol (6): An oil; ^1H NMR (60 MHz, $CDCl_3$) δ=1.40 (3H, s, CH_3), 1.55 (3H, m), 1.80 (4H, m), and 3.70 (2H, m, CH_2–OH); IR (neat) 3360, 1060, and 695 cm^{-1}.

2-[(2,2-Dibromo-1-methylcyclopropyl)methoxy]ethanol (7): An oil; ^1H NMR (60 MHz, $CDCl_3$) δ=1.50 (3H, s, CH_3), 1.6 (2H, m), 2.13 (1H, br s, OH), and 3.4—3.9 (6H, m); IR (neat) 3400, 1130, 1070, and 695 cm^{-1}.

4-(2,2-Dibromo-1-methylcyclopropyl)-1-butanol (8): An oil; ^1H NMR (60 MHz, $CDCl_3$) δ=1.37 (3H, s, CH), 1.43 (2H, m), 1.6 (6H, m), 2.25 (1H, m, OH), and 3.65 (2H, m, CH_2OH); IR (neat) 1660, 1130, 1085, 1040, and 890 cm^{-1}.

General Procedure for the Intramolecular Reaction of Dibromocyclopropyl Alcohols 6, 7, and 8. To a solution of a dibromocyclopropyl alcohol (**6**, **7**, or **8**)(1.0 mmol) in dry ether (5 ml) was slowly added methyllithium (ether solution, 2.0 mmol) at −85 °C under a nitrogen atmophere. The reaction mixture was gradually warmed up to 0 °C over a period of 5 h, and quenched by the addition of water. After the extraction with ether, the organic layer was dried over sodium sulfate, and concentrated in vacuo. After a capillary GLC analysis, the residual oil was subjected to flash chromatography (ethyl acetate/petroleum ether) to give a mixture of intramolecular insertion products and the allenyl alcohol. Analytically pure products were obtained after purification by preparative GLC. In the reaction of **8**, the reaction mixture was quenched by addition of benzoyl chloride (1.2 mmol) at 0 °C, and then stirred further for 14 h at a room temperature. By the similar workup procedure, a mixture of the benzoate ester of the insertion product *endo*-**12** and *exo*-**12**, and allenyl alcohol **13** was obtained.

***endo*-5-Methylbicyclo[3.1.0]hexan-2-ol (*endo*-9):**[17] An oil; ^1H NMR (200 MHz, $CDCl_3$) δ=0.25 (1H, dd, *J*=5.0 and 7.9 Hz, exo C(6)–H), 0.71 (1H, br dd, *J*=4.2 and 5.0 Hz, endo C(6)–H), 1.07 (1H, ddt, *J*=11.2, 12.8, and 8.2 Hz, exo C(3)–H), 1.14 (3H, s, CH_3), 1.20 (1H, ddd, *J*=3.7,.4.2, and 7.9 Hz, C(1)–H), 1.48 (1H, br s, OH), 1.56 (1H, ddt, *J*=0.8, 8.0, and 11.2 Hz, exo C(4)–H), 1.73 (1H, dd, *J*=8.3 and 12.2 Hz, endo C(4)–H), 1.89 (1H, dt, *J*=12.8 and 8 Hz, endo C(3)–H), and 4.53 (1H, *J*=3.7 and 8.2 Hz, exo C(2)–H); MS *m/z* (%) 112 (M^+, 6.9), 111 (4.9), 97 (69), 94 (31), 84 (16), and 70 (100); Found: *m/z* 112.0886, Calcd for $C_7H_{12}O$: 112.0889.

***exo*-5-Methylbicyclo[3.1.0]hexan-2-ol (*exo*-9):** An oil; ^1H NMR (200 MHz, $CDCl_3$) δ=0.21 (1H, dd, *J*=4.0 and 5.2 Hz, endo C(6)–H), 0.33 (1H, dd, *J*=5.2 and 8.4 Hz, exo C(6)–H), 1.05 (1H, dd, *J*=4.0 and 8.4 Hz, C(1)–H), 1.26 (3H, s, CH_3), 1.27—1.85 (5H, m), and 4.16 (1H, d, *J*=4.4 Hz, endo C(2)–H); MS *m/z* (%) 112 (M^+, 12), 97 (76), 94 (4.2), and 70 (100); Found: *m/z* 112.0892, Calcd for $C_7H_{12}O$: 112.0889.

4-Methyl-4,5-hexadien-1-ol (10):[16] An oil; ^1H NMR (200 MHz, $CDCl_3$) δ=1.50 (1H, br s, OH), 1.65—1.80 (5H, m, including t (3H, *J*=3.2 Hz, CH_3) at 1.68), 2.00 (2H, m, $-\mathrm{CH_2}-\overset{|}{\mathrm{C}}=$), 3.68 (2H, t, *J*=6.4 Hz, CH_2OH), and 4.61 (2H, m, CH_2=); MS *m/z* (%) 112 (M^+, 0.2), 97 (4.6), 94 (4.2), 84 (73), 81 (9.0), and 68 (100).

***endo*-5-Methyl-3-oxabicyclo[3.1.0]hex-2-ylmethanol (*endo*-11):** An oil; ^1H NMR (200 MHz, $CDCl_3$) δ=0.38 (1H, ddd, *J*=0.8, 4.8, and 7.4 Hz, exo C(6)–H), 0.64 (1H, dd, *J*=4.2 and 4.8 Hz, endo C(6)–H), 1.16 (1H, ddd, *J*=2.8, 4.2, and 7.4 Hz, C(1)–H), 1.24 (3H, s, CH_3), 1.56 (1H, br s, OH), 3.7 (3H, m), 3.76 (1H, d, *J*=8.0 Hz, C(4)–H), and 4.10 (1H, ddd, *J*=2.8, 4.2, and 7.6 Hz, exo C(2)–H).

***endo*-(5-Methylbicyclo[3.1.0]hex-2-yl)methyl Benzoate (*endo*-12):** An oil; ^1H NMR (200 MHz, $CDCl_3$) δ=0.17 (1H, ddd, *J*=0.8, 5.1, and 7.6 Hz, exo C(6)–H), 0.46 (1H, dd, *J*=3.4 and 5.1 Hz, endo C(6)–H), 1.05 (1H, ddd *J*=3.4, 3.7, and 7.6 Hz, C(1)–H), 1.5—1.8 (5H, m), 2.62 (1H, m, exo C(2)–H), 4.17 (1H, dd, *J*=7.8 and 9.8 Hz, $C\underline{H}OCOPh$), 4.23 (1H, dd, *J*=5.7 and 9.8 Hz, $C\underline{H}OCOPh$), 7.4—7.6 (3H, m), and 8.02 (2H, m); MS *m/z* (%) 122 (M^+, <1), 108 ($M^+ - PhCO_2H$, 100), and 105 (37). The fragment ion peak due to ($M^+ - PhCO_2H$) was observed at *m/z* 108.0940. Calcd for C_8H_{12}: $M^+ - PhCO_2H$, 108.0965.

***exo*-(5-Methylbicyclo[3.1.0]hex-2-yl)methyl Benzoate (*exo*-12):** An oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.32 (1H, dd, J=4.6 and 7.7 Hz, exo C(6)–H), 0.39 (1H, dd, J=3.4 and 4.6 Hz, endo C(6)–H), 0.95 (1H, dd, J=3.4 and 7.7 Hz, C(1)–H), 1.20 (3H, s, CH_3), 1.4—1.7 (4H, m), 2.36 (1H, q, J=6 Hz, endo C(2)–H), 4.15 (2H, d, J=7.1 Hz, CH_2OCOPh), 7.4—7.6 (3H, m), and 8.02 (2H, m); MS m/z (%) 230 (M^+, 0.5) and 108 (100); Found: m/z 230.1329, Calcd for $C_{15}H_{18}O_2$: 230.1307.

5-Methyl-5,6-heptadienyl Benzoate (13): An oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.4—1.9 (7H, m, including t (3H, J=3.2 Hz, CH_3) at 1.68), 1.99 (2H, m), 4.32 (2H, t, J=7.0 Hz, CH_2OCOPh), 4.58 (2H, m, CH_2=), 7.35—7.6 (3H, m), and 8.02 (2H, m); MS m/z (%) 230 (M^+, <1), 125 (13), 108 (39), 105 (56), and 93 (100); Found: m/z 230.1294, Calcd for $C_{15}H_{18}O_2$: 230.1307.

***endo*-(5-Methyl-3-oxabicyclo[3.1.0]hex-2-yl)methyl Acetate (15).** To a solution of *endo*-**11** (22.4 mg, 0.17 mmol) in acetic anhydride (0.032 ml) and pydridine (0.054 ml) was added 3 mg of 4-(dimethylamino)pyridine at a room temperature. After stirring for 3 h, the reaction mixture was diluted with water and extracted with ether. The organic layer was washed successively with 5% aq HCl and aq $NaHCO_3$, dried over sodium sulfate, and concentrated in vacuo. The residue was purified by preparative GLC to give **15**: an oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.40 (1H, dd, J=4.8 and 7.4 Hz, exo C(6)–H), 0.65 (1H, t, J=6 Hz, endo C(6)–H), 1.22 (1H, m, C(1)–H), 1.24 (3H, s, CH_3), 2.06 (3H, s, CH_3CO_2–), 3.59 (1H, br d, J=8.4 Hz, exo C(4)–H) 3.80 (1H, d, J=8.4 Hz, endo C(4)–H), 3.95 (1H, dd, J=9.2 and 12.7 Hz, $\mathrm{AcO}\overset{|}{\mathrm{C}}\underline{\mathrm{H}}$–), and 4.2 (2H, m, exo C(2)–H and $\mathrm{AcO}\overset{|}{\mathrm{C}}\underline{\mathrm{H}}$–).

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