7,7-Dimethyltricyclo[3.3.0.0^{2,8}]octan-3-ones as Synthetic Intermediates. IV.[1] A Further Examination of Cyclopropane Ring Opening in the Tricyclo[3.3.0.0^{2,8}]octan-3-one System

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The cyclopropane ring opening reaction of several tricyclo[3.3.0.0^{2,8}]octan-3-ones (8a—c) was examined. Under acid-catalyzed substitutional conditions, compounds 8a and 8b gave predominantly the bicyclo[3.2.1]octan-3-one derivatives (9a, b), while compound 8c afforded exclusively the bicyclo[3.3.0]octan-3-one (10c). A candidate precursor for the synthesis of quadrone, 13, was also successfully prepared.

Keywords cyclopropane ring opening; regioselectivity; tricyclo[3.3.0.0^{2,8}]octane; bicyclo[3.3.0]octane; bicyclo[3.2.1]octane; 1,2-carbonyl transposition; quadrone

Recently, we investigated the cylopropane ring opening of a tricyclo[3.3.0.0^{2,8}]octan-3-one (**1**).[2] Although C_2–C_8 bond fission took place exclusively under the Birch reduction conditions to give the bicyclo[3.3.0]octane derivative (**2**), an abnormal C_1–C_2 bond cleavage was found to occur predominantly under acid-catalyzed substitutional conditions to afford the bicylo[3.2.1]octanes (**3**), one (X=OH) of which was successfully transformed into (±)-descarboxyquadrone (**4**).[1] We wish to describe here a further examination of the cyclopropane ring opening reactions of some other tricyclo[3.3.0.0^{2,8}]octan-3-ones, in connection with a synthetic approach to an antitumor sesquiterpene quadrone (**5**).[3]

In order to synthesize quadrone,[4] it is necessary to introduce a functionalized one-carbon unit at the C_2-position in compound **3** with proper stereochemistry. The α-substitution reaction of ketone **3**, however, occurred exclusively at the unwanted C_4-position. For example, hydroxymethylenation of **3** (X=OMe) under usual conditions afforded the C_4 derivative (**6**) in 91% yield without formation of the desired isomer **7**, probably owing to steric hindrance. Therefore, a suitably functionalized one-carbon unit or requisite functional group at the C_2-position in **3** (equivalent to the C_4-position in **1**) should be introduced prior to the cyclopropane ring opening reaction of **1**.

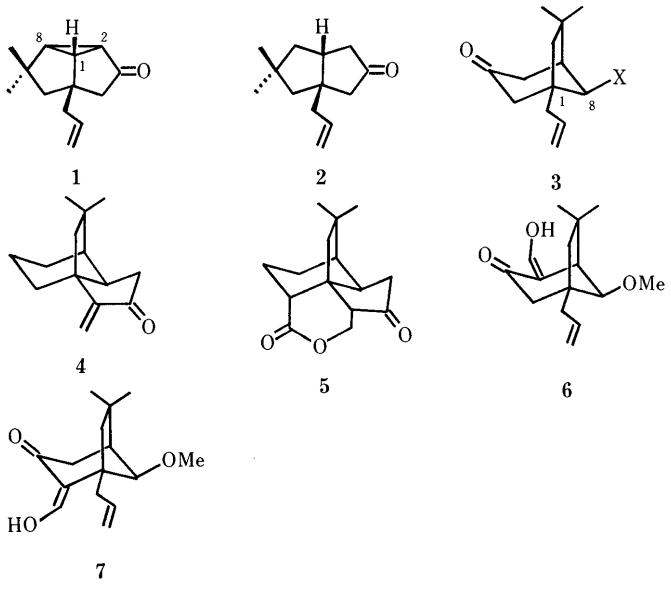


Chart 1

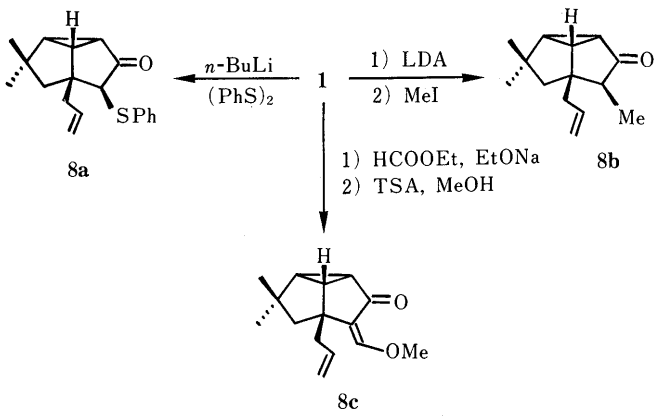
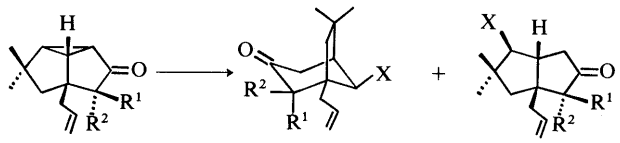


Chart 2

Some C_4-substituted tricyclo[3.3.0.0^{2,8}]octan-3-ones (**8a—c**) were prepared from **1** as illustrated in Chart 2.[5] The cyclopropane ring opening reaction of these compounds was examined under several conditions and the results obtained are summarized in Table I.[6] Treatment of compound **8a** with *p*-toluenesulfonic acid (TSA) in boiling methanol resulted in exclusive C_1–C_2 bond opening to afford a bicyclo[3.2.1]octan-3-one (**9a**; X=OMe) in 46% yield (run 1). The same treatments of **8b** and **8c**, however, gave different results: inseparable complex products from **8b** and only the C_2–C_8 bond-cleaved product (**10c**; X=OMe) from **8c** (run 2). On the other hand, when the reaction of **8b** was carried out in the presence of lithium bromide or tetramethylammonium bromide in aprotic solvents, the desired C_1–C_2 bond-cleaved compound (**9b**; X=Br) was obtained in moderate yield along with a smaller amount of the bicyclo[3.3.0]octan-3-one (**10b**; X=Br) (runs 3, 4). On the contrary, under similar conditions compound **8c** did not give the C_1–C_2 bond-cleaved product but underwent C_2–C_8 bond fission to afford a bicyclo[3.3.0]-octane (**10d**; X=I) as a sole product (run 5). Although such quite different behavior of the cyclopropane ring opening between compounds **8a** (or **8b**) and **8c** cannot be precisely explained at present, the results are interesting.

The bicyclo[3.2.1]octan-3-one (**9a**; X=OMe) was reduced with sodium borohydride to the alcohol (**11**; 86%), which was transformed into the olefin (**12**; 80%) *via* the mesylate in the usual manner. An acidic hydrolysis[7] of **12** afforded the ketone (**13**; 46%), which seems to be a potential intermediate for the synthesis of quadrone (**5**).

TABLE I. The Cyclopropane Ring Opening Reactions of **8**



8a—c **9a, b** **10b—d**

a: R^1=SPh, R^2=H **b**: R^1=Me, R^2=H **c**: R^1+R^2=CHOMe **d**: R^1+R^2=CHI

Run	Substrate	Conditions[a]	X	Products (Yield, %)[b]	
				9	**10**
1	**8a**	TSA (0.5), MeOH, refl., 40 h	OMe	**9a** (46)	
2	**8c**	TSA (0.5), MeOH, refl., 30 h	OMe		**10c** (72)
3	**8b**	TMSCl (2), LiBr (2), CH_2Cl_2, r.t., 4 h	Br	**9b** (57)	**10b** (30)
4	**8b**	TSA (1.5), PhCOOH (1.5), Me_4NBr (1.5), MeCN, refl., 15 h	Br	**9b** (62)	**10b** (17)
5	**8c**	TMSCl (5), NaI (5), MeCN, r.t., 15 h	I		**10d** (46)

a) In each run, *ca.* 0.5 mmol of the substrate was used. The numbers in parentheses indicate the equivalent(s) of each reagent. *b*) Isolated yield.

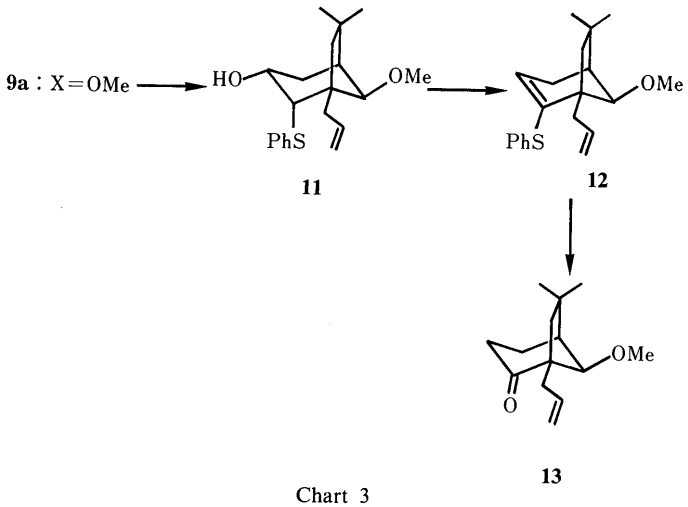


Chart 3

Experimental

The instruments used to obtain physical data, and the notations, were the same as described in the previous paper.[2])

(1*RS*,5*RS*,8*SR*)-4-Hydroxymethylene-8-methoxy-6,6-dimethyl-1-(2-propenyl)bicyclo[3.2.1]octan-3-one (6) Ethyl formate (0.2 ml) and EtOH (2 drops) were added to a suspension of NaH (60% in oil, 44 mg, 1.1 mmol, prewashed with hexane) in dry benzene (2 ml). A solution of **3** (X=OMe; 0.080 g, 0.36 mmol) in dry benzene (1 ml) was added to the resulting suspension at 0 °C, and the whole was stirred for 6 h at room temperature. The mixture was extracted with 15% aqueous NaOH. After acidification with concentrated HCl at 0 °C, the resulting mixture was extracted with $CHCl_3$. The extract was washed with brine, dried, and evaporated to leave an oil, which was chromatographed on silica gel with hexane–AcOEt (20:1) to give **6** (82 mg, 91%) as a pale yellow oil. Infrared (IR) (CCl_4) cm^{-1}: 3080, 1645, 1585, 995, 915. Proton nuclear magnetic resonance (^{1}H-NMR) ($CDCl_3$) δ: 0.89 and 1.25 (each 3H, s, 6-Me×2), 1.42 (1H, d, J=13 Hz, one of 7-H), 1.79 (1H, dd, J=3, 13 Hz, one of 7-H), 2.23 (1H, d, J=20 Hz, one of 2-H), 2.47 (1H, s, 5-H), 2.60 (1H, dd, J=3, 20 Hz, one of 2-H), 3.37 (4H, s, OMe and 8-H), 4.85—5.20 (2H, m, CH=C$\underline{H}_2$), 5.4—6.0 (1H, m, C$\underline{H}$=CH_2), 7.89 (1H, s, C=C$\underline{H}$OH). Mass spectra (MS) m/z (%): 250 (M^+, 14.6), 177 (71.0), 58 (100). High MS Calcd for $C_{15}H_{22}O_3$: 250.1567. Found: 250.1567.

(1*RS*,2*RS*,4*RS*,5*SR*,8*RS*)-7,7-Dimethyl-4-phenylthio-5-(2-propenyl)tricyclo[3.3.0.0^{2,8}]octan-3-one (8a) *n*-BuLi (1.6 M, 2.1 ml, 3.2 mmol) was added to a mixture of **1** (0.500 g, 2.6 mmol) and diphenyl disulfide (0.580 g, 2.7 mmol) in dry tetrahydrofuran (THF) (15 ml) at −15 °C, and the whole was warmed to 0 °C for 1 h. Stirring was continued for 4 h at room temperature, then saturated NH_4Cl solution was added to the mixture at 0 °C, and the resulting mixture was extracted with $CHCl_3$. The extract was washed with brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with benzene to give **8a** (0.448 g, 57%) as a colorless oil. IR (CCl_4) cm^{-1}: 3090, 3070, 3020, 1730, 1640, 1590, 990, 620. ^{1}H-NMR (CCl_4) δ: 1.06 and 1.22 (each 3H, s, 7-Me×2), 3.47 (1H, s, 4-H), 4.6—5.1 (2H, m, CH=C$\underline{H}_2$), 5.4—6.0 (1H, m, C$\underline{H}$=CH_2), 7.0—7.6 (5H, m, aromatic H×5). MS m/z (%): 298 (M^+, 53.8), 107 (100). High MS Calcd for $C_{19}H_{22}OS$: 298.1388. Found: 298.1388.

(1*RS*,2*RS*,4*RS*,5*SR*,8*RS*)-4,7,7-Trimethyl-5-(2-propenyl)tricyclo[3.3.0.0^{2,8}]octan-3-one (8b) A solution of **1** (0.500 g, 2.63 mmol) in dry THF (5.0 ml) was added dropwise to a stirred solution of lithium diisopropylamide (LDA) [prepared from iso-Pr_2NH (345 mg, 3.42 mmol) and *n*-BuLi (1.6 M, 2.14 ml, 3.42 mmol)] in dry THF (3 ml) at −78 °C. After being stirred for 10 min, the resulting mixture was treated with MeI (1.12 g, 7.89 mmol), stirred for 10 min at −78 °C, and then gradually warmed up to room temperature over 4 h. After addition of saturated NH_4Cl solution at 0 °C, the whole was extracted with ether. The extract was washed with brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with hexane–AcOEt (10:1) to give **8b** (0.427 g, 80%) as a colorless oil. IR (CCl_4) cm^{-1}: 3080, 3050, 3020, 1720, 1640, 920. ^{1}H-NMR (CCl_4) δ: 1.08 and 1.20 (each 3H, s, 7-Me×2), 1.09 (3H, d, J=7 Hz, 4-Me), 1.38 and 1.96 (each 1H, d, J=13 Hz, 6-H×2), 4.9—5.3 (2H, m, CH=C$\underline{H}_2$), 5.4—6.0 (1H, m, C$\underline{H}$=CH_2). MS m/z (%): 204 (M^+, 2.5), 91 (100). High MS Calcd for $C_{14}H_{20}O$: 204.1514. Found: 204.1515.

(1*RS*,2*RS*,5*SR*,8*RS*)-4-Methoxymethylene-7,7-dimethyl-5-(2-propenyl)-tricyclo[3.3.0.0^{2,8}]octan-3-one (8c) Ethyl formate (1.1 ml) and EtOH (5 drops) were added to a suspension of NaH (60% in oil, 0.190 g, 4.75 mmol, prewashed with hexane) in dry ether (20 ml). A solution of **1** (0.500 g, 2.63 mmol) in ether (5 ml) was added dropwise to the resulting suspension at 0 °C, and the whole was stirred for 15 h at room temperature. Work-up as described for **6** gave a crude product, which was chromatographed on silica gel with $CHCl_3$ to give the 4-hydroxymethylene derivative of **1** ((1*RS*,2*RS*,5*SR*,8*RS*)-4-hydroxymethylene-7,7-dimethyl-5-(2-propenyl)-tricyclo[3.3.0.0^{2,8}]octan-3-one) (0.404 g, 70%) as pale yellow needles, mp 99—100 °C (from hexane). IR ($CHCl_3$) cm^{-1}: 3080, 3020, 1670, 1610, 920. ^{1}H-NMR ($CDCl_3$) δ: 1.08 and 1.21 (each 3H, s, 7-Me×2), 1.55 and 2.10 (each 1H, d, J=12 Hz, 6-H×2), 2.42 (2H, br d, J=7 Hz, 5-CH_2), 2.69 (1H, t, J=6 Hz, 2-H), 4.9—5.3 (2H, m, CH=C$\underline{H}_2$), 5.5—6.1 (1H, m, C$\underline{H}$=CH_2), 6.76 (1H, s, C=C$\underline{H}$OH), 11.2 (1H, br, OH). Ultraviolet (UV) λ_{max}^{EtOH} nm (ε): 275 (12600). MS m/z (%): 218 (M^+, 8.4), 69 (100). *Anal.* Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.03; H, 8.54. A solution of the above product (0.395 g, 1.80 mmol) and TSA (0.010 g, 0.053 mmol) in dry MeOH (20 ml) was stirred for 18 h at room temperature. The mixture was neutralized with solid $NaHCO_3$ and the MeOH was evaporated off. The residue was taken up in ether, and the ethereal solution was washed with brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with hexane–AcOEt (5:1) to give **8c** (0.398 g, 96%) as a colorless oil. IR (CCl_4) cm^{-1}: 3080, 3050, 3010, 1705, 1640, 980, 920. ^{1}H-NMR (CCl_4) δ: 1.02 and 1.18 (each 3H, s, 7-Me×2), 2.32 (1H, br d, J=8, 14 Hz, 5-CH_2), 2.40 (1H, t, J=7 Hz, 2-H), 2.76 (1H, br d, J=6, 14 Hz, 5-CH_2) 3.80, (3H, s, OMe), 4.8—5.3 (2H, m,

CH=CH$_2$), 5.5—6.0 (1H, m, CH=CH$_2$), 6.80 (1H, s, =CHOMe). UV λ_{max}^{EtOH} nm (ε): 274 (12600). MS *m/z* (%): 232 (M^+, 27.9), 191 (100). High MS Calcd for $C_{15}H_{20}O_2$: 232.1464. Found: 232.1484.

The Ring Opening Reaction of 8: Typical Procedure Each reaction was carried out under the conditions described in Table I. Work-up as usual and purification by column chromatography (SiO_2) or high performance liquid chromatography (HPLC) (μ-Porasil) gave the results also shown in Table I. Physical data for each product are given below.

(1*RS*,2*SR*,5*SR*,8*RS*)-8-Methoxy-6,6-dimethyl-2-phenylthio-1-(2-propenyl)bicyclo[3.2.1]octan-3-one (**9a**: X=OMe): A colorless oil. IR (CCl_4) cm^{-1}: 3070, 1715, 1635, 1580, 995, 920. ^{1}H-NMR (CCl_4) δ: 0.90 and 1.15 (each 3H, s, 6-Me×2), 1.57 (2H, s, 7-H×2), 3.26 (3H, s, OMe), 3.46 and 3.50 (each 1H, s, 2-H and 8-H), 4.6—5.0 (2H, m, CH=CH$_2$), 5.0—5.9 (1H, m, CH=CH$_2$), 6.9—7.5 (5H, m, aromatic H×5). MS *m/z* (%): 330 (M^+, 7.3), 97 (100). High MS Calcd for $C_{20}H_{26}O_2S$: 330.1654. Found: 330.1655.

(1*RS*,5*RS*,8*RS*)-6-Methoxy-2-methoxymethylene-7,7-dimethyl-1-(2-propenyl)bicyclo[3.3.0]octan-3-one (**10c**: X=OMe): A colorless oil. IR (CCl_4) cm^{-1}: 3080, 1710, 1630, 920. ^{1}H-NMR (CCl_4) δ: 0.98 and 1.02 (each 3H, s, 7-Me×2), 1.80 (2H, s, 8-H×2), 2.18 (1H, br dd, *J*=5, 13 Hz, one of 1-CH$_2$), 2.58 (1H, br dd, *J*=6, 13 Hz, one of 1-CH$_2$), 3.40 (3H, s, 6-OMe), 3.87 (3H, s, =CHOMe), 4.8—5.2 (2H, m, CH=CH$_2$), 5.3—5.9 (1H, m, CH=CH$_2$), 6.96 (1H, s, =CHOMe). UV λ_{max}^{EtOH} nm (ε): 277 (10300). MS *m/z* (%): 264 (M^+, 0.9), 223 (100). High MS Calcd for $C_{16}H_{24}O_3$: 264.1722. Found: 264.1716.

(1*RS*,2*RS*,5*RS*,8*SR*)-8-Bromo-2,6,6-trimethyl-1-(2-propenyl)bicyclo-[3.2.1]octan-3-one (**9b**: X=Br): A colorless oil. IR (CCl_4) cm^{-1}: 3080, 1710, 1640, 990, 920. ^{1}H-NMR (CCl_4) δ: 0.93 and 1.46 (each 3H, s, 6-Me×2), 1.09 (3H, d, *J*=7 Hz, 2-Me), 1.62 (2H, s, 7-H×2), 4.49 (1H, s, 8-H), 4.9—5.3 (2H, m, CH=CH$_2$), 5.4—6.0 (1H, m, CH=CH$_2$). MS *m/z* (%): 286 (M^+ +2, 2.8), 284 (M^+, 3.0), 121 (100). High MS Calcd for $C_{14}H_{21}BrO$: 284.0776, 286.0754. Found: 284.0783, 286.0753.

(1*RS*,2*RS*,5*SR*,6*RS*)-6-Bromo-2,7,7-trimethyl-1-(2-propenyl)bicyclo-[3.3.0]octan-3-one (**10b**: X=Br): A colorless oil. IR (CCl_4) cm^{-1}: 3080, 1740, 1640, 990, 920. ^{1}H-NMR (CCl_4) δ: 0.97 (3H, d, *J*=7 Hz, 2-Me), 1.11 (6H, s, 6-Me×2), 1.67 and 1.83 (each 1H, d, *J*=13 Hz, 8-H×2), 2.75 (1H, q, *J*=7 Hz, 2-H), 3.80 (1H, d, *J*=16 Hz, 6-H), 4.9—5.2 (2H, m, CH=CH$_2$), 5.3—5.8 (1H, m, CH=CH$_2$). MS *m/z* (%): 286 (M^+ +2, 4.7), 284 (M^+, 4.6), 135 (100). High MS Calcd for $C_{14}H_{21}BrO$: 284.0776, 286.0754. Found: 284.0783, 286.0700.

(1*RS*,5*RS*,8*RS*)-6-Iodo-2-iodomethylene-7,7-dimethyl-1-(2-propenyl)-bicyclo[3.3.0]octan-3-one (**10d**: X=I): A colorless oil. IR (CCl_4) cm^{-1}: 3080, 1715, 1640, 1605, 1000, 920. ^{1}H-NMR (CCl_4) δ: 1.01 and 1.15 (each 3H, s, 7-Me×2), 3.45 and 3.47 (total 1H, each d, *J*=12 Hz, 6-H), 4.9—5.2 (2H, m, CH=CH$_2$), 5.2—5.9 (1H, m, CH=CH$_2$), 7.07 and 7.59 (total 1H, each s, =CHI). UV λ_{max}^{EtOH} nm (ε): 254 (6600). MS *m/z* (%): 456 (M^+, 1.3) 59 (100). High MS Calcd for $C_{14}H_{18}I_2O$: 455.9449. Found: 455.9434.

(1*RS*,2*SR*,3*SR*,5*SR*,8*RS*)-3-Hydroxy-8-methoxy-6,6-dimethyl-2-phenylthio-1-(2-propenyl)bicyclo[3.2.1]octan-3-one (11) $NaBH_4$ (0.100 g, 2.64 mmol) was added portionwise to a stirred solution of **9a** (X=OMe; 0.079 g, 0.24 mmol) in MeOH (3 ml) at 0 °C over 10 min, and the whole was stirred for 30 min at 0 °C. The MeOH was evaporated off, and the residue was taken up in $CHCl_3$. The $CHCl_3$ solution was washed with brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with benzene to give **11** (0.068 g, 86%) as a colorless oil. IR (CCl_4) cm^{-1}: 3450, 3070, 3010, 1640, 1590, 995, 920. ^{1}H-NMR (CCl_4) δ: 1.18 and 1.28 (each 3H, s, 6-Me×2), 2.51 (2H, br d, *J*=7 Hz, 1-CH$_2$), 3.02 (1H, s, OH), 3.17 (4H, s, OMe and 8-H), 3.3—3.5 (1H, m, 2-H), 3.5—3.8 (1H, m, 3-H), 4.9—5.3 (2H, m, CH=CH$_2$), 5.4—6.0 (1H, m, CH=CH$_2$), 6.9—7.5 (5H, m, aromatic H×5). MS *m/z* (%): 332 (M^+, 8.4), 97 (100). High MS Calcd for $C_{20}H_{28}O_2S$: 332.1810. Found: 332.1821.

(1*RS*,5*SR*,8*RS*)-8-Methoxy-6,6-dimethyl-2-phenylthio-1-(2-propenyl)-bicyclo[3.2.1]oct-2-ene (12) Methanesulfonyl chloride (0.2 ml) was added to a solution of **11** (0.134 g, 0.40 mmol) in dry pyridine (1.0 ml) at 0 °C, and the mixture was stirred for 3 h. After acidification with concentrated HCl, the mixture was extracted with $CHCl_3$. The extract was washed with brine, dried, and evaporated to give a crude mesylate. The crude mesylate was dissolved in dimethyl sulfoxide (2 ml), and *tert*-BuOK (0.250 g, 2.23 mmol) was added portionwise at 0 °C. The mixture was stirred for 30 min at room temperature. After dilution with water (20 ml), the whole was acidified with concentrated HCl and extacted with ether. The extract was washed with saturated $NaHCO_3$ solution and brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with hexane–benzene (3:1) to give **12** as colorless plates, mp 74—75 °C (from EtOH). IR (CCl_4) cm^{-1}: 3080, 3020, 1640, 1580, 990, 915. ^{1}H-NMR (CCl_4) δ: 0.99 and 1.07 (each 3H, s, 6-Me×2), 1.60 and 1.78 (each 1H, d, *J*=13 Hz, 7-H×2), 3.23 (3H, s, OMe), 3.48 (1H, s, 8-H), 4.7—5.2 (3H, m, CH=CH$_2$ and 3-H), 5.4—6.0 (1H, m, CH=CH$_2$), 7.0—7.5 (5H, m, aromatic H×5). UV λ_{max}^{EtOH} nm (ε): 216 (12500). MS *m/z* (%): 314 (M^+, 33.4), 99 (100). *Anal.* Calcd for $C_{20}H_{26}OS$: C, 76.38; H, 8.33; S, 10.20. Found: C, 76.44; H, 8.52; S, 10.15.

(1*RS*,5*SR*,8*RS*)-8-Methoxy-6,6-dimethyl-1-(2-propenyl)bicyclo[3.2.1]-octan-2-one (13) A mixture of **12** (0.239 g, 1.08 mmol), 3% HCl (15 ml), and MeOH (30 ml) was heated under reflux for 12 h. The MeOH was evaporated off, and the residue was extracted with ether. The extract was washed with saturated $NaHCO_3$ solution and brine, dried, and evaporated to leave an oil, which was chromatographed on silica gel with hexane–benzene (1:1) and then with benzene to give **13** (0.077 g, 46%) as a colorless oil. IR (CCl_4) cm^{-1}: 3080, 1710, 1630, 1000, 910. ^{1}H-NMR (CCl_4) δ: 1.09 and 1.24 (each 3H, s, 6-Me×2), 1.42 and 1.64 (each 1H, d, *J*=14 Hz, 7-H×2), 3.21 (1H, s, 8-H), 3.26 (3H, s, OMe), 4.7—5.1 (2H, m, CH=CH$_2$), 5.4—5.9 (1H, m, CH=CH$_2$). MS *m/z* (%): 222 (M^+, 14.8), 148 (100). High MS Calcd for $C_{14}H_{22}O_2$: 222.1620. Found: 222.1620.

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References and Notes

1) Part III: T. Imanishi, M. Yamashita, M. Matsui, T. Tanaka, and C. Iwata, *Chem. Pharm. Bull.*, **36**, 2012 (1988).
2) T. Imanishi, M. Yamashita, M. Matsui, F. Ninbari, T. Tanaka, and C. Iwata, *Chem. Pharm. Bull.*, **36**, 1351 (1988).
3) R. L. Ranieri and G. J. Calton, *Tetrahedron Lett.*, **1978**, 499; G. J. Calton, R. L. Ranieri, and M. A. Espenshade, *J. Antibiot.*, **31**, 38 (1978).
4) S. Danishefsky, K. Vaughan, R. C. Gadwood, and K. Tsuzuki, *J. Am. Chem. Soc.*, **102**, 4262 (1980); *idem*, *ibid.*, **103**, 4136 (1981); P. Magnus, L. M. Principe, and M. J. Slater, *J. Org. Chem.*, **52**, 1483 (1987) and references cited therein.
5) *Cf.* M. Demuth, S. Chandrasekhar, K. Nakano, P. R. Raghavan, and K. Schaffner, *Helv. Chim. Acta*, **63**, 2440 (1980).
6) The streochemistry of **8**, **9** and **10** is based on spectral considerations and/or chemical behavior as described in the previous paper.[2]
7) V. V. Kane, V. Singh, A. Martin, and D. L. Doyle, *Tetrahedron*, **39**, 345 (1983).