Construction of Asymmetric Quaternary Carbon Center Containing Heteroatom *via* Regioselective Cleavage of Cyclopropane Ring Mediated by Mercury(II) Salt

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Received April 5, 1993

(6*S*,7*S*)-1-Oxa-7-bromomethylspiro[5.5]undecanes (12 and 13) were synthesized from the optically active alkenyl sulfoxide (7). The key step involves a tandem regioselective cleavage of cyclopropane ring and stereoselective nucleophilic cyclization of the cyclopropylcarboxylic acid (11).

Keywords regioselective ring-opening; mercury(II) salt; chiral cyclopropane; oxaspiro[5.5]undecane; lactonization; asymmetric synthesis

Since many diastereoface-differentiating cyclopropanation reactions have been reported,[1] there seems to be considerable potential for utilization of chiral cyclopropyl compounds for the asymmetric synthesis of natural products. In the last decade, many elegant applications of cyclopropane derivatives for constructing several carbon frameworks of natural products have been explored, such as ring enlargement,[2] introduction of a three-carbon unit,[3] formation of heterocycles,[4] and so on.[5] Recently, we described an asymmetric cyclopropanation and a sulfur-assisted regioselective ring-opening reaction of cyclopropylsulfides *via* 'a'-bond cleavage mediated by mercury(II) cation (**1A**→**2**, Chart 1).[6] In this study, expecting to uncover another synthetic potentiality of **1**, we subjected the desulfurized compound (**1B**) to the mercury(II) salt-mediated reaction and obtained the 1-oxaspiro system (**3** and **4**), resulting from 'b'-bond cleavage, in moderate yield. It is important to note that these products are not only useful precursors for biologically important natural products, such as dactyloxene B and arteannuin B, but also plausible intermediates of the *cis*- and *trans*-decalins or indane system (**5** and **6**), which are difficult to synthesize stereoselectively (Chart 2).[7] Herein we wish to report a different carbon–carbon bond cleavage reaction of the 1,1,2-trisubstituted cyclopropyl compound (**11**) bearing no sulfur atom and the diastereoselectivity of the subsequent intramolecular nucleophilic cyclization depending on the reaction solvents.[8]

Chart 3 outlines the preparation of precursors (**11**) for examining the ring-opening reaction. Successive treatments of the cyclopropylsulfoxide (**7**)[6a)] by hydroboration with borane–dimethylsulfide complex and hydrogenolysis on Raney Ni provided the alcohol (**8**) in 64% yield. The mesylation of **8** with methanesulfonyl chloride in pyridine afforded the mesylate (**9**) in 99% yield. The nitrile (**10**) was obtained in 96% yield by exposure of **9** to potassium cyanide in the presence of a catalytic amount of 18-crown-6. Finally, the reaction of **10** with diisobutylaluminum hydride followed by oxidation with Jones reagent produced the desired compound (**11**) in 66% yield.

Cleavage of the cyclopropane ring was triggered by successive treatments of **11** with mercury(II) trifluoroacetate [$Hg(TFA)_2$] in methylene chloride (CH_2Cl_2), and then with lithium bromide and bromine under an oxygen atmosphere to afford only lactonization products *via* 'b'-bond cleavage in 34% yield. The products were obtained as a C_6-epimeric mixture of **12** and **13** with lack of stereoselectivity. The stereochemistry of C_6 of the lactones (**12** and **13**) was determined by the transformation of the minor lactone (**13**) into the diol (**14**), which was prepared as a major product from 2-methylcyclohexanone by the stereoselective 1,2-addition of Grignard reagent (**15**) followed by removal of the THP (tetrahydropyran) protecting group (Chart 4).[9] Change of the fissile bond from the 'a'-bond in the case of 1-cyclopropylsulfide (**1A**, Chart 1) to the 'b'-bond can reasonably be understood in terms of two factors, that is,

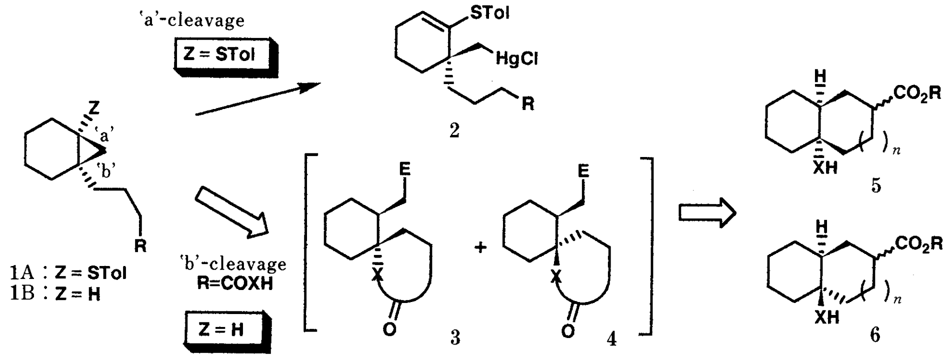
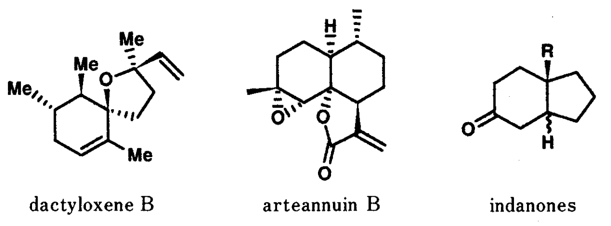


Chart 1

the stability of respective cationic carbon centers and the ease of approach by mercury cation.[10] The bond between less substituted carbon and more substituted carbon (*i.e.* the 'b'-bond in Fig. 1) of the cyclopropane should be cleaved in the case of **11**. We next searched for suitable reaction conditions to perform stereoselective intramolecular lactonization onto the tertiary carbocation center (C_1 of **11**). Table I shows some representative results. The reactions of **11** with $Hg(TFA)_2$ always provide the desired products as a diastereomixture in quite different ratios depending on the reaction solvents. The best stereoselectivity was obtained by using THF (tetrahydrofuran) in place of CH_2Cl_2 as the solvent (entry 4). At this stage, it is very hard to explain the solvent effect on the stereoselectivities of intramolecular lactonization.[11] The major product (**12**) obtained here may be a very versatile intermediate for the synthesis of natural products bearing *cis*-decalin and/or oxaspiro[5.5]undecane skeletons. We are now investigating analogous cyclopropane ring cleavages, and synthetic studies of several natural products are under way using **12** and **13**.



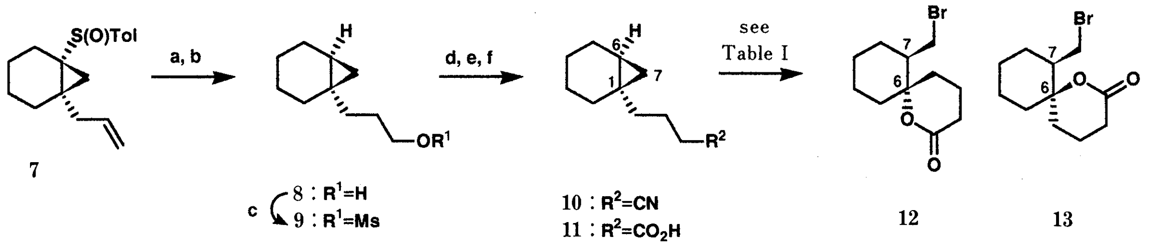
dactyloxene B arteannuin B indanones

Chart 2

Experimental

All melting points were determined with a Yanagimoto melting point apparatus and are uncorrected. Measurements of optical rotations were carried out using a JASCO DIP-360 digital polarimeter. IR measurements were performed with a Hitachi 260-10 IR spectrometer. ^{1}H-NMR spectra were measured with a Hitachi R-250 spectrometer (250 MHz) or a Varian VRX-200 spectrometer (200 MHz). ^{13}C-NMR spectra were measured with a Varian VRX-200 spectrometer (50 MHz). All signals are expressed as ppm downfield from tetramethylsilane used as an internal standard (δ value). The following abbreviations are used: singlet (s), doublet (d), triplet (t), multiplet (m), broad (br). Mass spectra were taken with a Shimadzu QP-1000 mass spectrometer and a JEOL JMS-D 300 mass spectrometer. Unless otherwise noted, all reactions were performed using anhydrous solvents. Merck Kiesel gel 60 was used as an adsorbent for column chromatography. All extracts were dried over anhydrous $MgSO_4$.

3-[(1*S*,6*S*)-Bicyclo[4.1.0]hept-1-yl]propanol (8) Borane–dimethylsulfide complex (0.374 ml, 10 M solution) was added to a solution of olefin (7)[6a)] (512 mg, 1.87 mmol) in THF (15 ml) at 0 °C under a nitrogen atmosphere. After being stirred at the same temperature for 2 h, the mixture was treated successively with ice, 3 N NaOH solution (0.89 ml), and 30% H_2O_2 solution (0.98 ml) and then stirring was continued for another 12 h at room temperature. After removal of THF, the mixture was extracted with ether. The ethereal layer was washed with brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 1 : 2) to give the alcohol (461 mg, 84%) as an oil, $[\alpha]_D^{29}$ +8.63° (c = 1.01, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.81 (1H, d, J = 5.7 Hz), 1.68 (1H, d, J = 5.7 Hz), 2.39 (3H, s), 3.10 (1H, br s), 3.64 (2H, t, J = 5.7 Hz), 7.21 (2H, d, J = 8.2 Hz), 7.42 (2H, d, J = 8.2 Hz). IR ($CHCl_3$): 3200—3600, 2950, 1050 cm^{-1}. MS m/z (%): 292 (M$^+$, 2), 135 (100), 109 (86), 93 (43). Activated Raney Ni (W-2) was added to a solution of the alcohol (897 mg,



a : $BH_3 \cdot SMe_2$, THF; 30% H_2O_2, 3 N NaOH (84%) b : Raney Ni (W2), EtOH (76%) c : CH_3SO_2Cl, pyridine (99%)
d : KCN, 18-crown-6, CH_3CN (96%) e : DIBAL, CH_2Cl_2 (78%) f : Jones reagent (84%)

Chart 3

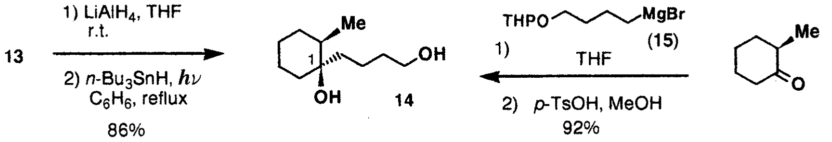


Chart 4

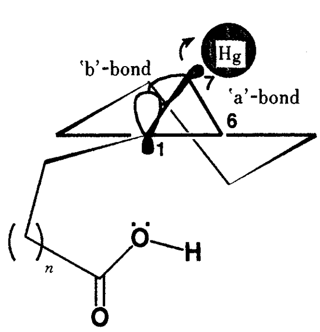


Fig. 1. Regioselective Reaction of 'b' Bond of **11** with Mercury(II) Ion

Table I. Mercury(II) Salt-Mediated Ring-Opening of the Cyclopropyl Carboxylic Acid (**11**)

Entry	HgX_2	Solvent	Base	Yield (%)	Ratio[a)] (**12** : **13**)
1	$Hg(TFA)_2$	CH_2Cl_2	$NaHCO_3$	47	50 : 50
2	$Hg(TFA)_2$	CH_2Cl_2	—	34	50 : 50
3	$Hg(TFA)_2$	CCl_4	—	21	71 : 29
4	$Hg(TFA)_2$	THF	—	63	92 : 8
5	$Hg(TFA)_2$	CH_3NO_2	—	47	48 : 52
6	$Hg(ClO_4)_2$	CH_2Cl_2	—	0[b)]	—

a) The ratios were determined from the 250 MHz ^{1}H-NMR spectra. *b)* The reaction provided a complex mixture without any desired products.

3.07 mmol) in EtOH (25 ml) and the mixture was heated at 60 °C with vigorous stirring. Further activated Raney Ni was added to the mixture, until the starting material disappeared on TLC chromatography. The insoluble material was filtered off through a Celite column and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 5 : 1) to give the desired product (**8**) (361 mg, 76%) as an oil, $[\alpha]_D^{26}$ $+2.77°$ ($c=0.95$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.16 (1H, dd, $J=4.3$, 4.7 Hz), 0.32 (1H, dd, $J=4.3$, 9.1 Hz), 0.67 (1H, m), 1.2—2.3 (13H, m), 3.63 (2H, t, $J=6.6$ Hz). IR ($CHCl_3$): 3600, 3450, 3000, 2930, 2860, 1460, 1020 cm^{-1}. MS m/z (%): 154 (M^+, 14), 136 (2), 95 (100), 81 (70). High MS Calcd for $C_{10}H_{18}O$: 154.1356. Found: 154.1356.

3-[(1*S*,6*S*)-Bicyclo[4.1.0]hept-1-yl]propyl Methanesulfonate (9) Methanesulfonyl chloride (79 μl, 2.8 mmol) was added to a solution of the alcohol (**8**) (361 mg, 2.34 mmol) in pyridine (15 ml) and the mixture was stirred at 0 °C for 2 h. The reaction was quenched with saturated $NaHCO_3$ solution, and the mixture was extracted with a mixture of 33% AcOEt in hexane. The organic layer was washed with saturated $NaHCO_3$ solution, water, and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 2 : 1) to give the sulfonate (**9**) (535 mg, 99%) as an oil, $[\alpha]_D^{22}$ $+1.35°$ ($c=1.03$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.20 (1H, t, $J=4.4$ Hz), 0.34 (1H, dd, $J=4.4$, 9.2 Hz), 0.7 (1H, m), 1.2—1.8 (11H, m), 3.00 (3H, s), 4.22 (2H, t, $J=6.6$ Hz). IR ($CHCl_3$): 2950, 2875, 1360, 1180, 980 cm^{-1}. MS m/z (%): 232 (M^+, 14), 108 (100), 95 (72), 81 (24). High MS Calcd for $C_{11}H_{20}O_3S$: 232.1131. Found: 232.1124.

4-[(1*S*,6*S*)-Bicyclo[4.1.0]hept-1-yl]butyronitrile (10) A mixture of the mesylate (**9**) (535 mg, 2.31 mmol), potassium cyanide (301 mg, 4.62 mmol), 18-crown-6 (17.2 mg, 0.231 mmol), and CH_3CN (30 ml) was refluxed for 2 h under a nitrogen atmosphere, then concentrated *in vacuo*. Water was added to the residue and the resulting mixture was extracted with a mixture of 50% AcOEt in hexane. The extract was washed with water and brine, and dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 2 : 1) to give the nitrile (**10**) (360 mg, 96%) as an oil, $[\alpha]_D^{25}$ $+1.81°$ ($c=0.77$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.19 (1H, dd, $J=4.6$, 5.4 Hz), 0.35 (1H, dd, $J=4.6$, 9.1 Hz), 0.69 (1H, m), 1.2—1.9 (12H, m), 2.33 (2H, t, $J=7.0$ Hz). IR ($CHCl_3$): 2980, 2850, 2250, 1450, 1120 cm^{-1}. MS m/z (%): 164 ($M^+ + 1$, 2), 163 (M^+, 10), 95 (100), 81 (33). High MS Calcd for $C_{11}H_{17}N$: 163.1361. Found: 163.1368.

4-[(1*S*,6*S*)-Bicyclo[4.1.0]hept-1-yl]butanoic Acid (11) A 1.0 M solution of diisobutylaluminum hydride (2.34 ml) in toluene was added to a solution of **10** (293 mg, 1.80 mmol) in CH_2Cl_2 (15 ml) at -78 °C under a nitrogen atmosphere. The mixture was stirred at -78 °C for 15 min, then the reaction was quenched with $NaHCO_3$ solution and the whole was filtered through a Celite column with AcOEt. The combined filtrate was concentrated *in vacuo* to give an oily residue, which was purified by column chromatography (hexane : AcOEt = 15 : 1) to give the aldehyde (232 mg, 78%) as an oil, $[\alpha]_D^{26}$ $+1.77°$ ($c=1.05$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 0.17 (1H, dd, $J=4.3$, 5.0 Hz), 0.32 (1H, dd, $J=4.3$, 8.9 Hz), 0.65 (1H, m), 1.2—1.9 (12H, m), 2.40 (2H, m), 9.76 (1H, t, $J=1.7$ Hz). IR ($CHCl_3$): 3000, 2950, 2880, 1730, 1460, 1250 cm^{-1}. MS m/z (%): 166 (M^+, 7), 148 (38), 95 (69), 81 (44), 58 (100). High MS Calcd for $C_{11}H_{18}O$: 166.1355. Found: 166.1349. A solution of the aldehyde (42.0 mg, 0.250 mmol) in acetone (3 ml) was treated with Jones reagent (0.2 ml, 2.7 M solution) at -10 °C and the mixture was stirred at room temperature for 15 min. The reaction was quenched with iso-propanol and the whole mixture was concentrated *in vacuo*. The residue thus obtained was diluted with AcOEt and washed with water. The organic layer was extracted with saturated $NaHCO_3$ solution. After being acidified with concentrated HCl under cooling, the mixture was extracted with AcOEt, and the combined extract was dried, and then concentrated *in vacuo* to give the carboxylic acid (**11**) (38 mg, 84%), which was used without further purification. ^{1}H-NMR ($CDCl_3$) δ: 0.16 (1H, dd, $J=4.1$, 5.0 Hz), 0.32 (1H, dd, $J=4.1$, 9.2 Hz), 0.63 (1H, m), 1.2—1.9 (12H, m), 2.33 (2H, t, $J=7.4$ Hz). IR ($CHCl_3$): 3500—3000, 1720, 1450, 1250 cm^{-1}. MS m/z (%): 182 (M^+, 28), 164 (13), 95 (100), 81 (34). High MS Calcd for $C_{11}H_{18}O_2$: 182.1304. Found: 182.1287.

(6*S*,7*R*)- and (6*R*,7*R*)-7-Bromomethyl-1-oxaspiro[5.5]undecan-2-one (12 and 13) Table I (Entry 4): A mixture of the carboxylic acid (**11**) (13.1 mg, 0.072 mmol), $Hg(TFA)_2$ (61.4 mg, 0.144 mmol), and THF (1 ml) was stirred at room temperature for 12 h under a nitrogen atmosphere. The reaction mixture was treated with saturated potassium bromide solution (1.5 ml), and the resulting mixture was stirred for 15 min and extracted with $CHCl_3$. The organic layer was dried and concentrated *in vacuo* to give an oily residue, which was dissolved in dry pyridine (1 ml), and then LiBr (12.5 mg, 0.144 mmol) and bromine (6 μl, 0.18 mmol) were added to this solution. After being stirred at room temperature for 3 h, the mixture was diluted with benzene, washed with $Na_2S_2O_5$ solution and brine, dried, and then concentrated *in vacuo*. The residue was purified by column chromatography (hexane : AcOEt = 3 : 1) to give a diastereomixture of the lactones (**12** and **13**) (11.1 mg, 63%) in a ratio of 92 : 8. These isomers were separated by flash column chromatography (hexane : AcOEt = 4 : 1). **12**: $[\alpha]_D^{28}$ $-4.53°$ ($c=1.01$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.2—2.1 (13H, m), 2.46 (2H, m), 3.18 (1H, dd, $J=9.6$, 9.6 Hz), 3.66 (1H, dd, $J=2.8$, 9.6 Hz). ^{13}C-NMR ($CDCl_3$) δ: 16.0, 23.0, 23.8, 24.2, 26.8, 29.5, 33.2, 36.3, 49.0, 86.3, 171.0. IR ($CHCl_3$): 3000, 2950, 2880, 1730, 1460, 1300, 1150 cm^{-1}. MS m/z (%): 261 (M^+, 0.5), 259 (0.5), 181 (100), 163 (38). High MS Calcd for $C_{11}H_{17}{}^{79}BrO_2$: 260.0412. Found: 260.0412. **13**: $[\alpha]_D^{28}$ $+0.42°$ ($c=0.76$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.2—2.1 (13H, m), 2.42 (2H, m), 3.23 (1H, dd, $J=8.9$, 10.2 Hz), 3.78 (1H, dd, $J=3.2$, 10.2 Hz). ^{13}C-NMR ($CDCl_3$) δ: 16.4, 21.4, 23.6, 26.2, 29.6, 30.7, 33.3, 36.5, 48.0, 84.3, 171.0. IR ($CHCl_3$): 3050, 2950, 2890, 1730, 1450, 1340, 1050 cm^{-1}. MS m/z (%): 261 (M^+, 2.6), 259 (2.6), 181 (100), 163 (37). High MS Calcd for $C_{11}H_{17}{}^{79}BrO_2$: 260.0413. Found: 260.0425.

(1*R*,6*R*)-1-(4-Hydroxybutyl)-6-methylcyclohexanol (14) From **13**: A solution of the lactone (**13**) (5.6 mg, 0.022 mmol) in THF (2 ml) was treated with lithium aluminum hydride (3.2 mg, 0.086 mmol) at 0 °C and the mixture was stirred at room temperature for 3 h. The reaction was quenched with 1 N sodium hydroxide solution under cooling, then the resulting suspension was filtered through a Celite column with ether. The collected filtrates were concentrated *in vacuo* to give an oily residue. A mixture of the residue, *n*-tributyltin hydride (12.5 mg, 0.043 mmol), and dry benzene (4 ml) was irradiated under a 60 W fluorescent lamp in an argon atmosphere at refluxing temperature for 12 h. The mixture was concentrated *in vacuo* and the residue was purified by column chromatography (hexane→hexane : AcOEt = 1 : 1) to give the diol (**14**) (3.5 mg, 86%).

(±)-**14** from 2-Methylcyclohexanone: To a stirred solution of 4-(2-tetrahydropyranoxy)butyl magnesium bromide (**15**), which was prepared from 2-(4-bromobutoxy)tetrahydropyran (237 mg, 1.00 mmol) and magnesium (24.3 mg, 1.00 mmol) in THF (4 ml), was added a solution of 2-methylcyclohexanone (50.0 mg, 0.446 mmol) in THF (2 ml) at -78 °C. The mixture was allowed to warm slowly to room temperature over a period of 8 h, then the reaction was quenched with 10% NH_4Cl solution and the resulting mixture was extracted with AcOEt. The extract was wahsed with water and brine, dried, and then concentrated *in vacuo*. A solution of the residue and *p*-toluenesulfonic acid monohydrate (2.1 mg, 0.011 mmol) in MeOH (4 ml) was stirred at room temperature for 6 h. The mixture was concentrated *in vacuo*, and the residue was purified by column chromatography (hexane : AcOEt = 1 : 1) to give the racemic diol (**14**) (76.4 mg, 92%) as colorless crystals, mp 91—92 °C (ether). ^{1}H-NMR ($CDCl_3$) δ: 0.87 (3H, d, $J=5.5$ Hz), 1.1—1.7 (17H, m), 3.67 (2H, t, $J=6.0$ Hz). IR (KBr): 3616, 3356, 2931, 2862, 1446, 1070 cm^{-1}. MS m/z (%): 186 (M^+), 113 (100). High MS Calcd for $C_{11}H_{22}O_2$: 186.1618. Found: 186.1613.

Acknowledgement We thank Ouchisinko Chemical Industrial Co., Ltd. for generous financial assistance.

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11) Although our result suggests that THF is the solvent of choice, Collum *et al.*[8b)] reported that the yield of the inversion product increased dramatically as lesser polar solvents, such as CCl_4 and hexane, were used.