Bull. Chem. Soc. Jpn., 70, 2215—2219 (1997)

Ring Expansion of Isopropenylcyclopropanes to Dihydromethyloxepins

Seiji Yamaguchi,* Akiko Arisawa, Naoko Katoh, Keiko Hatanaka, Hajime Yokoyama, and Yoshiro Hirai

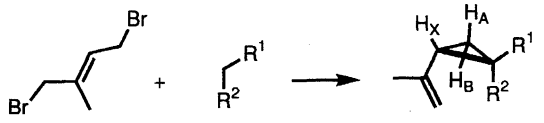
Department of Chemistry, Faculty of Science, Toyama University, Gofuku 3190, Toyama 930

(Received January 10, 1997)

The stereochemistry was studied concerning the ring expansion of some 2-isopropenylcyclopropane-1-carbonyl compounds to 2,5-dihydro-3-methyloxepin derivatives. The LAH reduction of dimethyl 2-isopropenylcyclopropane-1,1-dicarboxylate (**1aa**) gave the corresponding diol, and a subsequent Swern oxidation gave a seven-membered 4,7-dihydro-6-methyloxepin-3-carbaldehyde. A DIBAL reduction of **1aa** gave two isomeric hydroxymethyl carboxylic esters, and a subsequent Swern oxidation of methyl 1-hydroxymethyl-*t*-2-isopropenylcyclopropane-*r*-1-carboxylate caused a ring expansion to give methyl 4,7-dihydro-6-methyloxepin-3-carboxylate; however, a similar Swern oxidation of methyl 1-hydroxymethyl-*c*-2-isopropenyl-cyclopropane-*r*-1-carboxylate caused no ring expansion to give methyl 1-formyl-*c*-2-isopropenylcyclopropane-*r*-1-carboxylate.

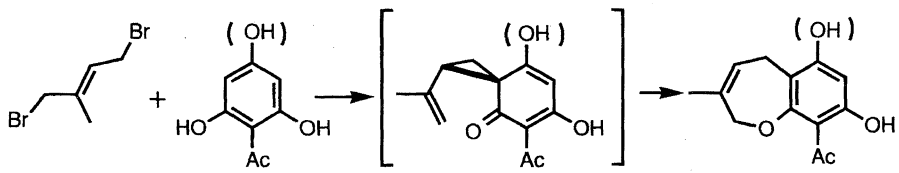
Some interconversions between *cis*-2-vinylcyclopropane-1-carbonyl compounds and dihydrooxepins were reported; the vinylcyclopropanes were generally favorable and the dihydrooxepins were favorable only in π-conjugated systems.[1] In our previous studies concerning naturally occurring isopropenyldihydrobenzofuran derivatives, the cyclization of 1-(2,6-dihydroxyphenyl)-1-ethanone or 1-(2,4,6-trihydroxyphenyl)-1-ethanone with (*E*)-1,4-dibromo-2-methyl-2-butene gave 1-(2,5-dihydro-3-methyl-1-benzoxepin-9-yl)-1-ethanone derivatives.[2] We proposed a [3,3] sigmatropic ring expansion of 1-isopropenylspiro[2.5]octa-5,7-dien-4-one intermediates, probably formed by C,C double alkylation; also, aromatization might be the driving force for the ring expansion. While expecting an effective preparation method for naturally occurring 2,5-dihydro-3-methyl-1-benzoxepin derivatives, we studied these ring expansions. In this paper we describe the ring expansion of 2-isopropenylcyclopropane-1,1-dicarbonyl compounds to 4,7-dihydro-6-methyloxepin-3-carbonyl derivatives (Chart 1).

According to a procedure reported by Nickl,[3] dimethyl 2-isopropenylcyclopropane-1,1-dicarboxylate (**1aa**) was effectively prepared by the cyclization of dimethyl malonate with (*E*)-1,4-dibromo-2-methyl-2-butene using potassium carbonate. Methyl 1-cyano-*t*-2-isopropenylcyclopropane-*r*-1-carboxylate (**1ac**) was similarly prepared from methyl cyanoacetate using sodium hydride (Chart 2). A lithium aluminium hydride (LAH) reduction of dimethyl ester **1aa** and a subsequent Swern oxidation of diol **1dd** gave seven-membered 4,7-dihydro-6-methyloxepin-3-carbaldehyde (**2e**), where none of corresponding three-membered dialdehyde **1ee** was observed. A diisobutylaluminium (DIBAL) reduction of dimethyl ester **1aa** and a subsequent Swern oxidation gave a 1 : 10 mixture of seven-membered methyl 4,7-dihy-



1aa) $R^1 = R^2 = CO_2Me$
1ba) $R^1 = CO_2$-*t*-Bu, $R^2 = CO_2Me$
1ac) $R^1 = CO_2Me$, $R^2 = CN$

Chart 2.



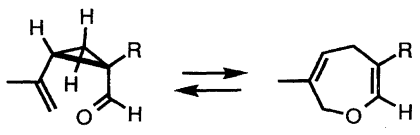


Chart 1.

dro-6-methyloxepin-3-carboxylate (**2a**) and three-membered methyl 1-formyl-*c*-2-isopropenylcyclopropane-*r*-1-carboxylate (**1ea**). These results might be explained as follows (Chart 3). A DIBAL reduction of **1aa** might give a mixture of two stereo-isomers, methyl 1-hydroxymethyl-*c*-2-isopropenylcyclopropane-*r*-1-carboxylate (**1da**) and methyl 1-hydroxymethyl-*t*-2-isopropenylcyclopropane-*r*-1-carboxylate (**1ad**), where **1da** is major because of a steric hindrance of the isopropenyl. Although methyl 1-formyl-*t*-2-isopropenylcyclopropane-*r*-1-carboxylate (**1ae**) derived from **1ad** might cause an expansion to give **2a**, **1ea** derived from **1da** might remain. This hypothesis was examined for each isomer **1ad** and **1da** isolated by repeating column chromatography, and confirmed that the Swern oxidation of **1ad** gave only **2a**, and that of **1da** gave only **1ea**. The stereochemistry was studied based on the ^{1}H NMR spectra. In the ^{1}H NMR spectra, dimethyl ester **1aa** showed three double doublets at $\delta = 1.47$ (3-H_A), 1.87 (3-H_B), and 2.49 (2-H_X) in a typical ABX pattern. Diol **1dd** showed them at $\delta = 0.67$ (3-H_A), 0.80 (3-H_B), 1.50 (2-H_X), where deshielding was observed in all ring protons: $\delta = -0.80$ (in 3-H_A), -1.07 (in 3-H_B), -0.99 (in 2-H_X). These might have been due to the disappearance of two ester carbonyls. Methyl 1-hydroxymethyl-*t*-2-isopropenylcyclopropane-*r*-1-carboxylate (**1ad**) showed them at $\delta = 1.11$ (3-H_B), 1.42 (3-H_A), 2.24 (2-H_X), where similar deshielding was observed in only one ring proton; $\delta = -0.76$ (in 3-H_B). And methyl 1-hydroxymethyl-*c*-isopropenylcyclopropane-*r*-1-carboxylate (**1da**) showed them at $\delta = 1.07$ (3-H_A), 1.70 (3-H_B), 1.88 (2-H_X), where similar deshielding was observed in two ring protons: $\delta = -0.40$ (in 3-H_A), -0.61 (in 2-H_X). Methyl 1-formyl-*c*-2-isopropenylcyclopropane-*r*-1-carboxylate (**1ea**), derived from **1da**, showed them at $\delta = 2.08$ (3-H_A), 1.83 (3-H_B), and 2.50 (2-H_X), where shielding was observed in two ring protons: $\delta = +1.01$ (in 3-H_A), +0.62 (in 2-H_X). These supported the stereochemistry of each isomer, and the idea that the carbaldehyde *cis* to the isopropenyl could cause only a ring expansion. A DIBAL reduction of the cyano ester **1ac** gave hydroxy carbonitrile **1dc**, and a subsequent Swern oxidation of **1dc** gave only three-membered 1-formyl-*c*-2-isopropenylcyclopropane-*r*-1-carbonitrile (**1ec**), and no ring expansion was observed. In the ^{1}H NMR spectra, the cyano ester **1ac** also showed three double doublets at $\delta = 1.86$ (3-H_A), 1.91(3-H_B), and 2.52 (2-H_X) in an ABX pattern. Hydroxy carbonitrile **1dc** showed them at $\delta = 1.21$ (3-H_A), 1.52 (3-H_B), and 1.83 (2-H_X), where deshielding was observed in two ring protons $\delta = -0.65$ (in 3-H_A) and -0.69 (in 2-H_X). Formyl carbonitrile **1ec** showed them at $\delta = 2.01$ (3-H_A), 1.99 (3-H_B), and 2.55 (2-H_X), where shielding was observed in two ring protons: $\delta = +0.80$ (in 3-H_A), +0.72 (in 2-H_X). These supported the structures of **1dc** and **1ec**. Then, 1-formyl-*c*-2-isopropenylcyclopropane-*r*-1-carbonitrile (**1ec**) was subjected to photo-isomerization. The photo-irradiation of **1ec** caused a partial expansion to give a mixture of 4,7-dihydro-6-methyloxepin-3-carbonitrile **2c** (43%) and the starting **1ec** (57%). These might be explained as follows. The 1-cyano-*t*-2-isopropenylcyclopropane-*r*-1-carboxylic ester (**1ac**) was either the major or only isomer in the cyclization, because either the bulky methoxycarbonyl group was directed trans to the isopropenyl group, or this isomer was only reduced with bulky DIBAL because of the smaller steric hindrance. Thus, *r*-*t*-butyl methyl *t*-2-isopropenylcyclopropane-1,1-dicarboxylate (**1ba**), prepared from *t*-butyl methyl malonate similarly, was subjected to a DIBAL reduction and subsequent Swern oxidation. A DIBAL reduction of **1ba** gave only *t*-butyl 1-hydroxymethyl-*t*-2-isopropenylcyclopropane-

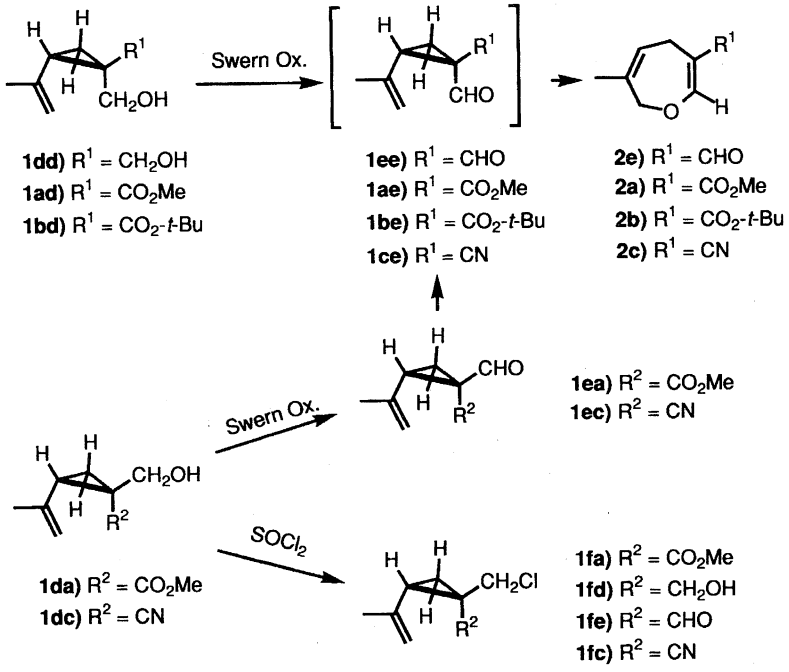


Chart 3.

r-1-carboxylate (**1bd**); a subsequent Swern oxidation of **1bd** gave *t*-butyl 6-methyl-4,7-dihydrooxepin-3-carboxylate (**2b**). The low yields in both formation of **1ba** and in the reduction of methyl ester *cis* to the isopropenyl group in **1ba** might show a steric hindrance of the bulky *t*-butyl.

The hydroxymethyl *trans* to the isopropenyl group in **1da** and **1dc** was chlorinated to the corresponding chlorides **1fa** and **1fc**, and then subjected to the conversion of the ester group in **1fa** or the carbonitrile group in **1fc** to the carbaldehyde **1fe**. 1-Chloromethyl-*c*-2-isopropenylcyclopropane-*r*-1-carboxylic ester (**1fa**) was reduced with DIBAL to give 1-chloromethyl-*c*-2-isopropenylcyclopropane-*r*-1-methanol (**1fd**), and a subsequent Swern oxidation of **1fd** gave three-membered 1-chloromethyl-*c*-2-isopropenylcyclopropane-*r*-1-carbaldehyde (**1fe**). A DIBAL reduction of 1-chloromethyl-*c*-2-isopropenylcyclopropane-*r*-1-carbonitrile (**1fc**) also gave the same carbaldehyde **1fe**. The ring expansion might need not only the *cis*-stereochemistry between the isopropenyl and the formyl, but also some other factors, such as the dipole repulsion of two carbonyls, in these cases.

Experimental

The melting points and boiling points were uncorrected (in boiling points: 1 mmHg = 133.322 Pa). Some concentrations were expressed in M (1 M = 1 mol dm^{-3}). Infrared spectra were recorded on a JASCO WS/IR-7300 spectrometer in liquid films or KBr disks. ^{1}H NMR spectra were recorded on a JEOL PMX-60Si, FX-90Q, or JNM A400 NMR spectrometer in $CDCl_3$ solutions, and abbreviated for multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br., broad. Mass spectra were measured on a JEOL JMS-OISG-2 mass spectrometer.

Preparation of Dimethyl 2-Isopropenylcyclopropane-1,1-dicarboxylate (1aa): According to a procedure described by Nickl,[3] to a sodium methylate solution, prepared from sodium metal (4.6 g, 202 mmol) in absolute methanol (250 ml), was added dimethyl malonate (3.2 g 100 mmol) and (*E*)-1,4-dibromo-2-methyl-2-butene (22.6 g, 99.1 mmol); the mixture was refluxed for 6 h. After cooling the mixture, it was filtered to remove sodium bromide, and concentrated under reduced pressure. The residue was treated with water and then extracted with ether. The ether layer was washed with a 5% aqueous solution of sodium hydroxide and a saturated sodium chloride solution and dried over anhydrous sodium sulfate. After removing the ether, an oily residue was distilled under reduced pressure to give dimethyl 2-isopropenylcyclopropane-1,1-dicarboxylate (**1aa**) (13.9 g, 70%) as fractions boiling at 118—122 °C/18 mmHg. IR 1732 cm^{-1} (CO). ^{1}H NMR δ = 1.47 (1H, dd, J = 4.9 and 8.7 Hz, 3-H_A), 1.79 (3H, d, J = 0.7 Hz, C=C–Me), 1.87 (1H, dd, J = 4.9 and 8.1 Hz, 3-H_B), 2.49 (1H, dd, J = 8.1 and 8.7 Hz, 2-H_X), 3.68 (3H, s, CO_2Me), 3.75 (3H, s, CO_2Me), 4.71 (1H, q, J = 0.7 Hz, C=CH_aH_b), 4.87 ppm (1H, br. s, C=CH$_a$H$_b$). MS *m/z* 198 (M^+). Found: C, 60.52; H, 7.15%. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12%.

Preparation of Methyl 1-Cyano-*t*-2-isopropenylcyclopropane-*r*-1-carboxylate (1ac): To a suspension of potassium carbonate (10.6 g, 76.7 mmol) in dry acetone (100 ml) was added methyl cyanoacetate (3.80 g, 38.4 mmol) and (*E*)-1,4-dibromo-2-methyl-2-butene (8.74 g, 38.4 mmol); the mixture was stirred at room temperature for 18 h. The acetone layer was collected by decantation, and concentrated under reduced pressure. The residue was treated with water and then extracted with ether. The ether layer was washed with a 5% aqueous solution of sodium hydroxide and a saturated sodium chloride solution and dried over anhydrous sodium sulfate. After removing the ether, an oily residue was chromatographed on a silica-gel column to give methyl 1-cyano-*t*-2-isopropenylcyclopropane-*r*-1-carboxylate (**1ac**) (3.69 g, 58%) as fractions eluted with benzene. IR 2243 (CN) and 1741 cm^{-1} (CO). ^{1}H NMR δ = 1.86 (1H, dd, J = 5.1 and 8.5 Hz, 3-H_A), 1.90 (3H, d, J = 0.7 Hz, C=C–Me), 1.91 (1H, dd, J = 5.1 and 8.5 Hz, 3-H_B), 2.52 (1H, t, J = 8.5 Hz, 2-H_X), 3.84 (3H, s, CO_2Me), 4.96 (1H, d, J = 1.0 Hz, C=CH_aH_b), 5.14 (1H, dq, J = 1.0 and 0.7 Hz, C=CH$_a$H$_b$). MS *m/z* 165 (M^+), 150 (M^+ – Me), 133 (M^+ – MeOH). High MS: Found: *m/z* M^+, 165.080. Calcd for $C_6H_{11}NO_2$: 1M, 165.079.

Preparation of *t*-Butyl *r*-Methyl *c*-2-Isopropenylcyclopropane-1,1-dicarboxylate (1ba): To a suspension of sodium hydride (60% oily 207 mg, 5.17 mmol) in dry benzene (50 ml) was added a solution of *t*-butyl methyl malonate (600 mg, 3.44 mmol) in dry benzene (20 ml). After the hydrogen gas evolution ceased, (*E*)-1,4-dibromo-2-methyl-2-butene (1.18 g, 5.17 mmol) was added to the mixture; the mixture was stirred at room temperature for 3 h. The mixture was treated with ice-water and extracted with ether. The ether layer was washed with a saturated sodium chloride solution and dried over anhydrous sodium sulfate. After removing the solvents, an oily residue was chromatographed on a silica-gel column to give *t*-butyl *r*-methyl *c*-2-isopropenylcyclopropane-1,1-dicarboxylate (**1ba**) (143 mg, 17%) as fractions eluted with hexane–ethyl acetate (98 : 2). IR 1732 cm^{-1} (CO). ^{1}H NMR δ = 1.38 (1H, dd, J = 5 and 9 Hz, 3-H_A), 1.46 (9H, s, O-*t*-Bu), 1.77 (1H, dd, J = 5 and 8 Hz, 3-H_B), 1.79 (3H, br. s, C=C–Me), 2.40 (1H, dd, J = 8 and 9 Hz, 2-H_X), 3.67 (3H, s, CO_2Me), 4.70 (1H, br. s, C=CH_aH_b), 4.85 (1H, br. s, C=CHaH_b). MS *m/z* 240 (M^+), 138 ($M^+ - CO_2$ – *t*-Bu).

LiAlH$_4$ Reduction of Dimethyl Ester 1aa: To a solution of dicarboxylic ester **1aa** (1.70 g, 8.59 mmol) in dry tetrahydrofuran (40 ml) was added a 0.3 M lithium aluminum hydride THF solution (42 ml, 12.6 mmol); the mixture was refluxed for 3 h. After cooling, the mixture was carefully treated with water, acidified with 10% hydrochloric acid, and extracted with ether. The ether layer was washed with a saturated sodium hydrogencarbonate solution and a saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After removing the ether, an oily residue was chromatographed on a silica-gel column to give 2-isopropenylcyclopropane-1,1-dimethanol (**1dd**) (714 mg, 58%) as fractions eluted with hexane–ethyl acetate (1 : 1). Mp 50—51 °C (crystallized from cyclohexane–benzene). IR 3280 cm^{-1} (OH). ^{1}H NMR δ = 0.6—1.0 (2H, m, 3-H_A and 3-H_B), 1.5 (1H, t, J = 7 Hz, 2-H_X), 1.8 (3H, br. s, C=C–Me), 2.8 (1H, br. s, CH_2OCH_a), 3.1 (1H, br. s, CH_2OH_b), 3.7 (4H, br. s, two CH_2O), 4.7 (1H, br. s, C=CH_aH_b), 4.8 (1H, br. s, C=CHaH_b). MS *m/z* 127 (M^+ – Me). Found: C, 67.41; H, 10.09%. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93%.

General Procedures for DIBAL Reductions: To a solution of ester **1aa**, **1ba**, **1ac**, **1fa** or nitrile **1fc** (ca. 5 mmol) in dry ether (70 ml) was added 1.0 M DIBAL heptane solution (12.0 ml, 12.0 mmol) over a period of 20 min under cooling with an acetone–liquid N_2 bath; the mixture was stirred for 2 h under cooling, and then stirred at room temperature for 3 h. After working up with methanol and a saturated ammonium chloride solution, the mixture was treated with 10% hydrochloric acid, and then extracted with ether. The ether layer was washed with a saturated sodium hydrogencarbonate solution, and dried over anhydrous sodium sulfate. After removing the ether, an oily residue was chromatographed on a silica-gel column. Dimethyl carboxylic ester **1aa** gave a mixture of **1ad** and **1da** (1 : 10) (49%) as fractions eluted with hexane–ethyl acetate (4 : 1).

Mixture of **1ad** and **1da**: IR 3435 (OH) and 1716 cm^{-1} (CO).

MS *m/z* 170 (M^+). High MS: Found: *m/z* M^+, 170.095. Calcd for $C_9H_{14}O_3$: M, 170.094.

Isolated **1ad**: ^{1}H NMR δ = 1.11 (1H, dd, J = 5.0 and 7.3 Hz, 3-H_A), 1.42 (1H, dd, J = 5.0 and 8.5 Hz, 3-H_B), 1.86 (3H, dd, J = 0.5 and 0.7 Hz, C=C–Me), 2.24 (1H, dd, J = 7.3 and 8.5 Hz, 2-H_X), 2.55 (1H, br. s, OH), 3.66 (1H, d, J = 12.5Hz, O–CH_aH_b), 3.69 (1H, d, J = 12.5 Hz, O–CH_aH_b), 3.74 (3H, s, CO_2Me), 4.74 (1H, d, J = 1.0 Hz, C=CH_aH_b), 4.94 (1H, dq, J = 0.5 and 1.0 Hz, C=CHaH_b).

Isolated **1da**: ^{1}H NMR δ = 1.07 (1H, dd, J = 5.0 and 8.7 Hz, 3-H_A), 1.70 (1H, dd, J = 5.0 and 7.7 Hz, 3-H_B), 1.72 (3H, dd, J = 0.5 and 0.7 Hz, C=C–Me), 1.87 (1H, dd, J = 7.7 and 8.7 Hz, 2-H_X), 2.77 (1H, br. s, OH), 3.55 (1H, d, J = 11.9 Hz, O–CH_aH_b), 3.66 (3H, s, CO_2M), 3.76 (1H, d, J = 11.9 Hz, O–CH_aH_b), 4.91 (1H, dq, J = 1.0 and 0.5 Hz, C=CH_aH_b), 4.93 (1H, dq, J = 1.0 and 0.7 Hz, C=CH_aH_b).

1-Cyano-*t*-2-isopropenylcyclopropane-*r*-1-carboxylic ester (**1ac**) gave 1-hydroxymethyl-*c*-2-isopropenylcyclopropane-*r*-1-carbonitrile (**1dc**) (45%) as fractions eluted with hexane–ethyl acetate (1 : 1). IR 2238 (CN) and 3425 cm^{-1} (OH). ^{1}H NMR δ = 1.21 (1H, dd, J = 5.7 and 8.4 Hz, 3-H_A), 1.52 (1H, dd, J = 5.7 and 7.2 Hz, 3-H_B), 1.83 (1H, dd, J = 7.2 and 8.4 Hz, 2-H_X), 1.90 (3H, d, J = 0.5 Hz, C=C–Me), 2.01 (1H, br. s, OH), 3.61 (1H, d, J = 11.5 Hz, O–CH_aH_b), 3.78 (1H, d, J = 11.5 Hz, O–CH_aH_b), 4.86 (1H, d, J = 1.0 Hz, C=CH_aH_b), 5.05 (1H, dq, J = 1.0 and 0.5 Hz, C=CHaH_b). MS *m/z* 137 (M^+), 122 (M^+ – Me). High MS: Found: *m/z* M^+, 137.079. Calcd for $C_8H_{11}NO$: M, 137.084.

t-Butyl *r*-methyl *c*-2-isopropenylcyclopropane-1,1-dicarboxylate (**1ba**) gave *t*-butyl 1-hydroxymethyl-*t*-2-isopropenylcyclopropane-*r*-1-carboxylate (**1bd**) (35%) as fractions eluted with hexane–ethyl acetate (95 : 5). IR 1724 (CO) and 3437 cm^{-1} (OH). ^{1}H NMR δ = 0.97 (1H, dd, J = 4 and 7 Hz, 3-H_A), 1.27 (1H, dd, J = 4 and 8 Hz, 3-H_B), 1.50 (9H, s, CO_2–*t*-Bu), 1.88(3H, br. s, C=C–Me), 2.07(1H, dd, J = 7 and 8 Hz, 2-H_X), 2.43 (1H, br. s, OH), 3.37(1H, d, J = 13 Hz, O–CH_aH_b), 3.63 (1H, d, J = 13 Hz, O–CH_aH_b), 4.75 (1H, br. s, C=CH_aH_b), 4.95 (1H, br. s, C=CHaH_b). MS *m/z* 156 ($M^+ - C_4H_8$).

1-Chloromethyl-*c*-2-isopropenylcyclopropane-*r*-1-carboxylic ester (**1fa**) gave 1-chloromethyl-*c*-2-isopropenylcyclopropane-*r*-1-methanol (**1fd**) (59%) as fractions eluted with hexane–ethyl acetate (97 : 3). IR 3417 cm^{-1} (OH). ^{1}H NMR δ = 0.77 (1H, d, J = 8 Hz, 3-H_A), 0.80 (1H, d, J = 11 Hz, 3-H_B), 1.30 (1H, dd, J = 8 and 11 Hz, 2-H_X), 1.67 (1H, br. s, OH), 1.83 (3H, br. s, C=C–Me), 3.50 (2H, br. s, O–CH_2), 3.57 (2H, br. s, –CH_2–Cl), 4.63 (1H, br. d, J = 1.0 Hz, C=CH_aH_b), 4.83 (1H, br. d, J = 1.0 Hz. C=CHaH_b). MS *m/z* 160 (M^+), (M^+ – HCl). Found: C, 59.55; H, 8.42%. Calcd for $C_8H_{13}OCl$: C, 59.81; H, 8.16%.

1-Chloromethyl-*c*-2-isopropenylcyclopropane-*r*-1-carbonitrile **1fc** gave 1-chloromethyl-*c*-2-isopropenyl-*r*-1-carbaldehyde (**1fe**) (24%) as fractions eluted with hexane–ethyl acetate (99 : 1). IR 1712 cm^{-1} (CO). ^{1}H NMR δ = 1.47 (1H, dd, J = 5.7 and 8.4 Hz, 3-H_A), 1.82 (1H, dd, J = 5.7 and 7.2 Hz, 3-H_B), 1.82 (3H, br. s, C=C–Me), 2.13 (1H, dd, J = 7.2 and 8.4 Hz, 2-H_X), 3.50 (1H, d, J = 12 Hz, –CH_aH_b–Cl), 3.83 (1H, d, J=12 Hz, –CH_aH_b–Cl), 4.90 (2H, br. s, C=CH_2), 8.77 (1H, s, CHO). MS *m/z* 158 (M^+), 123 (M^+ – HCl). Found: C, 60.55; H, 7.12%. Calcd for $C_8H_{11}OCl$: C, 60.57; H, 7.00%.

General Procedures for Swern Oxidation. Oxalyl chloride (480 mg, 3.79 mmol) was dissolved in dry dichloromethane (20 ml) under an argon atmosphere, and dimethyl sulfoxide (587 mg, 7.51 mmol) was added under cooling with a dry ice–acetone bath; the mixture was stirred for 10 min. To the mixture was added a solution of alcohol **1dd**, **1ad**, **1da**, **1dc**, **1bd**, **1fd** (1.00 mmol) in dry dichloromethane (15 ml) under cooling; the mixture was stirred for 30 min. Dry triethylamine (730 mg, 7.21 mmol) was then added to the mixture, and the mixture was stirred at room temperature for 1 h. After treating with 10% hydrochloric acid, the dichloromethane layer was washed with a saturated sodium hydrogencarbonate solution and a saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After removing the dichlomethane, the residue was chromatographed on a silica-gel column. Diol **1dd** gave 4,7-dihydro-6-methyloxepin-3-carbaldehyde (**2e**) (31%) as fractions eluted with chloroform. IR 1678 cm^{-1} (CO). ^{1}H NMR δ = 1.83 (3H, dt, J = 2 and 1 Hz, 6-Me), 3.05 (2H, dq, J = 6 and 1 Hz, 4-H), 4.73 (2H, s, 7-H), 6.00 (1H, tq, J = 6 and 2 Hz, 4-H), 7.03 (1H, s, 2-H), 9.05 (1H, s, CHO). MS *m/z* 138 (M^+), 123 (M^+ – Me). High MS: Found: *m/z* M^+, 138.068. Calcd for $C_8H_{10}O_2$: M, 138.068.

A mixture of two isomeric **1ad** and **1da**, obtained by DIBAL reduction of **1aa**, gave a 1 : 10 mixture of methyl 6-methyl-4,7-dihydrooxepin-3-carboxylate (**2a**) and methyl 1-formyl-*c*-2-isopropenylcyclopropane-*r*-1-carboxylate (**1ea**) in 63% yield as fractions eluted with hexane–ethyl acetate (99 : 1). Isolated methyl 1-hydroxymethyl-*c*-2-isopropenylcyclopropane-*r*-1-carboxylate **1ad** gave **2e** (58%) as fractions eluted with hexane–ethyl acetate (99 : 1). IR 1704 cm^{-1} (CO). ^{1}H NMR δ = 1.82 (3H, dt, J = 1.7 and 1.2 Hz, 6-Me), 3.13 (2H, dq, J = 6.3 and 1.2 Hz, 4-H), 3.69 (3H, s, CO_2Me), 4.60 (1H, s, 7-H), 5.01(1H, tq, J = 6.3 and 1.7 Hz), 7.49 (1H, s, 2-H). MS *m/z* 168 (M^+), 153 (M^+ – Me), 139(M^+ – CHO). High MS: Found: *m/z* M^+, 168.077. Calcd for $C_9H_{12}O_3$: M, 168.079.

Isolated 1-hydroxymethyl-*c*-isopropenylcyclopropane-*r*-1-carboxylic ester (**1da**) gave 1-formyl-*c*-2-isopropenylcyclopropane-*r*-1-carboxylic ester (**1ea**) (45%) as fractions eluted with hexane–ethyl acetate (99 : 1). IR 1714 (aldehyde CO) and 1744 cm^{-1} (ester CO). ^{1}H NMR δ = 1.72 (3H, dt, J = 0.7 and 1.5 Hz, C=C–Me), 1.84 (1H, dd, J = 4.1 and 9.1 Hz, 3-H_B), 1.87 (1H, dd, J = 4.1 and 8.8 Hz, 3-H_A), 2.49 (1H, qdd, J = 0.7, 8.8, and 9.1 Hz, 2-H_X), 3.77 (3H, s, CO_2Me), 4.89 (1H, dq, J = 1.0 and 1.5 Hz), 5.01 (1H, dq, J = 1.0 and 1.5 Hz), 10.25 (1H, s, CHO). MS *m/z* 168 (M^+), 153 (M^+ – Me). High MS: Found: *m/z* M^+, 168.078. Calcd for $C_9H_{12}O_3$: M, 168.079.

1-Hydroxymethyl-*c*-2-isopropenylcyclopropane-*r*-1-carbonitrile (**1dc**) gave 1-formyl-*c*-2-isopropenylcyclopropane-*r*-1-carbonitrile (**1ec**) (34%) as fractions eluted with hexane–ethyl acetate (4 : 1). IR 2244 (CN) and 1718 cm^{-1} (CO). ^{1}H NMR δ = 1.89 (3H, d, J = 0.7 Hz, C=C–Me), 1.99 (1H, dd, J = 5.3 and 8.5 Hz, 3-H_A), 2.01 (1H, dd, J = 5.3 and 8.5 Hz, 3-H_B), 2.55 (1H, t, J = 8.5 Hz, 2-H_X), 5.00 (1H, d, J = 1.0 Hz, C=CH_aH_b), 5.17 (1H, dq, J = 1.0 and 0.7 Hz, C=CHaH_b), 9.57 (1H, s, CHO). MS *m/z* 135 (M^+), 120 (M^+ – Me). High MS: Found: *m/z* M^+, 135.070. Calcd for C_8H_9NO: M, 135.068. *t*-Butyl 1-hydroxymethyl-*t*-2-isopropenylcyclopropane-*r*-1-carboxylate (**1bd**) gave *t*-butyl 4,7-dihydro-6-methyloxepin-3-carboxylate (**2b**) (34%) as fractions eluted with hexane–ethyl acetate (9 : 1). IR 1698 cm^{-1} (CO). ^{1}H NMR δ = 1.42 (9H, s, CO_2–*t*-Bu), 1.83 (3H, d, J = 1 Hz, 6-Me), 3.05 (2H, br. t, J = 6 Hz, 4-H), 4.53 (2H, s, 7-H), 5.87 (1H, tq, J = 6 and 2 Hz, 5-H), 7.25 (1H, s, 2-H). MS *m/z* 210 (M^+).

1- Chloromethyl- *c*- 2- isopropenylcyclopropane- *r*- 1- methanol (**1fd**) gave 1-chloromethyl-*c*-2-isopropenylcyclopropane-*r*-1-carbaldehyde (**1fe**) (61%), which was identical with the sample, was obtained by DIBAL reduction of **1fc**, as described above.

Photo-Isomerization of 1-Formyl-*c*-2-isopropenylcyclopropane-*r*-1-carbonitrile (1ec). A solution of cyano carbaldehyde **1ec** (200 mg, 1.45 mmol) in dry benzene (220 ml) was irradiated for 18 h using a 100-W high-pressure mercury lamp. After irradiation, the benzene was removed under reduced pressure, and an oily residue was chromatographed on a silica-gel column to recover the starting **1ec** (100 mg, 50%) as fractions eluted with hexane–ethyl

acetate (5 : 1), and give 4,7-dihydro-6-methyloxepin-3-carbonitrile (**2c**) (85 mg, 43%, conversion yield 86%) as fractions eluted with hexane. IR 2244 cm^{-1} (CN). ^1H NMR $\delta = 1.87$ (3H, dt, $J = 0.7$ and 1.5 Hz, 6-Me), 3.00 (2H, dqd, $J = 6.3$, 1.5, and 1.2 Hz, 4-H), 4.62 (2H, s, 7-H), 5.77 (1H, tq, $J = 6.3$ and 0.7 Hz, 5-H), 6.88 (1H, t, $J = 1.2$ Hz, 2-H). High MS: Found: *m/z* M^+, 135.065. Calcd for C_8H_9NO: M, 135.068.

Chlorination of 1da and 1dc. To a solution of thionyl chloride (238 mg, 2.01 mmol) in dry benzene (5 ml) was added a solution of hydroxymethyl ester (**1da** or **1dc** (ca. 1.00 mmol)) in dry pyridine (279 mg) and dry benzene (4 ml); the mixture was refluxed for 1 h. After cooling, the mixture was treated with 10% hydrochloric acid and then extracted with benzene. The benzene layer was washed with a saturated sodium hydrogencarbonate solution and a saturated sodium chloride solution, and dried over anhydrous sodium sulfate. After removing the benzene, the oily residue was chromatographed on a silica-gel column to give 1-chloromethyl-*c*-2-isopropenylcyclopropane-*r*-1-carboxylic ester (**1fa**) (69%) or 1-chloromethyl-*t*-2-isopropenylcyclopropane-*r*-1-carbonitrile (**1fc**) as fractions eluted with hexane–ethyl acetate (95 : 5).

Methyl 1-chloromethyl-*c*-2-isopropenylcyclopropane-*r*-1-carboxylate (**1fa**): IR 1728 cm^{-1} (CO). ^1H NMR $\delta = 1.05$ (1H, dd, $J = 5$ and 8 Hz, 3-H_A), 1.25 (1H, dd, $J = 5$ and 7 Hz, 3-H_B), 1.70 (3H, br. s, C=C–Me), 1.80 (1H, dd, $J = 7$ and 8 Hz, 2-H_X), 3.32 (1H, d, $J = 11$ Hz, –CH_aH_b–Cl), 3.65 (3H, s, CO_2Me), 4.17 (1H, d, $J = 11$ Hz, –CH_aH_b–Cl), 4.77 (1H, br. s, C=CH_aH_b), 4.88 (1H, br. s, C=CH_aH_b). MS *m/z* 187 (M^+), 153 ($M^+ - Cl$). Found: C, 57.02; H, 6.79%. Calcd for $C_9H_{13}O_2Cl$: C, 57.30; H, 6.95%.

1-Chloromethyl-*c*-2-isopropenylcyclopropane-*r*-1-carbonitrile **1fc**: IR 2238 cm^{-1} (CN). ^1H NMR $\delta = 1.33$ (1H, dd, $J = 5$ and 8 Hz, 3-H_A), 1.60 (1H, dd, $J = 5$ and 7 Hz, 3-H_B), 1.77 (1H, dd, $J = 7$ and 8 Hz, 2-H_X), 1.93 (3H, br. s, C=C–Me), 3.40 (1H, d, $J = 11$ Hz, –CH_aH_b–Cl), 3.73 (1H, d, $J = 11$ Hz, –CH_aH_b–Cl), 4.85 (1H, br. s, C=CH_aH_b), 5.05 (1H, br. s, C=CH_aH_b). MS *m/z* 155 (M^+), 120 ($M^+ - Cl$). Found: C, 61.76; H, 6.74; N, 8.74%. Calcd for $C_8H_{10}NCl$: C, 61.74; H, 6.48; N, 9.00%.

References

1) a) M. Rey and A. Dreing, *Helv. Chim. Acta*, **48**, 1985 (1965); b) M. T. Hughes and R. O. Williams, *J. Chem. Soc., Chem. Commun.*, **1968**, 587; c) S. J. Rhoads and R. D. Cockroft, *J. Am. Chem. Soc.*, **91**, 2815 (1969); d) S. J. Rhoads and N. R. Raulins, *Org. React.*, **22**, 1 (1975); e) M. E. Alonso, P. Jano, M. I. Hernandez, R. S. Greenberg, and E. Wenkert, *J. Org. Chem.*, **48**, 3047 (1983); f) E. Wenkert, R. S. Greenberg, and H. S. Kim, *Helv. Chim. Acta*, **70**, 2159 (1987); g) R. K. Boeckmann, Jr., M. D. Shair, J. R. Varges, and L. A. Stolz, *J. Org. Chem.*, **58**, 1295 (1993).

2) a) S. Yamaguchi, A. Saitoh, and Y. Kawase, *Bull. Chem. Soc. Jpn.*, **57**, 3983 (1986); b) S. Yamaguchi, M. Takai, I. Hanazome, Y. Okada, and Y. Kawase, *Bull. Chem. Soc. Jpn.*, **60**, 3603 (1987).

3) J. Nickl, *Chem. Ber.*, **91**, 553 (1958).