Bis(trimethylsilyl) Sulfate Catalysis in γ-Lactonization of Cyclopropanecarboxylates Activated by Carbonyl Substituents on α-Carbon

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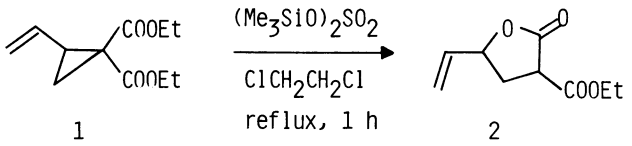
The title reaction of 1-carbonyl substituted cyclopropanecarboxylates proceeds under C(1)-C(2) bond cleavage to produce γ-lactones. Stereochemically, the reaction takes two pathways: (1) substrates with a cationstabilizing group like vinyl on C(2) give thermodynamically favored γ-lactones having the thermodynamically more stable arrangement of substituents irrespective of the configuration of the cyclopropane substrates, (2) substrates without such a cation-stabilizing group afford γ-lactones under *ca.* 70% inversion at C(2) reaction center.

Organosilicon reagents such as iodotrimethylsilane or cyanotrimethylsilane are silicon version of hydroiodic acid or hydrocyanic acid and exhibit characteristic Lewis acidity of trimethylsilyl silicon as well as remarkably increased nucleophilicity of iodide or cyanide group.[1-4] Among the silylated inorganic acids bis(trimethylsilyl) sulfate (BTS)[5-7] is characterized by its high Lewis acidity and low nucleophilicity, although the synthetic application of this reagent has been limited so far only to silylation of active hydrogen compounds.[8-10] Previous work has been related to the protective tetrahydropyranylation of alcohols as well as the deprotection.[11] We have found that the appropriately activated cyclopropanecarboxylates are readily transformed into γ-butyrolactones in the presence of BTS.[12]

Transformation of Doubly Activated Cyclopropane into γ-Butyrolactones. Treatment of diethyl 2-vinyl-1,1-cyclopropanedicarboxylate[13] (**1**) with BTS in 1,2-dichloroethane produces the γ-butyrolactone **2** in 98% yield. The reaction of dimethyl 2-vinyl-1,1-



1 2

Scheme 1.

cyclopropanedicarboxylate gave the lactone in a lower yield (46%) after prolonged reaction time (10 h). Other possible product such as ethyl 3-cyclopentene-1,1-dicarboxylate or a seven-membered ring lactone was not detected at all. The BTS catalyst is markedly expedient for this transformation as other Lewis acids induced rearrangement to **3** and/or nucleophilic ring opening leading to **4** at the expence of the yields of **2** as listed in Table 1. Ethyl chrysanthemate, *trans*-2-vinyl-1-(1-oxo-3-phenylpropyl)cyclopropane, and ethyl *trans*-2-phenylcyclopropanecarboxylate did not produce the corresponding γ-lactones. Obviously the *gem*-dicarbonyl substituents on a cyclopropane carbon are required for the lactonization of this kind. Notably, the catalyzed oxavinylcyclopropane rearrangement takes place under mild conditions (40—80 °C) as compared with the purely thermal reaction proceeding at over 280 °C.[14,15]

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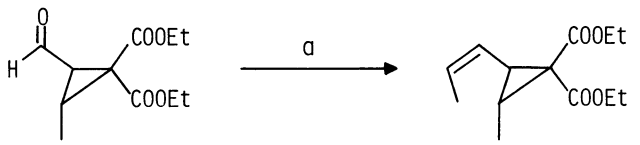
Extension of the reaction to other cyclopropanecarboxylates are summarized in Table 2. Diethyl *trans*-2-methyl-3-(*cis*-1-propenyl)-1,1-cyclopropanedicarboxylate (**5**) (Scheme 2) was converted into the lactone **6**



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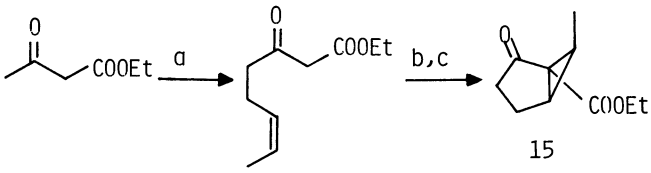
a: $Ph_3PCH_2CH_3Br$, n-BuLi.

Scheme 2.

of the depicted stereochemistry. Although the *trans* arrangement of the methyl and 1-propenyl appendages in **5** is retained in the product **6**, the isomerization of the *cis* C=C bond to *trans* is remarkable.[16] Retention of the stereochemistry at the cyclopropane carbon occurs also in the transformation of **7**[17] to the lactone **8**. The structure of **8** is based on ^{1}H-NMR spectral data (J_{ab}=6.7 Hz, J_{bc}=6.7 Hz, J_{bd}=3.1 Hz, J_{be}=9.3 Hz). Examination of the molecular model shows that dihedral angle of H_a-C-C-H_b is almost the same as that of H_b-C-C-H_c with respect to **8**. In contrast the *endo*-propenyl isomer of **8** is incapable of giving such a set of coupling constants. This is consistent with the *exo*-1-propenyl structure of **8**. Similar transformation of **9** gives **10** whose stereochemistry of phenyl substituent is tentatively assigned as *exo* on the basis of similar observations.

On the other hand, however, opposite stereochemistry prevails in the reaction of substrates having no cation-stabilizing substituent like 1-propenyl group. The dihydro derivative **11**[17] was transformed into an 82:18 mixture of the *endo*-propyl lactone **12a** and *exo*-isomer **12b**. The stereochemical assignment is



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a: NaH, n-BuLi, Br

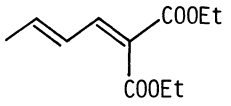
b: p-$CH_3C_6H_4SO_2N_3$, $(C_2H_5)_3N$, c: $Cu(acac)_2$, toluene, reflux.

Scheme 3.

Table 1. Transformation of diethyl 2-vinyl-1, 1-cyclopropanedicarboxylate (**1**) with Lewis acid catalyst

Reagent	Solvent	Temp/°C	Yield[a]/%		
			2	**3**	**4**
$(Me_3SiO)_2SO_2$	$ClCH_2CH_2Cl$	80	98	—	—
H_2SO_4	CH_2Cl_2	25	61	14	—
$Me_3SiOSO_2CF_3$	CH_2Cl_2	25	33[b]	33[b]	—
$Me_3SiOClO_3$[c]	PhH	25	39	—	47 (**4a**, X=Ph)
$Me_3SiOClO_3$	CH_2Cl_2	25	30	36	—
Me_3SiI	CH_2Cl_2	25	—	—	87 (**4b**, X=I)
$BF_3 \cdot OEt_2$	CH_2Cl_2[d]	25	0	0	0
Et_2AlCl-$AgBF_4$	CH_2Cl_2	25	—	48	31 (**4c**, X=Cl)
$TiCl_4$	CH_2Cl_2[e]	25	0	0	0

a) Isolated yield. b) Based on the consumed starting material. c) Prepared from $AgClO_4$ and Me_3SiCl. d) Complex mixture of products. e) Starting material was recovered quantitatively.



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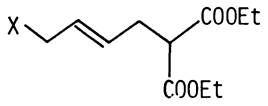

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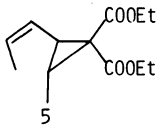
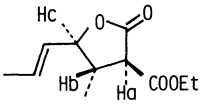
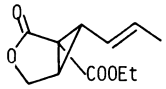
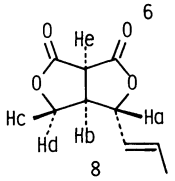
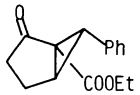
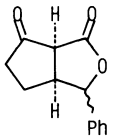
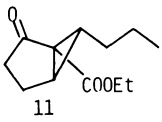
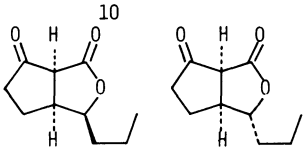
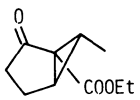
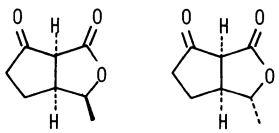
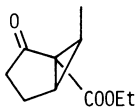
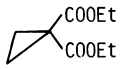
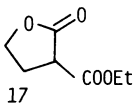
Table 2. Transformation of α-carbonyl substituted cyclopropanecarboxylates into γ-butyrolactone with BTS catalyst[a]

Substrate	Temp/°C	Yield/%	Product(s) (ratio)
 5	40[b]	60(98)[c]	 6
 7	80	39[d]	 8
 9	80	28[f]	 10
 11	80	79[e]	 12a (82 : 18) 12b

Substrate	Temp/°C	Yield/%	Product(s) (ratio)
 13	80	71	 14a (65 : 35) 14b
 15	80	28[d]	14a (23 : 77) 14b
 16	80	8(29)[c]	 17

a) Typically 1 mol of the substrate was heated in the presence of 2 mol of BTS in 1,2-dichloroethane. b) The reaction was carried out in dichloromethane. c) Based on the consumed starting material. d) Other product was polymeric material ($R_f \simeq 0$ on TLC) only. e) BTS (1 mol) was employed. f) A by-product, ethyl 2-benzyl-5-oxo-1-cyclopentene-1-carboxylate 18 (24%), was formed.

based on the fact that the *endo* hydrogen in the bicyclic system appears at higher field than the *exo* one (see experimental part).[18] Similarly, compound **13**[17] gave a 65:35 mixture of **14a** and **14b**. The somewhat sluggish reaction of the *endo* methyl isomer **15** (Scheme 3) gave the *exo* methyl lactone **14b** predominantly. Thus, the γ-lactonization of **11**, **13**, and **15** mostly accompanies the inversion of the configuration at C(2) center. Thermal vinylcyclopropane-cyclopentene rearrangement (*ca.* 300°C) proceeds with approximately 70% inversion at the migrating terminus.[19,20] Diethyl 1,1-cyclopropanedicarboxylate (**16**) isomerizes to γ-lactone[21] sluggishly.

Experimental

Distillation was carried out in Kugelrohr (Büchi). All mps and bps were not corrected. All ^{1}H-NMR spectra (tetramethylsilane as an internal standard) were obtained on a Varian EM 390 spectrometer, chemical shifts being given in ppm units. The IR spectra of neat liquid film samples (unless otherwise

noted) were measured on a Shimadzu IR-27G spectrometer, MS on a Hitachi RMU-6L spectrometer, and exact mass on a Hitachi M 80 spectrometer. Preparative TLC plates were prepared with Merck Kiesel-gel PF_{254}. Column chromatography was carried out with silica gel (Wakogel C-100) at atmospheric pressure.

Synthesis of Diethyl trans-*2-Methyl-3-(*cis-*1-propenyl)-1,1-cyclopropanedicarboxylate (5).* Butyllithium (1.44 M** hexane solution 3.2 ml, 4.6 mmol) was added to a THF (10 ml) solution of ethyltriphenylphosphonium bromide (1.70 g, 4.6 mmol) at 0 °C. After stirring for 15 min diethyl 2-formyl-3-methyl-1,1-cyclopropanedicarboxylate[22] (0.70 g, 3.1 mmol) in THF (4 ml) was added at 0 °C and the reaction mixture was stirred for 30 min. Workup followed by column chromatography (hexane–ethyl acetate=20:1) gave **5** (0.39 g, 53% yield): bp 70—75 °C (bath temperature)/0.03 Torr***: ^{1}H-NMR (CCl_4) δ=1.12 (J=7.2 Hz, 3H), 1.25 (t, J=6.0 Hz, 3H), 1.30 (t, J=6.0 Hz, 3H), 1.5—2.3 (m+dd (δ=1.77, J=1.5, 6.8 Hz), 4H), 2.38 (t, J=8.0 Hz, 1H), 3.9—4.3 (m, 4H), 4.91 (ddd, J=8.0, 10.5, 1.5 Hz, 1H), 5.48 (dq, J=10.5, 6.8 Hz, 1H); IR 2980, 1730, 1370, 1293, 1207, 1140, 1067 cm^{-1}; MS m/z (rel intensity) 241 (M^++1, 5), 240 (M^+, 21), 225 (11), 194 (63), 165 (51), 149 (99), 121 (38), 93 (100), 79 (61). Found: C, 65.18; H, 8.61%. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39%.

Synthesis of Ethyl endo-*6-Methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (15).* Ethyl acetoacetate (0.52 g, 4.0 mmol) dissolved in THF (5 ml) was added to sodium hydride (60% in oil, 0.19 g, 4.8 mmol) suspended in THF (15 ml) at 0 °C. After 20 min butyllithium (1.70 M hexane solution, 2.6 ml, 4.4 mmol) was added and the reaction mixture was stirred for 20 min at 0 °C. (*Z*)-1-Bromo-2-butene (0.60 g, 4.4 mmol) dissolved in THF (3 ml) was then added and stirred for 45 min. Workup and purification by column chromatography (benzene–ethyl acetate=30:1) gave ethyl (*Z*)-3-oxo-6-octenoate (0.65 g, 89% yield): bp 73 °C (bath temperature)/0.03 Torr; ^{1}H-NMR (CCl_4) δ=1.27 (t, J=6.9 Hz, 3H), 1.60 (d, J=5.1 Hz, 3H), 2.1—2.7 (m, 4H), 3.27 (s, 2H), 4.10 (q, J=6.9 Hz, 2H), 5.1—5.7 (m, 2H); IR 2980, 1745, 1326, 1237, 1032 cm^{-1}; MS m/z (rel intensity) 184 (M^+, 17), 166 (5), 112 (47), 97 (71), 69 (79), 55 (100). Found: C, 64.97; H, 8.79%. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75%.

The β-keto ester (0.57 g, 3.1 mmol) was converted into the corresponding diazo compound with *p*-toluenesulfonyl azide (0.64 g, 3.2 mmol) and triethylamine (0.49 ml, 3.5 mmol) in acetonitrile (10 ml) (r.t., 4 h). The diazo compound was then heated in toluene (10 ml) with $Cu(acac)_2$ (0.10 g) at reflux for 8 h. Concentration and column chromatography (benzene–ethyl acetate=30:1) gave **15** (0.36 g, 63% yield): bp 105—109 °C (bath temperature)/1 Torr; ^{1}H-NMR (CCl_4) δ=1.17 (d, J=6.6 Hz, 3 H), 1.32 (t, J=6.9 Hz, 3H), 1.5—2.7 (m, 6H), 4.12 (q, J=6.9 Hz, 2H); IR 3000, 1755, 1730 cm^{-1}; MS m/z (rel intensity) 183 (M^++1, 10), 182 (M^+, 10), 154 (44), 137 (88), 136 (86), 112 (100), 80 (66), 57 (97). Found: C, 65.88; H, 7.73%. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74%.

Synthesis of Ethyl 6-Phenyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (9). This compound was prepared similarly starting from (*E*)-3-chloro-1-phenyl-1-propene in 68% overall yield: mp 86.0—86.5 °C (hexane, prism); ^{1}H-NMR ($CDCl_3$) δ=0.88 (t, J=7.2 Hz, 3H), 2.0—2.5 (m, 4H), 2.90 (d, J=5.4 Hz, 1H), 3.1—3.3 (m, 1H), 3.91 (q, J=7.2 Hz, 2H), 7.2—7.4 (m, 5H); IR ($CHCl_3$) 2970, 1746, 1724, 1503, 1375, 1348, 1180, 1036 cm^{-1}; MS m/z (rel intensity) 245 (M^++1, 7), 244 (M^+, 20), 198 (53), 170 (30), 157 (28), 129 (100), 115 (43), 91 (40). Found: C, 73.82; H, 6.44%. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60%.

Transformation of 1 into Ethyl-2-Oxo-5-vinyltetrahydrofuran-3-carboxylate (2). *A Typical Procedure for the Transformation with BTS*: Diethyl 2-vinyl-1,1-cyclopropanedicarboxylate (**1**) (82 mg, 0.4 mmol) dissloved in 1,2-dichloroethane (2 ml) was heated to reflux in the presence of BTS (0.20 g, 0.8 mmol) for 1 h. The reaction mixture was poured into brine (10 ml) and extracted with ethyl acetate (10 ml×3). Column chromatography (silica gel, benzene–ethyl acetate=30:1) gave the γ-butyrolactone (**2**) (70 mg, 98% yield): bp 125—130 °C (bath temperature)/0.06 Torr; ^{1}H-NMR (CCl_4) δ=1.34 (t, J=6.9 Hz, 3H), 2.0—2.9 (m, 2H), 3.48 (dd, J=9.6, 5.7 Hz, 1H), 4.24 (q, J=6.9 Hz, 2H), 4.7—5.2 (m, 1H), 5.2—5.6 (m, 2H), 5.7—6.2 (m, 1H); IR 3000, 1780, 1740, 1162 cm^{-1}; MS m/z (rel intensity) 184 (M^+, 3), 183 (2), 155 (18), 137 (51), 110 (100). Found: C, 58.57; H, 6.65%. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57%.

Reaction of Diethyl 2-Vinyl-1,1-cyclopropanedicarboxylate with Sulfuric Acid. The compound **1** (72 mg, 0.34 mmol) dissolved in 1,2-dichloroethane (2 ml) was treated with sulfuric acid (97%, 0.01 ml) at 0 °C for 5 h. Workup and preparative TLC (hexane–ethyl acetate=2:1) gave **2** (R_f 0.40—0.50, 38 mg, 61% yield) and diene **3** (9 mg, 14% yield). The diene **3** gave bp 97 °C (bath temperature)/1 Torr; ^{1}H-NMR (CCl_4) δ=1.29 (t, J=6.9 Hz, 3H), 1.32 (t, J=6.9 Hz, 3H), 1.91 (d, J=6.0 Hz, 3H), 4.16 (q, J=6.9 Hz, 2H), 4.20 (q, J=6.9 Hz, 2H), 6.17 (dq, J=6.0, 15.0 Hz, 1H), 6.50 (dd, J=10.5, 15.0 Hz, 1H), 7.11 (d, J=10.5 Hz, 1H); IR 2999, 1738, 1728, 1643, 1605, 1240, 1058, 980 cm^{-1}; MS m/z (rel intensity) 210 (M^+, 50), 197 (19), 171 (56), 169 (60), 138 (67), 137 (67), 121 (100), 110 (86). Found: m/z 212.1054. Calcd for $C_{11}H_{16}O_4$: M, 212.1048.

Reaction of Diethyl 2-Vinyl-1,1-cyclopropanedicarboxylate with Trimethylsilyl Perchlorate. Trimethylsilyl perchlorate was prepared by mixing silver perchlorate (100 mg, 0.48 mmol) and chlorotrimethylsilane (72 mg, 0.48 mmol) in benzene at room temperature for 30 min and filtration of the precipitated salt. To the benzene solution of the catalyst, diethyl 2-vinyl-1,1-cyclopropanedicarboxylate **1** (53 mg, 0.25 mmol) in benzene (2 ml) was added and the mixture was stirred at room temperature for 2 h. Preparative TLC (hexane–ethyl acetate=10:1) gave **2** (18 mg, 39% yield) and **4a** (34 mg, 47% yield). The compound **4a** gave bp 110—113 °C (bath temperature)/0.05 Torr; ^{1}H-NMR (CCl_4) δ=1.23 (t, J=7.2 Hz, 4H), 1.24 (t, J=7.2 Hz, 2H), 2.4—2.9 (m, 2H), 3.0—3.5 (m, 3H), 4.08 (q, J=7.2 Hz, 2.7H), 4.11 (q, J=7.2 Hz, 1.3H), 5.3—5.8 (m, 2H), 6.9—7.4 (m, 5H); IR 3000, 1736, 1610, 970, 746, 698 cm^{-1}; MS m/z (rel intensity) 291 (M^++1, 1), 290 (M^+, 2), 271 (2), 199 (11), 130 (100), 115 (26), 91 (33). Found: C, 70.59; H, 7.81%. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64%.

Reaction of 1 with Iodotrimethylsilane. To diethyl 2-vinyl-1,1-cyclopropanedicarboxylate (0.07 g, 0.33 mmol) dissolved in 1,2-dichloroethane (2 ml), iodotrimethylsilane (0.07 ml, 0.72 mmol) was added at room temperature. The reaction mixture was stirred for 18 h. Column chromatography (silica gel, hexane–ethyl acetate=5:1) gave diethyl (4-iodo-2-butenyl)propanedioate (**4b**) whose structure was assigned spectrometrically (0.10 g, 87% yield): ^{1}H-NMR (CCl_4) δ=1.30 (t, J=6.9 Hz, 3H), 2.58 (dd, J=6.9, 4.8 Hz, 2H), 3.30 (t, J=6.9 Hz, 1H), 3.80 (t, J=6.6 Hz, 2H), 4.19 (q, J=6.9 Hz, 2H), 5.7—5.9 (m, 2H); IR 3000, 1758, 1738, 1235, 1155, 1035 968 cm^{-1}; MS m/z (rel intensity) 249 (14), 213 (M^+−I, 57), 181 (15), 139 (46), 111 (55), 95 (54), 67 (100).

*Ethyl 2-Oxo-5-(*trans-*1-propenyl)tetrahydrofuran-3-carboxylate (6)*: Bp 137—138 °C (bath temperature)/0.055 Torr; ^{1}H-NMR ($CDCl_3$) δ=1.13 (d, J=6.0 Hz, 3H), 1.35 (t, J=6.9 Hz, 3H), 1.80 (d, J=6.3 Hz, 3H), 2.53 (ddq, J=6.0, 11.8, 10.4 Hz, 1H, H_b), 3.10 (d, J=11.8 Hz, 1H, H_a), 4.24 (q(J=6.9 Hz)+dd (H_c), totally 3H), 5.51 (dd, J=14.7, 7.2 Hz, 1H), 5.80 (dq, J=14.7, 6.3 Hz, 1H); The coupling constant J_{ab}=11.8, J_{bc}=10.4 Hz is consistent to the *trans*-relationship of protons on γ-butyrolactone

** 1 M=1 mol dm^{-1}.

*** 1 Torr=133.322 Pa.

ring.[20] IR 2980, 1782, 1738, 1174, 966 cm^{-1}; MS *m/z* (rel intensity) 213 ($M^+ + 1$, 2), 212 (M^+, 2), 167 (33), 139 (94), 115 (52), 98 (84), 95 (88), 86 (100). Found: C, 62.29; H, 7.72%. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H. 7.60%.

*4-(1-*trans*-Propenyl)-3,7-dioxabicyclo[3.3.0]octane-2,8-dione (8)*: Bp 143—146°C (bath temperature)/0.04 Torr; ^{1}H-NMR (CCl_3) δ=1.85 (d, J=6.3 Hz, 3H), 3.2—3.6 (m, 1H, H_b), 3.73 (d, J=9.3 Hz, 1H, H_e), 4.34 (dd, J=10.3, 3.1 Hz, 1H, H_d), 4.65 (dd, J=10.3, 6.7 Hz, 1H, H_c), 4.83 (dd, J=7.4, 6.7 Hz, 1H, H_a), 5.61 (dd, J=7.4, 15.0 Hz, 1H), 6.06 (dq, J=6.3, 15.0 Hz, 1H); IR 2940, 1800, 1755, 1193, 964 cm^{-1}; MS *m/z* (rel intensity) 183 ($M^+ + 1$, 3), 182 (M^+, 14), 167 (18), 85 (100), 68 (81). Found: C, 59.18; H, 5.53%. Calcd for $C_9H_{10}O_4$: C, 59.33; H, 5.53%.

4-Propyl-3-oxabicyclo[3.3.0]octane-2,8-dione (12): Bp 128—130°C (bath temperature)/0.03 Torr; ^{1}H-NMR (CCl_4) δ= 1.01 (t, J=7.6 Hz, 3H), 1.1—2.6 (m, 8H), 2.9—3.4 (m, 1H), 3.4—3.6 (m, 1H), 4.2—4.4 (m, 0.18H), 4.5—4.8 (m, 0.82H); upon irradiation at δ 1.78 the multiplet at δ 4.2—4.4 (ascribed to **12b**) turned into a doublet (J=4.2 Hz) and the one at δ 4.5—4.8 (attributed to **12a**) to a doublet of J=5.0 Hz. IR 2960, 1786, 1738, 1187, 1139 cm^{-1}; MS *m/z* (rel intensity) 183 ($M^+ + 1$, 1), 182 (M^+, 5) 139 (19), 110 (27), 68 (100). Found: C, 65.75; H, 7.90%. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74%.

4-Methyl-3-oxabicyclo[3.3.0]octane-2,8-dione (14) Obtained by the Reaction of exo*-6-Methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (13)*: Bp 110—115°C (bath temperature)/0.03 Torr; ^{1}H-NMR ($CDCl_3$) δ=1.49 (d, J=6.9 Hz, 3H), 1.8—2.6 (m, 4H), 2.9—3.4 (m, 1H), 3.43 (d, J=7.6 Hz, 0.65H), 3.50 (dd, J=7.8, 1.6 Hz, 0.35H), 4.49 (dq, J=6.3, 4.5 Hz, 0.35H), 4.84 (dq, J=6.3, 5.1 Hz, 0.65H); upon irradiation at δ 1.49 the double of quartet at higher field turned to a doublet (J=4.5 Hz) and the one at lower field to a doublet of J= 5.1 Hz. IR 2980, 1784, 1734, 1186, 1140 cm^{-1}; MS *m/z* (rel intensity) 155 ($M^+ + 1$, 12), 154 (M^+, 12), 110 (45), 82 (25), 68 (100). Found: C, 62.07; H, 6.56%. Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.54%.

4-Methyl-3-oxabicyclo[3.3.0]octane-2,8-dione from endo*-6-Methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (15)*: ^{1}H-NMR ($CDCl_3$) δ=1.48 (d, J=6.9 Hz, 3H), 1.6—2.6 (m, 4H), 2.8—3.5 (m+d (δ 3.38, J=8.4 Hz), 1H), 4.2—4.4 (m, 0.77H), 4.4—4.8 (m, 0.23H).

4-Phenyl-3-oxabicyclo[3.3.0]octane-2,8-dione (10): Bp 148—155°C (bath temperature)/0.04 Torr; ^{1}H-NMR (CCl_4) δ= 1.9—2.7 (m, 4H), 3.2—3.5 (m+d (δ 3.45, J=7.7 Hz), 2H), 5.23 (d, J=4.2 Hz, 1H), 7.1—7.6 (m, 5H); IR 3030, 2960, 1785, 1748, 1496, 1457, 1163, 699 cm^{-1}; MS *m/z* (rel intensity) 217 ($M^+ + 1$, 5), 216 (M^+, 14), 198 (24),174 (14), 149 (36), 110 (41), 105 (56), 91 (22), 67 (100). Found: C, 72.46; H, 5.46%. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59%.

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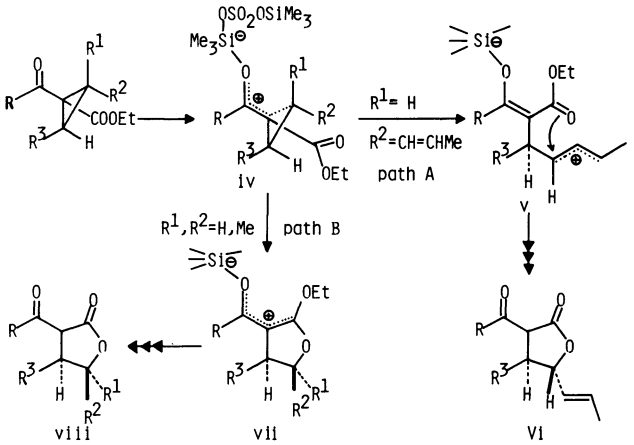

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