Studies on 5-8 Fused Ring Compounds. VI. Synthesis of Tricyclo[9.3.0.0^{3,7}]tetradec-3-ene-5,10-dione and Related Compounds

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(Received August 26, 1992)

The C_5–C_8–C_5 fused ring compounds (the title compound, **11**) constituting the carbon skeletal ring of ophiobolane sesterterpenes have been synthesized from one of the photoadducts, 1-acetoxytricyclo[5.4.0.0^{2,6}]undecan-8-one (**4a**) of cyclopentene and 3-acetoxy-2-cyclohexen-1-one. The photoadduct **4a** was converted via bromination and retro-aldol cleavage into 5-bromobicyclo[6.3.0]undecane-2,6-dione (**8**). The allylation of **8** with allyltributyltin and oxidation of the allyl group with palladium(II) chloride-copper(I) chloride yielded 5-acetonylbicyclo[6.3.0]undecane-2,6-dione (**10a**). Under basic conditions, the intramolecular cyclization of **10a** afforded the title compound **11**, and was accompanied by tetracyclo[9.3.0^{1,5}.0^{5,8}]tetradecane-2,7-dione (**12**). Under acidic conditions, **10a** cyclized to 2-methyl-4,5,6a,7,8,9,9a,10-octahydro-6*H*-cyclopenta[6,7]cycloocta[1,2-*b*]furan-6-one (**13**). The structures of **8**, **11**, **12**, and **13** were determined by X-ray analyses.

The C_5–C_8–C_5 fused ring system exists amongst ophiobolins[1] and celoplastols[2] of sesterterpenes, or fusicoccin[3] and cotylenins[4] of diterpenes. In the preceding papers[5] we reported that the photocycloaddition of bicyclo[4.3.0]nonane-2,4-dione to cyclopentene afforded directly C_5–C_8–C_5 fused ring compounds. In the major product, however, the carbon skeleton of the C_5–C_8–C_5 fused ring differs from that of ophiobolins, fusicoccin, etc. Previously we reported photocycloaddition of dimedone enol acetate to cyclopentene, and indicated that the isolated photoadducts, 1-acetoxy-10,10-dimethyltricyclo[5.4.0.0^{2,6}]undecan-8-one (**1a** and **1b**), undergo retro-aldol cleavage under acidic conditions to give 4,4-dimethylbicyclo[6.3.0]-undecane-2,6-dione (**2**) containing a C_5–C_8 fused ring.[6] Whereas under basic conditions both **1a** and **1b** do not undergo retro-aldol cleavage, and they readily lose the acetic acid to yield an α,β-unsaturated ketone (**3**).[6] The object of the present study is to synthesize the C_5–C_8–C_5 fused ring compounds such as the ophiobolane ring by retro-aldol cleavage of photoadducts.

Results and Discussion

The irradiation of 3-acetoxy-2-cyclohexen-1-one in cyclopentene by high-pressure mercury arc,[7] yielded a mixture of two stereoisomeric photoadducts, **4a** and **4b**, in a ratio of ca. 2:1. The configurations of **4a** and **4b** were assigned by comparing ^{1}H NMR and IR spectral data with those of **1a** (cis-transoid-cis) and **1b** (trans-cisoid-cis), of which the relative configurations were determined by lanthanide induced shifts of ^{1}H NMR in a previous report.[6] The ^{1}H NMR spectra of **1b** and **4b** have signals for the H(C6) atom at δ=3.30 and 3.25, respectively, in unusually low magnetic field. While those of **1a** and **4a** show the signals with normal δ values, 2.48 and 2.55, respectively. The difference can be explained in terms of the anisotropic low-field shift due to the proximity of the ester carbonyl group in **1b** and **4b**. In addition, IR spectrum of **4b** shows a ketonic carbonyl absorption at the unusually large wave number of 1732 cm^{-1} similar to **1b** (1730 cm^{-1}) which indicates the presence of a large strain in the six-membered ring of **4b**. Therefore **4a** corresponds to **1a** (cis-transoid-cis configuration), and **4b** to **1b** (trans-cisoid-cis configuration).

The photoadducts, **4a** and **4b** underwent retro-aldol cleavage in methanol containing hydrochloric acid[8] at room temperature to yield a mixture of two stereoisomers of bicyclo[6.3.0]undecane-2,6-dione, **5a** and **5b**. The major product was **5a**, and **5b** isomerized readily to **5a** at room temperature in acidic or alkaline methanol (Fig. 1). Begley et al.[9] have synthesized **5a** and determined the trans-fusion of the rings by X-ray analysis. Therefore, the ring fusion of **5a** is trans and that of **5b** is cis. In such C_5–C_8 fused ring compounds, a trans isomer is more stable than a cis isomer.[10]

Under basic conditions **4a** and **4b** readily lost acetic acid to yield an α,β-unsaturated ketone **6**.[7] Therefore, the alkylation of **4a** or **4b** is unsuccessful under basic conditions.

The reaction of the photoadduct **4a** with pyridinium tribromide gave a monobromide **7**, as the major product. Under acidic conditions **7** underwent retro-aldol cleavage to yield **8**. The molecular structure of **8** was determined by X-ray analysis.[11] By treating **8** in toluene with allyltributyltin in the presence of azobisisobutyronitrile (AIBN) at 80°C,[12] the bromine atom was substituted by an allyl group to yield **9a** predominantly. In this reaction small amount of **9b** was also yielded, and **9b** was isomerized readily to **9a** at room temperature in alkaline methanol.

The oxidation of **9a** with palladium(II) chloride and

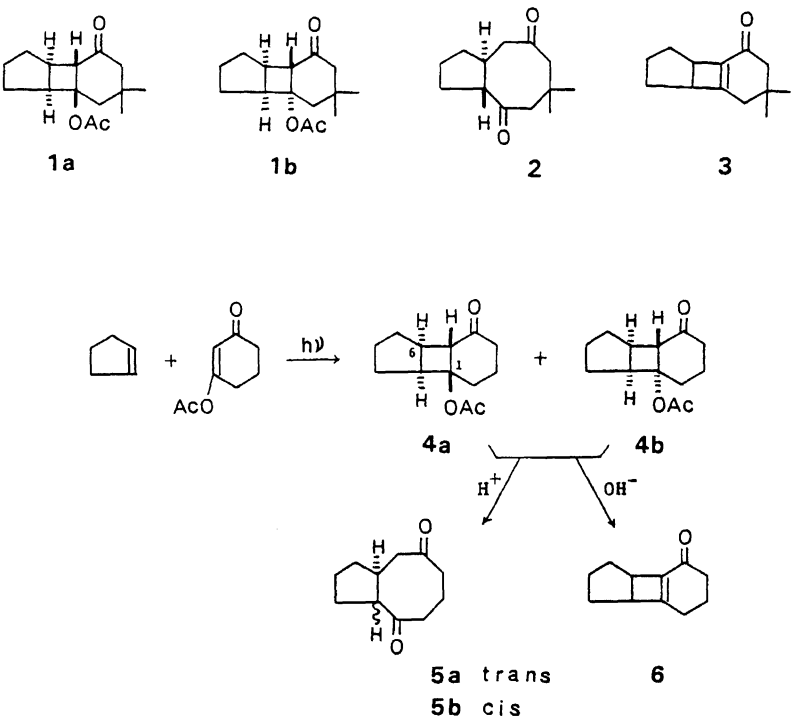


Fig. 1.

copper(I) chloride in *N*,*N*-dimethylformamide (DMF) under oxygen atmosphere[13] afforded the acetonyl compound **10a**, while **9b** was oxidized to **10b** in a similar manner. Compounds **10a** and **10b** are epimers. Their relative configurations were elucidated by nuclear Overhauser effect (NOE) experiments of ^{1}H NMR spectroscopy at 400 MHz. An NOE enhancement of either H(C5) or H(C8) was observed in **10a** upon irradiation of H(C8) or H(C5), whereas NOE enhancement between H(C1) and H(C5) was not observed. Therefore in **10a** H(C5) and H(C8) exist in cis-configuration, while H(C1) and H(C5) exist in trans. With a similar procedure the configuration of **10b** was assigned as shown in Fig. 2.

The intramolecular aldolization of the acetonyl compound **10a** under basic conditions at room temperature, though unsatisfactory yields, afforded the desired C_5–C_8–C_5 fused ring compound, tricyclo[9.3.0.0^{3,7}]tetradec-3-ene-5,10-dione (**11**) accompanying with tetracyclo[9.3.0.0^{1,5}.0^{6,9}]tetradecane-2,7-dione (**12**). The structures of **11** and **12** were determined by X-ray analyses (Fig. 3).[14] The configurations of H(C1), H(C7), and H(C11) in **11** at ring junctions are the same as those of ophiobolin G.[15] The configuration of H(C7) in **11** is different from that of H(C5) in **10a**, suggesting that in the intramolecular aldolization of **10a** to **11** the epimerization of H(C5) in **10a** occurred under basic conditions. Conformation of the eight-membered ring in **11** is a boat-chair (BC) form,[14] as in bromo dione **8**[11] (Fig. 4). Torsion angles for the eight-membered ring in these compounds are compared in Table 1. The deviation parameter, ΔBC,[16] which is a measure of fit to the symmetrical BC conformation, is 4.8° for **11** and 18.7° for **8**.[6] It is remarkable that the BC form of **11** is excellent in symmetry comparing with other C_5–C_8–C_5 fused ring compounds prepared in preceding paper.[5] The larger distortion of **8** may be attributed to the steric interactions involving the Br atom. The compound **12** has a C_5–C_5–C_5–C_5 fused ring, which might be formed by a transannular reaction in the eight-membered ring of **10a**. Formation of a compound similar to **12** has been reported for ophiobolin D derivative.[17]

Under acidic conditions (HCl–methanol) at room temperature the acetonyl compound **10a** afforded furan compound **13** in a high yield. The structure of **13** was also confirmed by X-ray analysis.[11]

Experimental

Melting points were uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL-400 (400 MHz) spectrometer in $CDCl_3$ with TMS as the internal standard. The IR spectra were recorded using JASCO IR-G spectrometer. The mass spectra were obtained with a Hitachi M-80B mass spectrometer. The GC analyses were carried out on a 263-50 Hitachi gas chromatography. Column chromatography was carried out with silica gel (Wacogel C-300).

1- Acetoxytricyclo[5.4.0.0^{2,6}]undecan- 8- one (4a and 4b). A solution of 3-acetoxy-2-cyclohexen-1-one (30.0 g, 0.195 mol) in cyclopentene (350 ml) was irradiated for 20 h in a Pyrex tube with 400 W high-pressure mercury arc at 12—15°C in a nitrogen atmosphere. After removal of the cyclopentene with distilation, the remaining residue was subjected to column chromatography on silica gel (hexane–ether, 3:1). From the first fraction **4a** was obtained and the second fraction was a mixture of **4a** and **4b**. From the third elution **4b** was obtained. (Total 29.4 g, 0.132 mol,

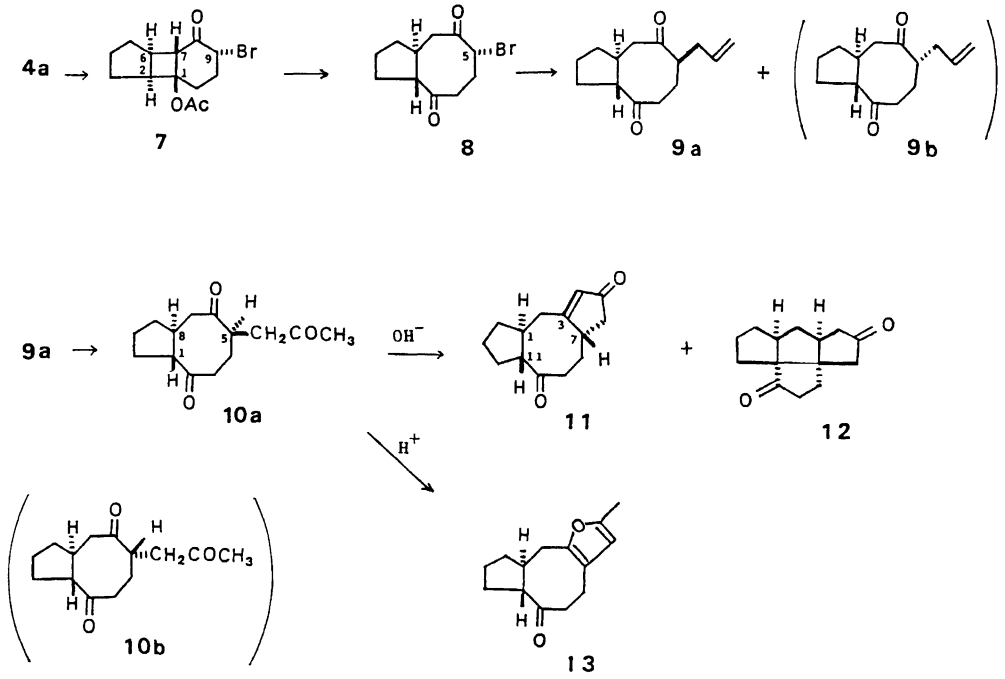


Fig. 2.

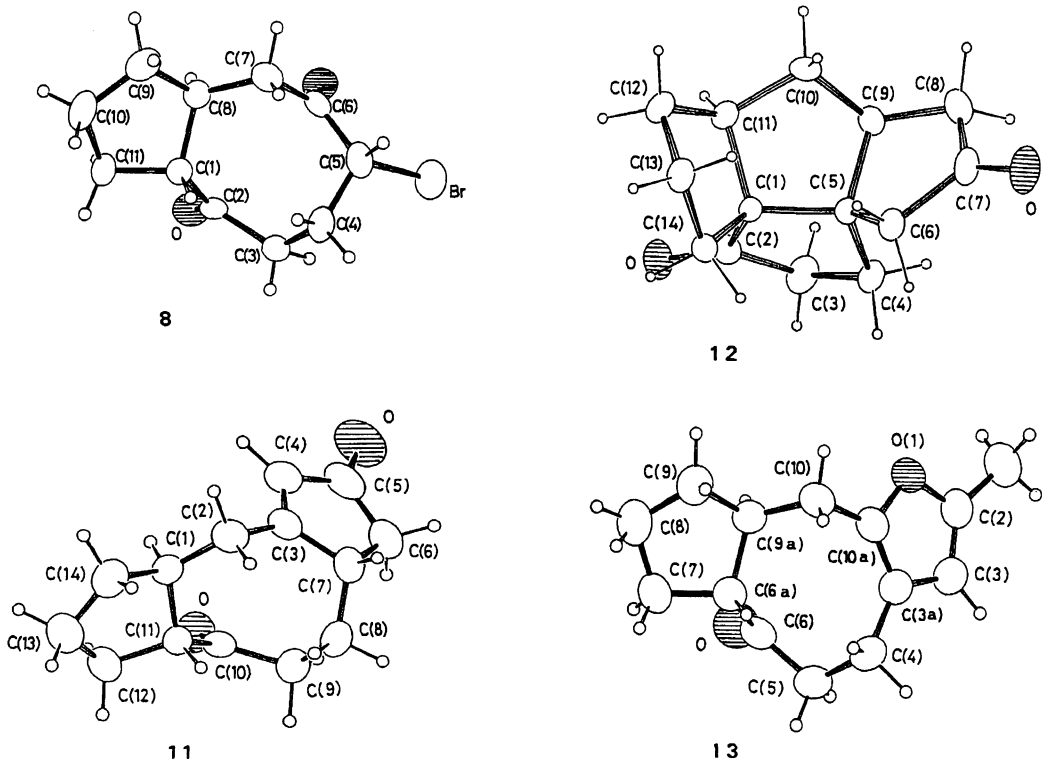
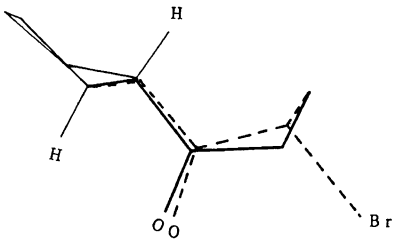


Fig. 3. Perspective views of the molecules **8**, **11**, **12**, and **13**.

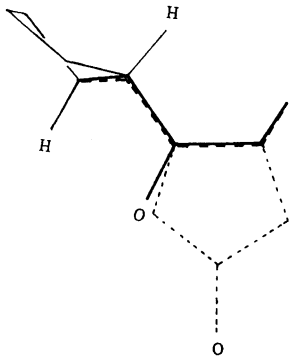
68% yield, as a mixture of **4a** and **4b**). In GC analysis of the photoadduct mixture the ratio of **4a** to **4b** was ca. 2 : 1.

4a: Mp 50—51°C (lit,[7] 48—49°C); IR (Nujol) 1730 cm^{-1} (ester C=O), 1700 cm^{-1} (ketone C=O); ^{1}H NMR ($CDCl_3$) δ=2.8 (t, 1H, H(C2)), 2.48 (m, 1H, H(C6)), 2.55 (m, 1H, H(C7)), 2.02 (s, 3H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$) δ=21.5 (OCH_3), 18.7, 25.4, 26.9, 32.6, 32.7, and 38.1 (CH_2), 39.0 (C6, CH), 47.7 (C2, CH), 55.7 (C7, CH), 78.5 (C–OAc), 169.9 (O–C=O), 210.6 (C=O); MS *m/z* (rel intensity) 222 (M^+, 3), 180(3), 162 (4), 155 (16), 134 (3), 113 (100), 84 (8), 67 (4), 55 (3), 43 (40). Found: C, 70.02; H, 8.24%. Calcd for $C_{13}H_{18}O_3$: C, 70.25; H, 8.16%.

4b: Mp 76—77°C; IR (Nujol) 1730 cm^{-1} (ester C=O), 1720 cm^{-1} (ketone C=O); ^{1}H NMR ($CDCl_3$) δ=3.30 (m, 1H,



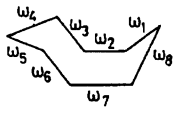
8



11

Fig. 4. The side views of the molecules **8** and **11**.

Table 1. Torsion Angles ω_{1-8}[a] (°) for Eight-Membered Rings



Compounds	Torsion angles ω_4	ω_3	ω_2	ω_1	ΔBC(°)[b]
	ω_5	ω_6	ω_7	ω_8	
8[c]	65.2	−112.3	64.2	50.4	18.7
	−70.2	98.8	−30.3	−72.7	
11[d]	65.8	−105.4	50.4	60.8	4.8
	−69.8	103.5	−41.8	−65.4	

	8	**11**
ω_1	C(3)–C(4)–C(5)–C(6)	C(9)–C(8)–C(7)–C(3)
ω_2	C(4)–C(5)–C(6)–C(7)	C(8)–C(7)–C(3)–C(2)
ω_3	C(5)–C(6)–C(7)–C(8)	C(7)–C(3)–C(2)–C(1)
ω_4	C(6)–C(7)–C(8)–C(1)	C(3)–C(2)–C(1)–C(11)
ω_5	C(7)–C(8)–C(1)–C(2)	C(2)–C(1)–C(11)–C(10)
ω_6	C(8)–C(1)–C(2)–C(3)	C(1)–C(11)–C(10)–C(9)
ω_7	C(1)–C(2)–C(3)–C(4)	C(11)–C(10)–C(9)–C(8)
ω_8	C(2)–C(3)–C(4)–C(5)	C(10)–C(9)–C(8)–C(7)

a) The positions of the torsion angles ω_{1-8} are shown below. b) Ref. 15, $\Delta BC=(|\omega_1+\omega_8|+|\omega_2+\omega_7|+|\omega_3+\omega_6|+|\omega_4+\omega_5|)/4$. c) Ref. 11. d) Ref. 14.

H(C6)), 2.90 (m, 1H, H(C2)), 2.77 (d, 1H, H(C7)), 2.00 (s, 3H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$) δ=21.9 (OCH_3), 22.6, 25.3, 26.9, 27.4, 30.4, and 39.0 (CH_2), 41.8 (C6, CH), 50.0 (C2, CH), 55.8 (C7, CH), 90.8 (C–OAc), 170.0 (O–C=O), 206.7 (C=O); MS *m/z* (rel intensity) 180 (M^+-CH_2CO, 4), 179 (M^+-CH_3CO, 6), 162 (8), 155 (6), 134 (9), 113 (100), 84 (9), 69 (9), 67 (7), 55 (6), 43 (37). Found: C, 70.31; H, 8.09%. Calcd for $C_{13}H_{18}O_3$: C, 70.25; H, 8.16%.

Bicyclo[6.3.0]undecane-2,6-dione (5a and 5b). A solution of **4a** (0.50 g, 2.25 mmol) in 5% HCl–methanol (3 ml of concd HCl and 18 ml of methanol) was left to stand for 10 d at room temperature. The reaction mixture was diluted with water and extracted with ether. The ethereal extracts were neutralized with aqueous sodium hydrogencarbonate, washed with water, and then dried over sodium sulfate. The remaining residue after the removal of the ether was subjected to silica-gel column chromatography (hexane–ether, 2:1). From the first fraction, 20 mg (0.11 mmol) of **5b** was obtained and further elution gave **5a** (0.27 g, 1.50 mmol). (total 1.61 mmol, 72%). Similarly, a solution of **4b** (0.50 g, 2.25 mmol) in 3% HCl-methanol (2 ml of concd HCl and 22 ml of methanol) was left to stand for 2 d at room temperature and worked up in the same procedure described for **4a**, 0.14 g (0.77 mmol) of **5a** and 0.10 g (0.55 mmol) of **5b** were obtained (total 1.33 mmol, 58%). **5a** and **5b** were crystallized from hexane.

5a: Mp 65—66°C (lit,[9] 64.5°C); IR (Nujol) 1700, 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=2.71 (m, 1H, H(C1)), 2.08 (m, 1H, H(C8)); ^{13}C NMR ($CDCl_3$) δ=21.5, 22.6, 29.3, 34.2, 42.8, 42.9, and 46.7 (CH_2), 44.3 (C8, CH), 56.4 (C1, CH), 211.9 and 214.5 (C2 and C6, C=O); MS *m/z* (rel intensity) 180 (M^+, 25), 152 (22), 124 (42), 113 (100), 95 (35), 84 (85), 83 (52), 81 (23), 71 (16), 67 (73), 55 (56), 43 (39), 42 (41). Found: *m/z* 180.1157. Calcd for $C_{11}H_{16}O_2$: M, 180.1152.

5b: Mp 67—68°C; IR (Nujol) 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=3.13 (m, 1H, H(C1)), 2.73 (m, 1H, H(C8)); ^{13}C NMR ($CDCl_3$) δ=23.2, 23.2, 26.0, 33.1, 43.1, 43.8, and 44.8 (CH_2), 40.9 (C8, CH), 53.7 (C1, CH), 213.1 and 214.9 (C=O); MS *m/z* (rel intensity) 180 (M^+, 49), 152 (31), 124 (97), 113 (32), 109 (15), 95 (100), 84 (62), 83 (35), 81 (45), 71 (24), 67 (76), 55 (65), 43 (47), 42 (40). Found: *m/z* 180.1155. Calcd for $C_{11}H_{16}O_2$: M, 180.1152.

Isomerization of 5b to 5a. A solution of **5b** (20 mg, 0.11 mmol) in 5% HCl-methanol (5 ml) was left to stand at room temperature for one week. The reaction mixture was extracted with ether. The usual work-up of the extracts gave a crystalline residue, and the IR spectrum was essentially identical with that of **5a**.

A solution of **5b** (30 mg, 0.17 mmol) in 2% KOH–methanol (5 ml) was left to stand at room temperature for 5 days, and extracted with ether. The usual work-up of the extracts gave a crystalline residue, and also the IR spectrum was essentially identical with that of **5a**.

1- Acetoxy- 9- bromotricyclo[5.4.0.0^{2,6}]undecan- 8-one (7). To a solution of **4a** (0.50 g, 2.25 mmol) in ethanol (12 ml), pyridinium tribromide (0.75 g, 2.3 mmol) was added with stirring. The reaction mixture was slightly warmed until orange color disappeared. The reaction mixture was diluted with water and extracted with ether. After the usual work-up of the extracts, crude product was chromatographed on silica gel (hexane–ether, 2:1), and 0.45 g (1.49 mmol, 66%) of **7** was isolated. Small amount (ca. 20

mg) of stereoisomer of **7** was also yielded but it could not be isolated as a pure form.

7: Mp 84—85°C (from hexane); IR (Nujol) 1720 cm^{-1} (ester C=O), 1710 cm^{-1} (ketone C=O); ^1H NMR ($CDCl_3$) δ=4.48 (m, 1H, CHBr), 2.02 (s, 3H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$) δ=21.4 (OCH_3), 25.3, 26.6, 30.1, 31.3, and 32.7 (CH_2), 41.5 (C6, CH), 48.2 (C2, CH), 48.5 (C9, CHBr), 54.9 (C7, CH), 77.7 (C–OAc), 169.9 (O–C=O), 202.3 (C=O); MS *m/z* (rel intensity) 243 (M^++2−CH_3COOH, 7), 241 (M^+−CH_3COOH, 7), 235 (9), 233 (9), 221 (19), 193 (98), 191 (100), 179 (21), 161 (12), 112 (25), 95 (5), 91 (12), 85 (13), 81 (8), 79 (11), 77 (8), 67 (29), 55 (21), 53 (13). Found: C, 51.97; H, 5.73%. Calcd for $C_{13}H_{17}O_3Br$: C, 51.84; H, 5.69%.

5-Bromobicyclo[6.3.0]undecane-2,6-dione (8). A solution of **7** (0.50 g, 1.66 mmol) in 6% HCl–methanol (4 ml of concd HCl and 19 ml of methanol) was left to stand at room temperature for two weeks and crystalline **8** was precipitated. After filtration of **8**, the filtrate was evaporated under reduced pressure and additional crystalline **8** was obtained (total 0.26 g, 1.00 mmol, 61%).

8: Mp 153—154°C (from acetone), sparingly soluble in various solvents; IR (Nujol) 1720, 1685 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=4.82 (dd, 1H, CHBr), 2.71 (m, 1H, H(C1)), 2.28 (m, 1H, H(C8)); ^{13}C NMR ($CDCl_3$) δ=22.1, 28.8, 30.2, 33.6, 38.7, and 43.6 (CH_2), 44.0 (C8, CH), 55.4 (C1, CH), 56.8 (C5, CHBr), 202.5 (C2, C=O), 211.9 (C6, C=O); MS *m/z* (rel intensity) 260 (M^++2, 8), 258 (M^+, 8), 232 (2), 230 (2), 193 (2), 191(3), 179 (29), 152 (94), 124 (95), 123 (57), 111 (14), 109 (12), 95 (82), 83 (97), 81 (37), 67 (100), 55 (62). Found: C, 50.86; H, 5.91%. Calcd for $C_{11}H_{15}O_2Br$: C, 50.98; H, 5.83%.

5-Allylbicyclo[6.3.0]undecane-2,6-dione (9a and 9b). A mixture of allyltributyltin (2.6 g, 7.9 mmol) and **8** (1.0 g, 3.86 mmol) in toluene (3 ml) solution containing AIBN (0.1 g, 0.6 mmol) was stirred at 80°C for 9 h in a nitrogen atmosphere.[9] The reaction mixture was extracted with ether. After the usual work-up of the extracts, the crude product was subjected to chromatography on silica gel (hexane–ether, 2:1). From the first fraction, small amount of stereoisomer **9b** was obtained (22 mg, 0.10 mmol, 2.6%), and further elution gave **9a** (0.62 g, 2.8 mmol, 73%).

9a: Mp 84—85°C (from hexane); IR (Nujol) 1700 and 1688 cm^{-1} (C=O), 1645 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ= 5.62 (m, 1H, =CH), 5.00 (m, 2H, $=CH_2$), 2.65 (m, 1H, H-(C5)), 2.59 (m, 1H, H(C1)), 2.22 (m, 1H, H(C8)); ^{13}C NMR ($CDCl_3$) δ=22.7, 28.4, 28.9, 34.1, 37.4, 41.3, and 46.5 (CH_2), 43.4 (C8, CH), 51.2 (C5, CH), 57.1 (C1, CH), 117.4 ($=CH_2$), 134.7 (=CH), 213.9 and 214.2 (C=O); MS *m/z* (rel intensity) 220 (M^+, 31), 192 (18), 164 (21), 152 (47), 137 (13), 124 (100), 110 (19), 109 (21), 95 (93), 83 (69), 67 (87), 55 (53), 41 (53). Found: *m/z* 220.1448. Calcd for $C_{14}H_{20}O_2$: M, 220.1454.

9b: Mp 79—81°C (from hexane); IR (Nujol) 1700 (shoulder) and 1695 cm^{-1} (C=O), 1645 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=5.68 (m, 1H, =CH), 5.02 (m, 2H, $=CH_2$), 2.85 (m, 1H, H(C1)), 2.76 (m, 1H, H(C5)); ^{13}C NMR ($CDCl_3$) δ=22.3, 25.8, 29.5, 33.3, 34.5, 40.9, and 46.9 (CH_2), 46.6 (C8, CH), 51.6 (C5, CH), 55.8 (C1, CH), 117.1 ($=CH_2$), 135.7 (=CH), 213.2 and 214.6 (C=O); MS *m/z* (rel intensity) 220 (M^+, 32), 192 (12), 164 (18), 152 (43), 137 (14), 124 (100), 110 (18), 109 (21), 95 (86), 83 (67), 67 (83), 55 (50), 41 (52). Found: *m/z* 220.1451. Calcd for $C_{14}H_{20}O_2$: M, 220.1454.

Isomerization of 9b to 9a. A solution of **9b** (10 mg, 0.045 mmol) in 2% KOH-methanol (2 ml) was left to stand at room temperature for 5 h. The reaction mixture was extracted with ether. The usual work-up of the extracts gave a crystalline residue, and the IR spectrum was essentially identical with that of **9a**.

5-Acetonylbicyclo[6.3.0]undecane-2,6-dione (10a and 10b). CuCl (0.10 g, 1.01 mmol) and $PdCl_2$ (36 mg, 0.2 mmol) were suspended in DMF (1 ml) and water (0.12 ml). The mixture was shaken under oxygen atmosphere until absorption of oxygen ceased. Then **9a** (0.22 g, 1.00 mmol) was added and the mixture was shaken under oxygen at room temperature for 20 h.[10] The reaction mixture was extracted with ether. After the usual work-up of the extracts, the solution was subjected to silica-gel chromatography (hexane-ether, 2:1), and 0.17 g (0.72 mmol, 72%) of **10a** was yielded.

The oxidation of **9b** (0.10 g, 0.45 mmol) with oxygen by the same procedure as **9a**, in the solution of CuCl (0.05 g, 0.50 mmol), $PdCl_2$ (16 mg, 0.09 mmol), DMF (1 ml), and water (0.1 ml) for 12 h gave 63 mg (0.27 mmol, 60%) of **10b**.

10a: Mp 109—110°C (from hexane); IR (Nujol) 1712, 1690 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=3.22 (m, 1H, H-(C5)), 2.60 (m, 1H, H(C8)), 2.40 (m, 1H, H(C1)), 2.07 (s, 3H, $COCH_3$); ^{13}C NMR ($CDCl_3$) δ=22.6, 28.6, 29.4, 30.5, 33.9, 38.6, and 49.6 (CH_2), 40.6 (C8, CH), 42.3 (C5, CH), 59.8 (C1, CH), 206.9 (C13, CH=O), 214.7 and 214.5 (C2 and C6, C=O); MS *m/z* (rel intensity) 236 (M^+, 1.5), 218 (3), 208 (12), 165 (12), 152 (14), 137 (8), 124 (35), 111 (8), 109 (7), 95 (20), 83 (33), 67 (33), 55 (57), 43 (100). Found: C, 71.23; H, 8.34%. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53%.

10b: Mp 100—101°C (from hexane); IR (Nujol) 1720, 1685 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=3.27 (m, 1H, H-(C5)), 2.85 (m, 1H, H(C1)), 2.16 (s, 3H, $COCH_3$), 1.94 (m, 1H, H(C8)); ^{13}C NMR ($CDCl_3$) δ=22.3, 26.6, 29.5, 30.0, 34.5, 41.3, 44.1, and 46.4 (CH_2), 46.7 (C8, CH), 47.2 (C5, CH), 56.1 (C1, CH), 206.9 (C13, C=O), 212.6 and 214.4 (C2 and C6, C=O). Found: C, 71.11; H, 8.58. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53%

Intramolecular Cyclization of 10a. Tricyclo-[9.3.0.$0^{3,7}$]tetradec-3-ene-5,10-dione (11) and Tetracyclo[9.3.0.$0^{1,5}$.$0^{5,9}$]tetradecane-2,7-dione (12). A solution of **10a** (0.60 g, 2.54 mmol) in 3% NaOH/methanol–water (1:1) (40 ml) was left to stand at room temperature for 20 h. The reaction mixture was neutralized with 1 M hydrochloric acid (1 M=1 mol dm^{-3}) and extracted with ether. After the usual work-up of the extracts, the crude products was subjected to silica-gel chromatography (hexane-ether, 2:1), and **12** was eluted (33 mg, 0.15 mmol, 5.5%). In following elution with hexane-ether (1:1) starting material **10a** (75 mg, 0.34 mmol) was eluted, and further elution gave **11** (102 mg, 0.47 mmol, 18.5%).

11: Mp 108—110°C; IR (Nujol) 1700—1680 cm^{-1} (C=O), 1602 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=5.91 (s, 1H, =CH), 3.16 (m, 1H, H(C7)), 2.87 (m, 1H, H(C11)), 1.86 (m, 1H, H(C1)); ^{13}C NMR ($CDCl_3$) δ=22.5 (C13), 23.1 (C8), 29.3 (C12), 34.4 (C14), 35.0 (C2), 38.8 (C6), and 39.6 (C9) (CH_2), 43.3 (C7, CH), 52.0 (C1, CH), 53.8 (C11, CH), 133.9 (C4, =CH), 181.4 (C3, =C<), 207.5 (C5, C=O), 214.0 (C10, C=O); MS *m/z* (rel intensity) 218 (M^+, 65), 200 (44), 190

(6), 175 (5), 162 (12), 150 (23), 133 (14), 122 (15), 108 (18), 105 (16), 95 (100), 91 (23), 79 (22), 77 (19), 67 (26), 55 (21). Found: m/z 218.1302. Calcd for $C_{14}H_{18}O_2$: M, 218.1307.

12: Mp 78—80°C; IR (Nujol) 1735 (shoulder) and 1725 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=2.55 and 2.47 (m, 1H, H(C9) and H(C11)); ^{13}C NMR ($CDCl_3$) δ=27.4, 31.9, 32.0, 33.3, 36.2, 39.7, 41.5, and 45.9 (CH_2), 47.0 and 54.1 (CH), 59.2 and 63.2 (quaternary C), 218.1 and 224.1 (C=O); MS m/z (rel intensity) 218 (M^+, 12), 190 (6), 177 (40), 149 (14), 133 (13), 119 (24), 105 (35), 91 (100), 79 (72), 77 (61), 67 (46), 55 (42), 41 (94). Found: m/z 218.1310. Calcd for $C_{14}H_{18}O_2$: M, 218.1307.

2-Methyl-4,5,6a,7,8,9,9a,10-octahydro-6*H*-cyclopenta[6,7]cycloocta[1,2-*b*]furan-6-one (13). A solution of **10a** (0.30 g, 1.27 mmol) in 5% HCl-methanol (20 ml) was left to stand at room temperature for 2 d. After the removal of methanol under reduced pressure, crystalline **13** was obtained by filtration. (0.23 g, 1.06 mmol, 83%): Mp 70—71°C (from hexane); IR (Nujol) 1695 cm^{-1} (C=O), 1635 and 1575 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=5.73 (s, 1H, =CH), 2.85 (m, 1H, H(C6a)), 2.15 (s, 3H, CH_3), 1.9 (m, 1H, H(C9a)); ^{13}C NMR ($CDCl_3$) δ=13.4 (CH_3), 19.9 (C10), 23.6 (C9), 30.8 (C7), 32.0 (C4), 33.6 (C8) and 46.9 (C5) (CH_2), 47.9 (C9a, CH) and 55.5 (C6a, CH), 107.6 (C3, =CH), 118.6 (C3a, =C<), 149.2 and 149.3 (=C–O), 215.17 (C=O); MS m/z (rel intensity) 218 (M^+, 100), 190 (10), 175 (10), 150 (58), 122 (48), 108 (70), 79 (13), 95 (13), 67 (8), 43 (25). Found: m/z 218.1304. Calcd for $C_{14}H_{18}O_2$: M, 218.1307.

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