Synthesis of α-Methylene-γ-lactones involving Baeyer–Villiger Oxidation of α-Substituted Cyclobutanones

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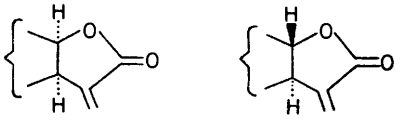
The previously reported 7-*exo*-halogeno-7-*endo*-methylbicyclo[3.2.0]heptan-6-ones (3) and (13) and 7-*exo*-bromo-7-*endo*-methylbicyclo[3.2.0]hept-2-en-6-one (1) were converted into the corresponding α-methylene-γ-lactones (31) and (33) in two steps, involving Baeyer–Villiger oxidation and dehydrohalogenation. Similarly, 7-*exo*-bromo-7-*endo*-isopropylbicyclo[3.2.0]hept-2-en-6-one (11) gave the isopropylidene-lactone (34), and the bromomethylbicyclo-octanone (5) gave the lactone (32). In contrast, oxidation and dehydrobromination of 7-*endo*-bromo-7-*exo*-methylbicyclo[3.2.0]hept-2-en-6-one (2) and 7-*endo*-bromo-7-*exo*-methylbicyclo[3.2.0]-heptan-6-one (4) gave the αβ-unsaturated lactones (36) and (35), respectively.

THE biological activity of compounds possessing the α-methylene-γ-lactone unit [1] has led to recent interest in the development of synthetic routes to this system.[2] In particular, pathways to compounds in which the α-methylene-γ-lactone system is *cis*- (A) or *trans*-fused (B) to an alicyclic ring have been sought.

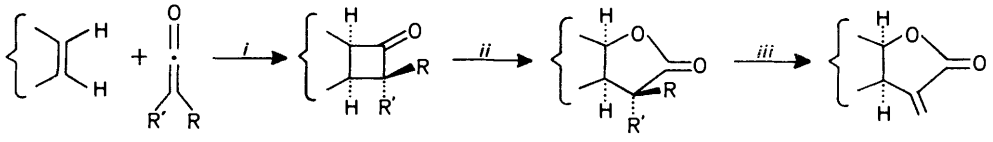


(A) (B)

A route to *cis*-fused bicyclic α-methylene-γ-lactones [type (A)] that had been overlooked hitherto involves the three-step elaboration of an alkene as illustrated in Scheme 1.[3] The route entails cycloaddition of a keten and olefin (step i), Baeyer–Villiger oxidation of the resultant cyclobutanone (step ii) and modification of R and R′ to give the exocyclic methylene group (step iii).

The role of the substituents R and R′ is twofold: first they must be readily convertible into the exocyclic-methylene function and, secondly, they must direct the mode of ring expansion in the preceding oxidation step. With these two factors in mind we chose to investigate the feasibility of the sequence using R′ = halogen and R = alkyl; advantageously, the properties of the appropriate ketens had been described previously.[4]

Various cyclic alkenes were used as substrates for the alkylhalogenoketens in the initial cycloaddition reaction; the results are summarized in the Table. By employing hexane as the solvent and by conducting the cyclo-additions at or above room temperature *endo*-alkyl-*exo*-halogenocyclobutanone derivatives were formed as major products.[5,6] Separations of the isomeric products were achieved readily by distillation and/or column chromatography.



SCHEME 1

Cycloaddition of alkylhalogenoketens to cyclic olefins

Olefin	Keten	Reaction temp. (°C)	Yield (%)	Products (isomer ratio)	Reference [yield (%); isomer ratio]
Cyclopentadiene	Bromo(methyl)keten	25	70	(1), (2) (1.4 : 1)	5 [—; 1.1 : 1]
Cyclopentene		65	40	(3), (4) (8 : 1)	6 [37; 1.3 : 1]
Cyclohexene		65	50	(5), (6) (1.1 : 1)	
Dihydropyran		25	70	(7), (8) (1.5 : 1)	*a* [50; 0.6 : 1]
Cyclopentadiene	Chloro(methyl)keten	40	86	(9), (10) (4.5 : 1)	6 [61; 4.5 : 1]
Cyclopentadiene	Bromo(isopropyl)keten	40	74	(11), (12) (7 : 1)	5 [78; 7.4 : 1]

[a] W. T. Brady and R. Roe, *J. Amer. Chem. Soc.*, 1971, **93**, 1662.

As expected, the oxidations of the bicycloalkanones (3)—(5), (7), and (13) with *m*-chloroperbenzoic acid proceeded with migration of the bridgehead carbon atom exclusively to give the corresponding lactones (14)—(18) in high yield.[7] Baeyer–Villiger oxidations of the

[1] A. T. McPhail, K. D. Onan, K.-H. Lee, T. Ibuka, and H.-C. Huang, *Tetrahedron Letters*, 1974, 3203; K.-H. Lee, T. Ibuka, M. Kozuka, A. T. McPhail and K. D. Onan, *ibid.*, 1975, 2287; K.-H. Lee, T. Ibuka, S.-H. Kim, B. R. Vestal, and I. H. Hall, *J. Medicin. Chem.*, 1975, **18**, 812 and references therein.

[2] P. A. Grieco, *Synthesis*, 1975, 67; R. B. Gammill, C. A. Wilson, and T. A. Bryson, *Synth. Comm.*, 1975, **4**, 245; T. Minami, I. Niki, and T. Agawa, *J. Org. Chem.*, 1974, **39**, 3236; L. S. Hegedus, S. D. Wagner, E. L. Waterman, and K. Siirala-Hansen, *ibid.*, 1975, **40**, 593; J. A. Marshall and W. R. Snyder, *ibid.*, p. 1656; *Synth. Comm.*, 1975, **5**, 43; P. A. Grieco, N. Marinovic, and M. Miyashita, *J. Org. Chem.*, 1975, **40**, 1670; M. Kato, M. Kageyama, R. Tanaka, K. Kuwahara, and A. Yoshikoshi, *ibid.*, p. 1932; D. Caine and G. Hasenhuettl, *Tetrahedron Letters*, 1975, 743; P. A. Grieco, C. J. Wang, and S. D. Burke, *J.C.S. Chem. Comm.*, 1975, 537; A. D. Harmon and C. R. Hutchinson, *J. Org. Chem.*, 1975, **40**, 3474.

[3] Preliminary communication, S. M. Ali and S. M. Roberts, *J.C.S. Chem. Comm.*, 1975, 887.

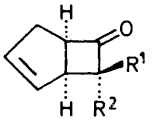
[4] W. T. Brady, *Synthesis*, 1971, 415.

[5] W. T. Brady and R. Roe, *J. Amer. Chem. Soc.*, 1970, **92**, 4618.

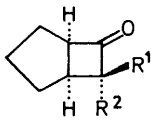
[6] W. T. Brady, R. Roe, E. F. Hoff, and F. H. Parry, *J. Amer. Chem. Soc.*, 1970, **92**, 146.

[7] J. B. Lee and B. C. Uff, *Quart. Rev.*, 1967, **21**, 429; P. A. Grieco, *J. Org. Chem.*, 1972, **37**, 2363.

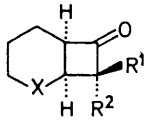
analogous bicycloalkenones (1), (2), and (9)—(11) were conducted under milder conditions in order to minimize concurrent epoxidation. Buffered peracetic acid oxi-



(1) R^1=Me, R^2=Br
(2) R^1=Br, R^2=Me
(9) R^1=Me, R^2=Cl
(10) R^1=Cl, R^2=Me
(11) R^1=Pr^i, R^2=Br
(12) R^1=Br, R^2=Pr^i

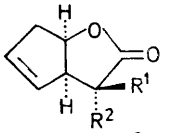


(3) R^1=Me, R^2=Br
(4) R^1=Br, R^2=Me
(13) R^1=Me, R^2=Cl

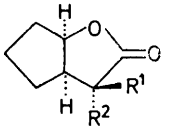


(5) R^1=Me, R^2=Br, X=CH_2
(6) R^1=Br, R^2=Me, X=CH_2
(7) R^1=Me, R^2=Br, X=O
(8) R^1=Br, R^2=Me, X=O

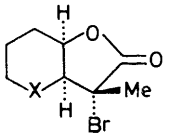
dized the *endo*-halogenobicycloheptenones (2) and (10) to the corresponding lactones (19) and (20) exclusively. More vigorous oxidation of the ketone (2) gave



(19) R^1=Br, R^2=Me
(20) R^1=Cl, R^2=Me
(25) R^1=Me, R^2=Br
(26) R^1=Me, R^2=Cl
(29) R^1=Pr^i, R^2=Br

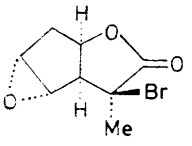


(14) R^1=Me, R^2=Br
(15) R^1=Br, R^2=Me
(18) R^1=Me, R^2=Cl



(16) X=CH_2
(17) X=O

a mixture containing the lactone (19) and the epoxylactone (21) as major products. Omission of buffer in



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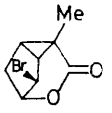

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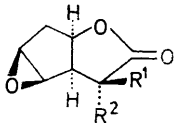


(27) R^1=Me, R^2=Br
(28) R^1=Me, R^2=Cl
(30) R^1=Pr^i, R^2=Br

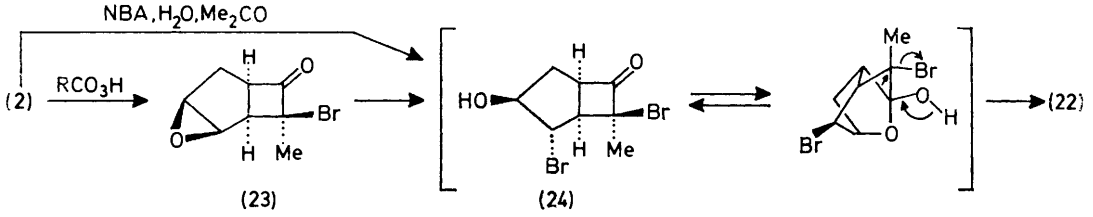
the peracetic acid oxidation of compound (2) led to a decreased yield of the lactone (19) and production of the tricyclic lactone (22). We envisage that the latter compound is formed from the *endo*-epoxyketone (23) by reaction with HBr and subsequent rearrangement (Scheme 2).[8] The lability of the bromohydrin (24) was demonstrated by treating the ketone (2) with *N*-bromoacetamide (NBA) in aqueous acetone; a good yield of the rearranged lactone (22) was obtained.

The *exo*-halogenobicyclo[3.2.0]hepten-6-ones (1) and (9) underwent Baeyer–Villiger ring expansion more slowly than the *endo*-halogeno-isomers, owing, no doubt, to the unfavourable influence of the halogen atom on the approach of the peracetic acid to the carbonyl carbon atom from the *exo*-face in the rate-determining step of the oxidation.[9] However, oxidation conditions were established whereby the sole product isolated from reactions of compounds (1) and (9) was the corresponding lactone (25) or (26). Prolonged oxidation gave rise to appreciable amounts of the corresponding *endo*-epoxylactone (27) or (28).

Baeyer–Villiger oxidation of the bromo-ketone (11) proceeded very slowly and, after chromatography, the lactone (29) and the *endo*-epoxy-lactone (30) were isolated in poor yield.

The configuration of the three-membered ring in the oxirans (21), (27), (28), and (30) is conveniently ascertained by n.m.r. spectroscopy: most noticeably, that proton at C-8 which is adjacent to the oxiran oxygen atom, resonates at lower field. It is noteworthy that 7-*exo*-halogenobicyclo[3.2.0]heptenones give *endo*-epoxylactones,[10] whereas 7-*endo*-halogenobicyclo[3.2.0]heptenones yield *exo*-epoxylactones preferentially.

The required elimination of HBr from the 7-*exo*-bromolactones (14), (16), (25), and (29) occurred readily on treatment with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in hot toluene to give the corresponding α-alkylidene-γ-lactones (31)—(34).[11] Similarly, the 7-*exo*-chloro-lactone

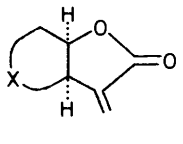


SCHEME 2

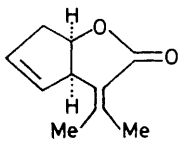
[8] Z. Grudzinski and S. M. Roberts, *J.C.S. Perkin I*, 1975, 1767.
[9] J. L. Mateos and H. Menchaca, *J. Org. Chem.*, 1964, **29**, 2026.
[10] E. J. Corey and R. Noyori, *Tetrahedron Letters*, 1970, 307.
[11] A. E. Green, J.-C. Muller, and G. Ourisson, *Tetrahedron Letters*, 1972, 2489, 3375.

(18) eliminated HCl to give compound (31) on more prolonged treatment with DBN. In contrast, the halogeno-lactones (17) and (26) gave no identifiable products when treated with the base.

Not unexpectedly, base-catalysed elimination of HBr from the 7-*endo*-bromolactone (15) gave the αβ-unsaturated lactone (35),[12] whereas the unsaturated analogue (19) gave the diene (36) as the sole product in almost quantitative yield. We believe that (36) is formed from the expected product (37) by a series of base-induced 1,3- and 1,5-hydrogen shifts (Scheme 3);[12] molecular models



(31) X = $[CH_2]_2$
(32) X = $[CH_2]_3$
(33) X = CH:CH



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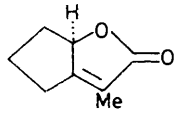
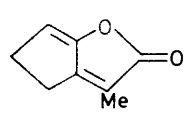


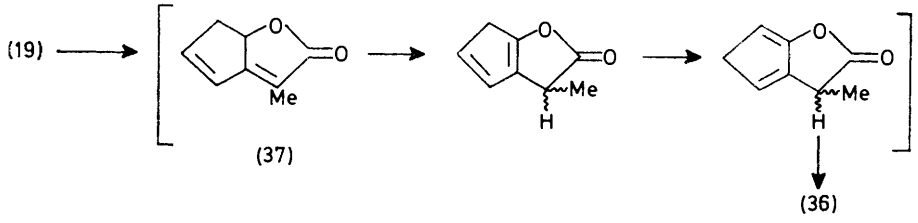
(35)



(36)

indicate that the observed product (36) is considerably less strained than the postulated intermediate (37).

In conclusion, the route described in Scheme 1 has been shown to be useful for the synthesis of compounds in which an α-methylene-γ-lactone unit is *cis*-fused to an alicyclic ring system. However, there are two major inadequacies. First, the requisite α-halogen atom (R′ in Scheme 1) must be *trans*-oriented to a vicinal β-substituent to avoid formation of an endocyclic double bond. Secondly, the synthetic sequence will be of limited utility when the cycloaddition of keten and an



(19) (37) (36)

SCHEME 3

unsymmetrical alkene is non-specific. Further studies are being pursued in an effort to circumvent these difficulties.

EXPERIMENTAL

M.p.s were taken by the capillary tube method. Distillations were accomplished by using the Büchi Kugelröhr (bulb-to-bulb) system and the b.p.s reported are oven temperatures at distillation. N.m.r. spectra were obtained with a Varian EM-360 or Perkin Elmer R-32 spectrometer (CCl_4 or $CDCl_3$ as solvent). I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer for neat films unless otherwise stated. Silica gel MFC was used for column chromatography. Anhydrous sodium sulphate was used as a drying agent for solutions in organic solvents.

Preparation of the Bicyclic Ketones (1)—(13). These were prepared by reported methods.[5,6] The isomeric products were separated by distillation and/or column chromatography ($CHCl_3$).

Preparation of the Bicyclic Lactones (14)—(20), (25), (26), *and* (29).—*Method A*. To the appropriate bicyclic ketone (0.01 mol) in chloroform (30 ml) were added *m*-chloroperbenzoic acid (0.015 mol) and sodium hydrogen carbonate (0.015 mol). The mixture was stirred at room temperature. The excess of peroxy-acid was decomposed by washing with aqueous 10% sodium sulphite. Finally the chloroform layer was washed with saturated sodium hydrogen carbonate solution, dried, and evaporated. The products were purified by column chromatography with chloroform as eluant.

Method B. To the bicyclic ketone (0.01 mol) in acetic acid (10 ml) were added a solution of hydrogen peroxide (30% in water; 0.03 mol) in acetic acid (5 ml) and sodium acetate (0.01 mol). When the reaction was complete the solution was diluted with water (100 ml) and extracted with ether (3 × 25 ml). The combined extracts were washed with aqueous sodium sulphite solution (10%; 2 × 15 ml) and water (3 × 15 ml), dried, and evaporated. The residue was purified as in method A.

(a) 4-exo-*Bromo*-4-endo-*methyl*-2-*oxabicyclo*[3.3.0]*octan*-3-*one* (14) was obtained from the bicyclic ketone (3) (method A; 24 h) as an oil (60%), b.p. 87—90° at 0.003 mmHg, $\nu_{max.}$ 1 770, 1 450, 1 150, and 1 080 cm^{-1}, δ 4.75 (1 H, m, H-1), 2.8 (1 H, m, H-5), 1.6 (3 H, s, Me), and 1.5 (6 H, m) (Found: C, 44.0; H, 5.0. $C_8H_{11}BrO_2$ requires C, 43.8; H, 5.0%).

(b) 4-endo-*Bromo*-4-exo-*methyl*-2-*oxabicyclo*[3.3.0]*octan*-3-*one* (15), from the bicyclic ketone (4) (method A; 15 h), was an oil (93%), b.p. 90—92° at 0.05 mmHg, $\nu_{max.}$ 1 780, 1 450, 1 210, and 1 085 cm^{-1}, δ 4.9 (1 H, m, H-1), 2.75 (1 H, m, H-5), 2.0 (3 H, s, Me), and 1.8 (6 H, m) (Found: M^+, 217.9938. $C_8H_{11}BrO_2$ requires M, 217.9942).

(c) 9-*exo*-Bromo-9-*endo*-methyl-7-oxabicyclo[4.3.0]nonan-8-one (16) [12] was obtained from the bicyclic ketone (5) (method A; 20 h) as an oil (63%), $\nu_{max.}$ 1 770, 1 450, and 1 130 cm^{-1}, δ 4.8 (1 H, m, H-6), 2.3 (1 H, m, H-1), 1.7 (3 H, s, Me), and 1.5 (8 H, m).

(d) 9-exo-*Bromo*-9-endo-*methyl*-2,7-*dioxabicyclo*[4.3.0]-*nonan*-8-*one* (17), from the bicyclic ketone (7) (method A;

[12] A. E. Green, J.-C. Muller, and G. Ourisson, *J. Org. Chem.*, 1974, **39**, 186.

16 h), was an oil (65%), b.p. 95—97° at 0.04 mmHg, $\nu_{max.}$ 1 780, 1 450, 1 190, and 1 090 cm^{-1}, δ 4.7 (1 H, m, H-6), 4.0 (1 H, d, *J* 2 Hz, H-1), 3.6 (2 H, m, 2 × H-3), 1.7 (4 H, m), and 1.8 (3 H, s, Me) (Found: *M*$^+$, 233.9894. $C_8H_{11}BrO_3$ requires *M*, 233.9891).

(e) 4-exo-*Chloro*-4-endo-*methyl*-2-*oxabicyclo*[3.3.0]*octan*-3-*one* (18), from the bicyclic ketone (13) (method A; 16 h), was a liquid (91%), b.p. 85—86° at 0.02 mmHg, $\nu_{max.}$ 1 780, 1 450, 1 150, and 1 090 cm^{-1}, δ 5.0 (1 H, m, H-1), 2.9 (1 H, m, H-5), 1.8 (6 H, m), and 1.65 (3 H, s, Me) (Found: C, 55.2; H, 6.3. $C_8H_{11}ClO_2$ requires C, 55.2; H, 6.3%).

(f) 4-endo-*Bromo*-4-exo-*methyl*-2-*oxabicyclo*[3.3.0]*oct*-6-*en*-3-*one* (19), from the bicyclic ketone (2) (method A; 5 °C; 3 h), was an oil (75%), b.p. 90—95° at 0.005 mmHg, $\nu_{max.}$ 1 770, 1 440, 1 180, and 1 095 cm^{-1}, δ 5.75 (2 H, m, H-6 and -7), 5.1 (1 H, m, H-1), 3.5 (1 H, m, H-5), 2.75 (2 H, m, 2 × H-8), and 2.0 (3 H, s, Me) (Found: *M*$^+$, 215.9786. $C_8H_9BrO_2$ requires *M*, 215.9786).

Reaction under the same conditions but at room temperature gave the lactone (19) 25% and the exo-*epoxy-lactone* (21) as fine needles (28%), m.p. 117—118°, $\nu_{max.}$ (Nujol) 1 770, 1 450, 1 180, and 1 040 cm^{-1}, δ 4.66 (1 H, ddd, *J* 8.0, 8.0, and 6.0 Hz, H-1), 3.7 (2 H, m, H-6 and -7), 3.03 (1 H, d, *J* 8.0 Hz, H-5), 2.7 (1 H, dd, *J* 15.0 and 8.0 Hz, H-8), 2.1 (1 H, dd, *J* 15.0 and 6.0 Hz, H-8), and 2.06 (3 H, s, Me) (Found: C, 40.9; H, 3.9. $C_8H_9BrO_3$ requires C, 41.2; H, 3.8%).

When the bicyclic ketone (2) was oxidised according to method B in the absence of sodium acetate, a mixture of the lactone (19) (25%) and 6-exo-*bromo*-2-exo-*methyl*-4-*oxatricyclo*[3.2.1.0^{2,7}]*octan*-3-*one* (22) (15%), b.p. 100—105° at 0.01 mmHg, $\nu_{max.}$ 1 730, 1 370, 1 230, and 1 110 cm^{-1}, δ 4.5 (1 H, m, H-5), 4.2 (1 H, s, H-8), 2.49 (1 H, ddd, *J* 13.0, 3.0, and 3.0 Hz, H-6), 2.0 (3 H, m), and 1.25 (3 H, s, Me) (Found: *M*$^+$, 215.9786. $C_8H_9BrO_2$ requires *M*, 215.9786), was obtained. The same lactone (22) was obtained by addition of NBA (1.4 g) to a solution of the bicyclic ketone (2) (2 g) in acetone (3 ml) and water (15 ml). The mixture was left in the dark for 10 h at room temperature. The acetone was evaporated off and the residue was extracted with ether (3 × 20 ml). The combined extracts were washed with water (3 × 15 ml), dried, and evaporated. Distillation afforded compound (22) (2.0 g, 92%).

(g) 4-endo-*Chloro*-4-exo-*methyl*-2-*oxabicyclo*[3.3.0]*oct*-6-*en*-3-*one* (20), from the bicyclic ketone (10) (method B; 90% acetic acid; 6 h at 10 °C) was a liquid (75%), b.p. 97—100° at 0.01 mmHg, $\nu_{max.}$ 1 780, 1 450, 1 200, and 1 100 cm^{-1}, δ 5.8 (2 H, m, H-6 and -7), 5.1 (1 H, m, H-1), 3.55 (1 H, m, H-5), 2.7 (2 H, m, 2 × H-8), and 1.8 (3 H, s, Me) (Found: *M*$^+$, 172.0294. $C_8H_9ClO_2$ requires *M*, 172.0290).

(h) 4-exo-*Bromo*-4-endo-*methyl*-2-*oxabicyclo*[3.3.0]*oct*-6-*en*-3-*one* (25), from the bicyclic ketone (1) (method B; 45 h) was an oil (34%), b.p. 75—80° at 0.01 mmHg, $\nu_{max.}$ 1 780, 1 450, 1 180, and 1 070 cm^{-1}, δ 5.75 (2 H, m, H-6 and -7), 5.1 (1 H, m, H-1), 3.8 (1 H, m, H-5), 2.7 (2 H, m, 2 × H-8), and 1.9 (3 H, s, Me) (Found: *M*$^+$, 215.9786. $C_8H_9BrO_2$ requires *M*, 215.9786).

When the oxidation was carried out by method A, the reaction was complete after 24 h and the lactone (25) was obtained in 60% yield. In addition the endo-*epoxy-lactone* (27) was isolated as an oil (16%), b.p. 110—114° at 0.03 mmHg, δ 5.0 (1 H, dd, *J* 6.0 and 6.0 Hz, H-1), 3.65 (2 H, m, H-6 and -7), 3.35 (1 H, dd, *J* 8.0 and 2.0 Hz, H-5), 2.48 (1 H, d, *J* 16.0 Hz, H-8), 2.15 (1 H, dd, *J* 16.0 and 6.0 Hz, H-8), and 2.1 (3 H, s, Me) (Found: *M*$^+$, 231.9740. $C_8H_9BrO_3$ requires *M*, 231.9735).

(i) 4-exo-*Chloro*-4-endo-*methyl*-2-*oxabicyclo*[3.3.0]*oct*-6-*en*-3-*one* (26), from the bicyclic ketone (9) (method B; 90% acetic acid; 16 h) was an oil (36%), b.p. 85—86° at 0.02 mmHg, $\nu_{max.}$ 1 780, 1 450, 1 190, and 1 110 cm^{-1}, δ 5.7 (2 H, m, H-6 and -7), 5.15 (1 H, m, H-1), 3.6 (1 H, m, H-5), 2.7 (2 H, m, 2 × H-8), and 1.75 (3 H, s, Me) (Found: C, 55.6; H, 5.4. $C_8H_9ClO_2$ requires C, 55.8; H, 5.2%).

When the oxidation was carried out in glacial acetic acid, the lactone (26) was obtained in 25% yield along with the endo-*epoxy-lactone* (28) (8%) as an oil, $\nu_{max.}$ (Nujol) 1 770, 1 450, 1 200, and 1 100 cm^{-1}, δ 4.9 (1 H, dd, *J* 6.0 and 6.0 Hz, H-1), 3.5 (2 H, m, H-6 and -7), 3.14 (1 H, dd, *J* 6.0 and 2.0 Hz, H-5), 2.5 (1 H, d, *J* 15.0 Hz, H-8), 2.05 (1 H, dd, *J* 15.0 and 7.0 Hz, H-8), and 1.9 (3 H, s, Me) (Found: C, 50.8; H, 4.6. $C_8H_9ClO_3$ requires C, 51.1; H, 4.8%).

(j) 4-exo-*Bromo*-4-endo-*isopropyl*-2-*oxabicyclo*[3.3.0]*oct*-6-*en*-3-*one* (29), from the bicyclic ketone (11) (method B; 120 h) (6%) was an oil, $\nu_{max.}$ 1 780, 1 460, 1 190, and 1 170 cm^{-1}, δ 5.8 (2 H, m, H-6 and -7), 5.05 (1 H, m, H-1), 3.74 (1 H, m, H-5), 2.7 (2 H, m, 2 × H-8), 1.85 (1 H, m, H-9), and 1.33 and 1.13 (6 H, 2 × d, *J* 6.0 Hz, 2 × Me), was obtained along with the endo-*epoxy-lactone* (30), an oil (4%), δ 5.0 (1 H, dd, *J* 6.0 and 6.0 Hz, H-1), 3.6 (2 H, m, H-6 and -7), 3.25 (1 H, d, *J* 6.0 Hz, H-5), 2.55 (1 H, d, *J* 16.0 Hz, H-8), 2.0 (1 H, dd, *J* 16.0 and 6.0 Hz, H-8), 2.1 (1 H, m, H-9), and 1.4 and 1.2 (6 H, 2 × d, *J* 6.0 Hz, 2 × Me) (Found: C, 46.3; H, 4.9. $C_{10}H_{13}BrO_3$ requires C, 46.0; H, 5.0%).

Dehydrohalogenation of the Bicyclic Lactones (14)—(16), (18), (19), (25), *and* (29).—To a solution of the α-halogenolactone (0.001 mol) in dry toluene (10 ml) was added 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) (0.004 mol) and the mixture was heated under reflux. When the reaction was complete, ether (20 ml) was added and the mixture was washed with hydrochloric acid (10%; 2 × 10 ml) and with saturated sodium chloride solution (2 × 10 ml). The combined aqueous washings were extracted with ether (10 ml). The combined ether extracts were dried and evaporated. The products were purified by distillation or by preparative t.l.c.

(a) 4-*Methylene*-2-*oxabicyclo*[3.3.0]*octan*-3-*one* (31), from the lactone (14) (30 min) was an oil (75%), b.p. 95° at 0.08 mmHg, $\nu_{max.}$ 1 760, 1 665, 1 150, and 1 110 cm^{-1}, δ 6.0 and 5.55 (2 H, 2 × d, *J* 2.5 Hz, :CH$_2$), 4.85 (1 H, m, H-1), 3.4 (1 H, m, H-5), and 1.7 (6 H, m) (Found: *M*$^+$, 138.0689. $C_8H_{10}O_2$ requires *M*, 138.0681.)

Treatment of the lactone (18) under the basic reaction conditions (24 h) also gave the lactone (31) (65%).

(b) 9-Methylene-7-oxabicyclo[4.3.0]nonan-8-one (32) was obtained (72%) from the lactone (16) after 30 min; b.p. 75° at 0.08 mmHg (lit.,[13] 60° at 0.06 mmHg), $\nu_{max.}$ 1 760 1 670, 1 450, and 1 130 cm^{-1}, δ 6.02 and 5.47 (2 H, 2 × d, *J* 3 Hz, :CH$_2$), 4.47 (1 H, m, H-6), 3.0 (1 H, m, H-1), and 1.6 (8 H, m).

(c) 4-*Methylene*-2-*oxabicyclo*[3.3.0]*oct*-6-*en*-3-*one* (33) was obtained from the lactone (25) as an oil (60%), b.p. 80° at 0.08 mmHg, $\nu_{max.}$ 1 760, 1 670, 1 400, and 1 130 cm^{-1}, δ 6.0 and 5.53 (2 H, 2 × d, *J* 2.0 Hz, :CH$_2$), 5.65 (2 H, m, H-6 and -7), 5.25 (1 H, m, H-1), 4.25 (1 H, m, H-5), and 2.85 (2 H, m, 2 × H-8) (Found: *M*$^+$, 136.0533. $C_8H_8O_2$ requires *M*, 136.0524).

[13] J. A. Marshall and M. Cohen, *J. Org. Chem.*, 1965, **30**, 3475.

(d) 4-*Isopropylidene*-2-*oxabicyclo*[3.3.0]*oct*-6-*en*-3-*one* (34) was obtained from the lactone (29) as an oil (75%), b.p. 90° at 0.08 mmHg, $\nu_{max.}$ 1 735, 1 660, 1 180, and 1 065 cm^{-1}, δ 5.6 (2 H, m, H-6 and -7), 4.85 (1 H, m, H-1), 3.9 (1 H, m, H-5), 2.7 (2 H, m, 2 × H-8), and 2.2 and 2.0 (6 H, 2 × s, 2 × Me) (Found: M^+, 164.0845. $C_{10}H_{12}O_2$ requires M, 164.0837).

(e) 4-*Methyl*-2-*oxabicyclo*[3.3.0]*oct*-4-*en*-3-*one* (35) was obtained from the lactone (15) as an oil (78%), b.p. 90° at 0.08 mmHg, $\nu_{max.}$ 1 750, 1 690, 1 450, and 1 130 cm^{-1}, δ 4.75 (1 H, m, H-1), 2.2 (6 H, m), and 1.7 (3 H, s, Me) (Found: M^+, 138.0682. $C_8H_{10}O_2$ requires M, 138.0680).

(f) 4-*Methyl*-2-*oxabicyclo*[3.3.0]*octa*-4,8-*dien*-3-*one* (36), from the reaction of DBN with the lactone (19), was a semi-solid (80%), $\nu_{max.}$ ($CHCl_3$), 1 760, 1 660, and 1 000 cm^{-1}, δ 5.6 (1 H, t, J 2.0 Hz, H-8), 2.8 (4 H, m), and 1.9 (3 H, s, Me) (Found: M^+, 136.0525. $C_8H_8O_2$ requires M, 136.0524).

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