General Synthetic Route to γ-Butyrolactones *via* Stereoselective Radical Cyclization by Organotin Species†

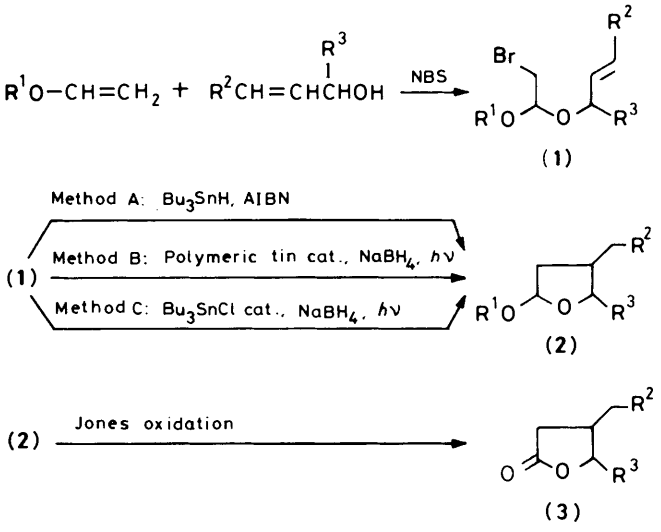
Yoshio Ueno,‡ Osamu Moriya,*§ Kunitake Chino, Masaru Watanabe, and Makoto Okawara
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

A new method for the preparation of γ-butyrolactones is described in which the key step is the highly stereoselective radical cyclization of bromoacetals to 2-alkoxytetrahydrofurans in the presence of polymeric or low-molecular weight organotin species. 2-Alkoxytetrahydrofurans can be easily converted into γ-butyrolactones by Jones oxidation.

Much work concerned with intramolecular radical cyclization *via* carbon-centred or heteroatom-centred free radical intermediates has been reported.[1]

Application of the radical process to organic synthesis has been made difficult by a lack of understanding of the resulting product- and stereo-selectivities, although recent preliminary reports claim to have overcome these.[2,3] Such radical cyclizations effected under neutral conditions are free from rearrangements or eliminations observed in ionic process and they have, therefore, aroused much interest. Further, the protection of many functional groups in such reactions is unnecessary since they are inert towards the radical species involved. The value of this process has been greatly enhanced as a useful method for the preparation of heterocyclic and carbocyclic compounds by developments in methodologies for the generation of radical intermediates.[4]

During the course of our studies in this field,[5] we have found a new synthetic route to γ-butyrolactones starting from bromoacetals. Independently, Stork *et al.* have discovered the same route;[6] their observations on the high-stereoselectivity of the cyclization, correspond with our own observations (see later).

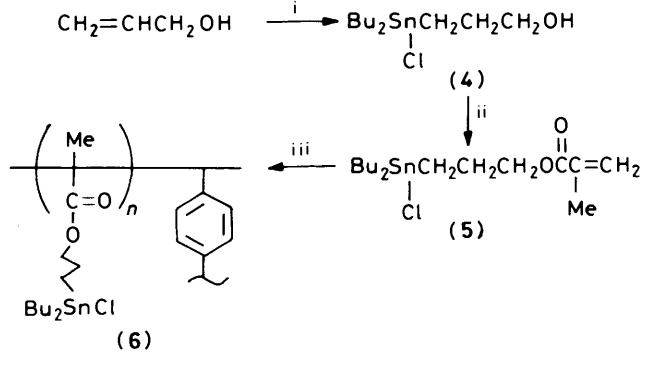


Scheme 1.

Results and Discussion

The synthesis of γ-butyrolactones was attained *via* the three steps shown in the Scheme 1. The starting bromo acetals (**1**) were readily obtained by alkoxy-brominations of vinyl ethers with allylic alcohols in the presence of *N*-bromosuccinimide (NBS). The cross-linked polymeric tin compound (**6**) was prepared *via* the methacrylate monomer (**5**) by copolymerization in the presence of 5% divinylbenzene and a catalytic amount of azo-isobutyronitrile (AIBN). The content of tin moiety was estimated by elemental analysis (styrene:Sn = 85:15).

The radical cyclization of the bromo acetals (**1**) to give 2-alkoxytetrahydrofurans (**2**) was carried out by the following Methods A—C. To a solution of (**1**) and a catalytic amount of AIBN in dry benzene was added dropwise over 30 min an equimolar amount of tributyltin hydride either at room temperature or at 50 °C. After being stirred for 2—4 h at 50 °C, the mixture was distilled under reduced pressure to give the tetrahydrofurans (**2**) (Method A, Table 1 and 2). The catalytic reactions using polymeric tin compound (**6**) or tributyltin chloride with sodium tetrahydroborate in a degassed benzene–



Scheme 2. *Reagents:* i, Bu_2SnClH (W. P. Newman and J. Pedain, *Tetrahedron Lett.*, 1964, 2461); ii, CH=C(Me)COCl/base; iii, $PhCH=CH_2$/AIBN

ethanol mixture when subjected to u.v.-irradiation for 1—2 h at room temperature afforded (**2**) (Methods B and C, Tables 1 and 2). The resulting tetrahydrofurans (**2**) were converted into γ-butyrolactones (**3**) by oxidation with Jones reagent in high yields[7] (Tables 1 and 2).

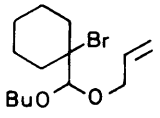
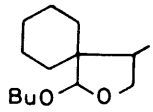
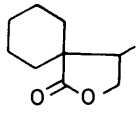
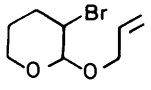
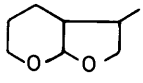
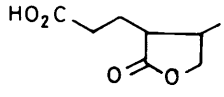
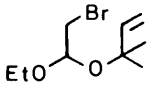
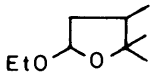
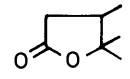
In all the cases studied here, radical cyclization of (**1**) gave only five-membered cyclic products (**2**), not six-membered ones.

† Presented in part at the 2nd IUPAC Symposium on Organometallic Chemistry Directed toward Organic Synthesis, Abstr. P. 80, 1983, Dijon and *J. Am. Chem. Soc.*, 1982, **104**, 5564.

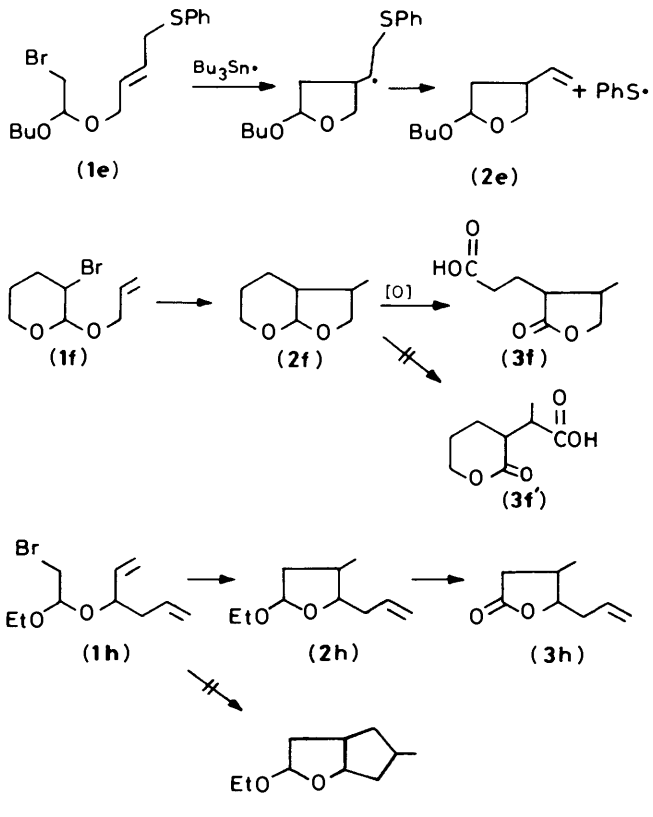
‡ Deceased February 27, 1985.

§ *Present address:* Department of Chemistry, National Defense Academy, Hashirimizu, Yokosuka 239, Japan.

Table 1. Preparation of the 2-alkoxytetrahydrofurans (**2a**—**h**) and γ-butyrolactones (**3a**—**h**) from the bromoacetals (**1a**—**h**)

Entry no.	(1) R¹	R²	R³	Yield of (2) Method A	Method B	Yield of (3)[a] (%)
a	BuO	H	H	59	91	87
b	BuO	Me	H	59	86	79
c	BuO	Pr	H	65	96	91
d				 50	73	 70
e	BuO	$PhSCH_2$	H	78	91	95
f				 68	84	 81
g				 71	—	 72
h	EtO	H	CH_2=$CHCH_2$	63	—	65

[a] Based on the tetrahydrofurans (**2**).



Scheme 3.

The predominance of this exocyclic mode of cyclization is in agreement with previous results for simpler compounds,[2,3] and gives an efficient route to the tetrahydrofurans (**2**).

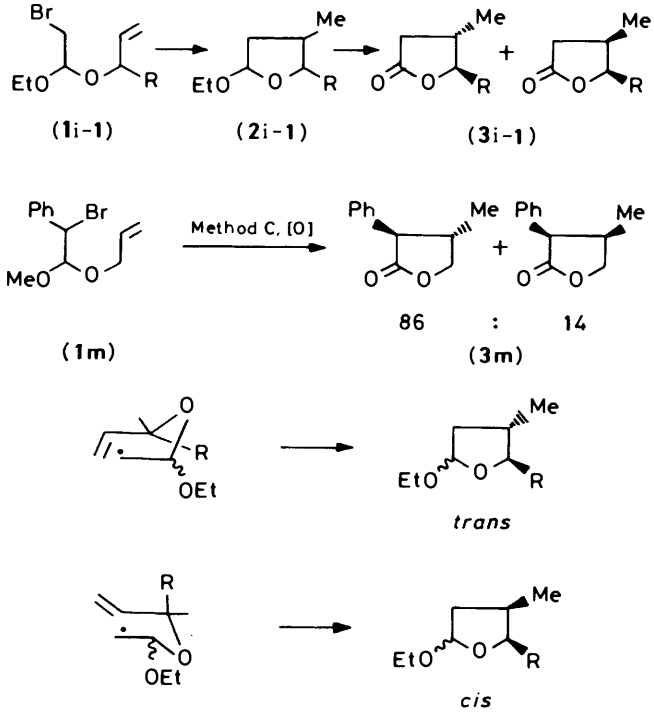
This method seems to be particularly useful for C–C bond formation where a sterically hindered carbon is involved since such bond formation in polar reactions, involving carbocations or carbanions and often accompanying an elimination reaction or a skeletal rearrangement, is well known to be strongly effected by the steric hindrance and generally give poor results. In this respect the advantage of the method was demonstrated in the successful preparation of the spirocyclic lactone (**3d**). Further, the method was developed for the facile synthesis of functionalized γ-butyrolactones. The vinyl substituted tetrahydrofuran (**2e**) gave the lactone (**3e**) in good yield by an effective combination of radical cyclization and the intramolecular S_H' process (Scheme 3).[5a] Adoption of the 2,3-dihydropyran as starting material enabled the preparation of the bicyclic tetrahydrofuran (**2f**), which afforded, exclusively, by Jones oxidation the carboxy lactone (**3f**); none of the six-membered product (**3f'**) was formed. The bromo acetal (**1h**), containing a 1,5-diene structure, reacted to give the allyl substituted lactone (**3h**); formation of a bicyclic tetrahydrofuran *via* a double cyclization was not observed. Reactions using polymeric organotin hydride[8] and Bu_3SnCl[9] have been described and their use gives simpler product isolation. In view of this, we investigated their use in reactions of the type described here, fractional distillation to remove organotin by-products having been found to cause a decreased yield of tetrahydrofurans (**2**), and known methods[10] for the separation of organotin species giving less than satisfactory results. The capacity of the reported polymeric organotin hydride to be regenerated, however, was limited, a result it is thought of its deactivation *via* coupling of tin radicals to give distannane. We, therefore, employed the polymer tin chloride (**6**) to solve the

Table 2. Preparation of 2-ethoxytetrahydrofurans (**2i—l**) and γ-butyrolactones (**3i—l**) from bromo acetals (**1i—l**)

Entry no.	(1)	Method	(2) Yield (%)	(3) Yield (%)[a]	(3) *trans*/*cis*[b]
i	Me	A	52	75	96/4
j	Et	A	71	86	96/4
k	Pr^i	C	66	92	98/2
l	Ph	C	—	73[c]	95/5

[a] Based on the tetrahydrofurans (**2**). [b] Estimated by ^{1}H n.m.r. (100 MHz) analysis. [c] Based on the bromo acetal (**1**).

problem by utilizing the 'site-isolation' effect of cross-linked polymers.[11] As shown by the results recorded in Table 1, use of a catalytic quantity of (**6**) promoted the efficient synthesis of (**2**), the procedure being simpler and the yield of products higher. Use of Bu_3SnCl as a catalyst is also a practical possibility as shown by the last run in Table 2. Here, the lactone (**3l**) was synthesized in increased overall yield from the bromo acetal (**1l**) without isolation of the intermediate tetrahydrofuran.



Scheme 4.

The high stereoselectivity observed in the preparation of 3,4-disubstituted lactones (**3i—l**) is particularly noteworthy. The stereochemistry of compounds (**3i—l**) was assigned by comparison of their ^{1}H n.m.r. data with reported results.[12,13] Estimation of isomeric ratios was based on the signals for the *O*-methine proton at C-4 in the case of (**3i—k**) and the 3-methyl proton in the case of (**3l**). Such inspections revealed that all the lactones (**3i—l**) consisted of over 95% of the major isomer corresponding to the *trans*-lactone (Table 2), a result in accord with that of Stork *et al.*[6] Further, similar predominant *trans*-selectivity was observed in the analogous examples of radical cyclization reported very recently.[5d,14]

The observed isomeric ratios appeared to be independent of steric factors arising from C-4 substituents, a finding which suggests that the high *trans*-selectivity is a result of conformational effects in the chair-like transition state.[15] That is, when substituent R is located at pseudo-equatorial position, the product will be a *trans*-isomer (see Scheme 4).

Finally, we examined the stereoselectivity of the 2,3-disubstituted system. 3-Methyl-2-phenyl-γ-butyrolactone (**3m**),[16] prepared by Method C in 60% yield, also existed predominantly as the *trans*-isomer, ^{1}H n.m.r. results indicating a *trans*:*cis* ratio 86:14. This result differed from our expectations, based as it was on previous work with simple disubstituted carbocyclic compounds, where the reactions occurred in a completely *trans*-selective fashion.[2,3]

Experimental

I. r. spectra were recorded on a Hitachi EPI-S2 IR spectrometer and ^{1}H n.m.r. on a JEOL JNM-PMX 60 or JEOL-C 100 instrument, using tetramethylsilane as an internal standard. The silica gel used for column chromatography was Wakogel C-200 (100—200 mesh). All the reactions employing organotin species were carried out under nitrogen. The following materials were prepared by literature methods: butyl cyclohexylidene ether[17] and β-methoxystyrene.[18]

General Procedure for the Preparation of Bromoacetals (**1**).—*Bromoacetaldehyde allyl butyl acetal* (**1a**). *N*-Bromosuccinimide (3.56 g, 20 mmol) was added to a stirred solution of butyl vinyl ether (2.00 g, 20 mmol) in allyl alcohol (10 ml) at −20 °C—−50 °C; the mixture was then stirred for 2—3 h, the temperature being kept below −20 °C. The precipitate so formed was filtered off and washed with hexane and the combined filtrate and washings treated successively with 5% aqueous KOH, water, and brine. After being dried ($MgSO_4$), the solution was concentrated *via* a rotary evaporator and the residual oil was distilled (Kugelrohr) to give the acetal (**1a**) (3.56 g, 75%), b.p. 120—123 °C/15 mmHg (Kugelrohr) (Found: C, 45.6; H, 7.4. $C_9H_{17}BrO_2$ requires C, 45.59; H, 7.23%); $\nu_{max.}$(neat) 1 183, 1 115, and 1 045 cm^{-1}; δ_H($CDCl_3$) 0.70—1.80 (7 H, m), 3.30—3.70 (4 H, m), 4.08 (2 H, d, *J* 5.5 Hz), 4.67 (1 H, t, *J* 5.5 Hz), 5.00—5.50 (2 H, m), and 5.60—6.30 (1 H, m).

Bromoacetaldehyde but-2-enyl butyl acetal (**1b**). This compound was obtained from butyl vinyl ether and but-2-enol in 84% yield, b.p. 142—144 °C/15 mmHg (Kugelrohr) (Found: C, 48.0; H, 8.0. $C_{10}H_{19}BrO_2$ requires C, 47.82; H, 7.62%); $\nu_{max.}$(neat) 1 040, 1 110, and 962 cm^{-1}; δ_H($CDCl_3$) 0.80—1.90 (10 H, m), 3.30–3.70 (4 H, m), 3.90—4.20 (2 H, m), 4.71 (1 H, t, *J* 5.0 Hz), and 5.50—5.80 (2 H, m).

Bromoacetaldehyde hex-2-enyl butyl acetal (**1c**). This compound was obtained from butyl vinyl ether and hex-2-enol in 77% yield, b.p. 76—80 °C/0.1 mmHg (Kugelrohr) (Found: C, 51.3; H, 8.7. $C_{12}H_{23}BrO_2$ requires C, 51.62; H, 8.30%); $\nu_{max.}$(neat) 1 040, 1 115, and 967 cm^{-1}; δ_H($CDCl_3$) 0.70–2.20 (14 H, m), 3.30—3.80 (4 H, m), 4.05 (2 H, dd, *J* 4.4, 1.5 Hz), 4.69 (1 H, t, *J* 5.8 Hz), and 5.73 (2 H, m).

1-*Bromocyclohexanecarbaldehyde allyl butyl acetal* (**1d**). This compound was obtained from butyl cyclohexylidene ether and allyl alcohol in 80% yield, b.p. 133–134 °C/0.33 mmHg (Kugelrohr) (Found: C, 55.35; H, 7.8. $C_{14}H_{25}BrO_2$ requires C, 55.09; H, 8.25%); $\nu_{max.}$(neat) 1 050 cm^{-1}, δ_H($CDCl_3$) 1.00 (3 H, d, *J* 6.4 Hz), 1.10—1.20 (13 H, m), 3.40—4.50 (6 H, m), 5.00—5.50 (2 H, m), and 5.70—6.30 (1 H, m).

Bromoacetaldehyde 4-phenylthiobut-2-enyl butyl acetal (**1e**). This compound was obtained from butyl vinyl ether and *cis*-4-phenylthiobut-2-en-1-ol in 92% yield (purified by column chromatography on silica gel and elution with benzene); $\nu_{max.}$(neat) 1 660, 1 180, 1 112, and 1 030 cm^{-1}; δ_H($CDCl_3$)

0.80—1.60 (7 H, m), 3.30—4.10 (8 H, m), 4.61 (1 H, t, *J* 5.7 Hz), 5.60—5.80 (2 H, m), and 7.20—7.40 (5 H, m).

2-*Allyloxy*-3-*bromotetrahydropyran* (**1f**). This compound was obtained from 2,3-dihydropyran and allyl alcohol in 65% yield, b.p. 88—89 °C/6 mmHg (Kugelrohr) (Found: C, 43.6; H, 6.15. $C_8H_{13}BrO_2$ requires C, 43.46; H, 5.93%); $\nu_{max.}$(neat) 1 130, 1 073, and 1 030 cm^{-1}; $\delta_H(CDCl_3)$ 1.40—2.80 (4 H, m), 3.40—4.30 (5 H, m), 4.66 (1 H, d, *J* 4.2 Hz), 5.10—5.50 (2 H, m), and 5.70—6.30 (1 H, m).

Bromoacetaldehyde 1,1-*dimethylprop*-2-*enyl ethyl acetal* (**1g**). This compound was obtained from ethyl vinyl ether and 1-methylbut-2-en-3-ol in 81% yield, b.p. 97—100 °C/25 mmHg (Kugelrohr) (Found: C, 45.3; H, 7.2. $C_9H_{17}BrO_2$ requires C, 45.57; H, 7.22%); $\nu_{max.}$(neat) 2 975, 2 920, 1 100, and 1 050 cm^{-1}; $\delta_H(CDCl_3)$ 1.10—1.50 (9 H, m), 3.30—3.80 (4 H, m), 4.80 (1 H, t, *J* 5.5 Hz), 5.00—5.40 (2 H, m), and 5.80—6.20 (1 H, dd, *J* 10.0, 10.0 Hz).

Bromoacetaldehyde 1-*vinylbut*-3-*enyl ethyl acetal* (**1h**). This compound was obtained from ethyl vinyl ether and hexa-1,5-dien-3-ol in 76% yield, b.p. 135—137 °C/35 mmHg (Kugelrohr) (Found: C, 48.35; H, 7.0. $C_{10}H_{17}BrO_2$ requires C, 48.19; H, 6.87%); $\nu_{max.}$(neat) 1 110 and 1 020 cm^{-1}; $\delta_H(CDCl_3)$ 1.22 (3 H, t, *J* 6.0 Hz), 2.34 (2 H, t, *J* 7.0 Hz), 3.20—4.80 (5 H, m), 4.73 (1 H, t, *J* 5.5 Hz), and 4.90—6.80 (6 H, m).

Bromoacetaldehyde ethyl 1-*methylprop*-2-*enyl acetal* (**1i**). This compound was obtained from ethyl vinyl ether and but-1-en-3-ol in 82% yield, b.p. 96—99 °C/20 mmHg (Kugelrohr) (Found: C, 43.0; H, 6.55. $C_8H_{15}BrO_2$ requires C, 43.05; H, 6.73%); $\nu_{max.}$(neat) 2 970, 1 100, and 1 000 cm^{-1}; $\delta_H(CDCl_3)$ 1.00—1.60 (6 H, m), 3.10—3.90 (4 H, m), 4.10—4.30 (1 H, m), 4.70 (1 H, t, *J* 5.5 Hz), and 4.95—6.10 (3 H, m).

Bromoacetaldehyde 1-*ethylprop*-2-*enyl ethyl acetal* (**1j**). This compound was obtained from ethyl vinyl ether and pent-1-en-3-ol in 68% yield, b.p. 102—104 °C/18 mmHg (Kugelrohr) (Found: C, 45.55; H, 7.45. $C_9H_{17}BrO_2$ requires C, 45.57; H, 7.17%); $\nu_{max.}$(neat) 2 975, 1 120, and 990 cm^{-1}; $\delta_H(CDCl_3)$ 0.75—1.81 (8 H, m), 3.67—4.12 (5 H, m), 4.72 (1 H, t, *J* 5.5 Hz), and 5.00—6.14 (3 H, m).

Bromoacetaldehyde ethyl 1-*isopropylprop*-2-*enyl acetal* (**1k**). This compound was obtained from ethyl vinyl ether and 1-isopropylprop-2-en-1-ol in 60% yield, b.p. 92—94.5 °C/10 mmHg (Kugelrohr) (Found: C, 46.95; H, 7.65. $C_{10}H_{19}BrO_2$ requires C, 47.81; H, 7.63%); $\nu_{max.}$(neat) 2 975, 1 110, and 1 030 cm^{-1}; $\delta_H(CDCl_3)$ 0.80—1.40 (9 H, m), 1.40—2.05 (1 H, m), 3.25—4.00 (5 H, m), 4.70 (1 H, dd, *J* 6.0, 5.5 Hz), and 5.00—6.20 (3 H, m).

Bromoacetaldehyde ethyl 1-*phenylprop*-2-*enyl acetal* (**1l**). This compound was obtained from ethyl vinyl ether and 1-phenylprop-2-en-1-ol in 63% yield, b.p. 109—110 °C/0.35 mmHg (Kugelrohr) (Found: C, 54.7; H, 6.1; Br, 28.4. $C_{13}H_{17}BrO_2$ requires C, 54.73; H, 6.01; Br, 28.03%); $\nu_{max.}$(neat) 1 120, 1 020, and 700 cm^{-1}; $\delta_H(CDCl_3)$ 1.00—1.35 (3 H, m), 3.30—3.80 (5 H, m), 4.65 (1 H, m), 5.00—5.55 (2 H, m), 5.60—6.30 (1 H, m), and 7.35 (5 H, s).

Bromophenylacetaldehyde allyl ethyl acetal (**1m**). This compound was obtained from β-methoxystyrene and allyl alcohol in 68% yield, b.p. 114 °C/2 mmHg (Kugelrohr) (Found: C, 53.4; H, 5.55. $C_{12}H_{15}BrO_2$ requires C, 53.14; H, 5.57%); $\nu_{max.}$(neat) 1 100 and 1 050 cm^{-1}; $\delta_H(CDCl_3)$ 3.21 (3 H, s), 3.80—4.30 (2 H, m), 4.80 (1 H, d, *J* 2.5 Hz), 5.15—6.30 (4 H, m), and 7.36 (5 H, m).

General Procedures for the Radical Cyclization.—Method A: 2-*Butoxy*-4-*methyltetrahydrofuran* (**2a**). Tributyltin hydride (2.91 g, 10 mmol) was added dropwise over 30 min to a solution of the bromoacetal (**1a**) (2.37 g, 10 mmol) and AIBN (0.016 g, 0.1 mmol) in benzene (40 ml) at 50 °C under nitrogen. After being stirred for 2 h at the same temperature, the solution was concentrated *via* a rotary evaporator. The residue was then distilled with a Kugelrohr apparatus to give 2-butoxy-4-methyltetrahydrofuran (**2a**) (1.00 g, 59%), b.p. 49—50 °C/5 mmHg (Kugelrohr) (Found: C, 68.15; H, 11.65. $C_9H_{18}BrO_2$ requires C, 68.31; H, 11.46%); $\nu_{max.}$(neat) 1 100 and 1 080 cm^{-1}; $\delta_H(CDCl_3)$ 0.80—2.50 (13 H, m), 3.20—4.20 (4 H, m), and 5.22 (1 H, m).

Method B. A solution of the bromoacetal (**1a**) (1.00 g, 4.22 mmol), the polymeric tin compound (**6**) (1.00 g), and $NaBH_4$ (0.24 g, 6.33 mmol) in degassed benzene–ethanol (3:1; 30 ml) was irradiated (100 W high-pressure mercury lamp) and cooled with a fan at room temperature for 2 h under nitrogen. After the irradiation, the polymeric tin compound was filtered off and water added to the filtrate. The aqueous mixture was extracted several times with chloroform and the extracts were dried ($MgSO_4$). Work-up gave (**2a**) (0.61 g, 91%).

Method C. The reaction was carried out in a manner similar to that employed in Method B except that tributyltin chloride (0.1 equiv.) was used in the place of polymeric tin compound (**6**).

2-*Butoxy*-4-*ethyltetrahydrofuran* (**2b**), b.p. 59—60 °C/6 mmHg (Kugelrohr) (Found: C, 69.8; H, 11.9. $C_{10}H_{20}O_2$ requires C, 69.72; H, 11.70%); $\nu_{max.}$(neat) 1 080 and 1 025 cm^{-1}; $\delta_H(CDCl_3)$ 0.70—1.10 (6 H, m), 1.10—1.80 (7 H, m), 1.80—2.50 (2 H, m), 3.20—4.10 (4 H, m), and 5.12 (1 H, dd, *J* 5.4, 5.2 Hz).

2-Butoxy-4-butyltetrahydrofuran (**2c**), b.p. 104—105 °C/6 mmHg (Kugelrohr) (Found: C, 71.5; H, 12.15. $C_{12}H_{24}O_2$ requires C, 71.95; 12.08%); $\nu_{max.}$(neat) 1 090 and 1 025 cm^{-1}; $\delta_H(CDCl_3)$ 0.80—2.40 (19 H, m), 3.20—4.10 (4 H, m), and 5.08 (1 H, dd, *J* 8.2, 7.2 Hz).

2′-Butoxy-4′-methylcyclohexanespiro-3′-(tetrahydrofuran) (**2d**), b.p. 90—107 °C/0.4 mmHg (Kugelrohr) (Found: C, 74.0; H, 11.9. $C_{14}H_{26}O_2$ requires C, 74.29; H, 11.58%); $\nu_{max.}$(neat) 1 060 and 1 020 cm^{-1}; $\delta_H(CDCl_3)$ 0.60—2.00 (21 H, m), 3.30—4.50 (4 H, m), and 4.92 (1 H, s).

2-Butoxy-4-vinyltetrahydrofuran (**2e**), b.p. 82—83 °C/12 mmHg (Kugelrohr) (Found: 70.25; H, 10.5. $C_{10}H_{18}O_2$ requires C, 70.55; H, 10.66%); $\nu_{max.}$(neat) 3 075, 1 650, and 912 cm^{-1}; $\delta_H(CDCl_3)$ 0.92 (3 H, t, *J* 6.4 Hz), 1.10—3.80 (11 H, m), 3.97 (1 H, t, *J* 7.3 Hz), 4.80—5.20 (2 H, m), and 5.50—6.20 (1 H, m).

3-Methylfuro[2,3-*b*]pyran (**2f**), b.p. 126—127 °C/30 mmHg (Kugelrohr) (Found: C, 67.75; H, 9.9. $C_8H_{14}O_2$ requires C, 67.57; H, 9.92%); $\nu_{max.}$(neat) 1 140 and 1 020 cm^{-1}; $\delta_H(CDCl_3)$ 0.95 (3 H, d, *J* 6.5 Hz), 1.50—2.70 (6 H, m), 3.40—4.10 (4 H, m), and 5.27 (1 H, d, *J* 3.4 Hz).

2-Ethoxy-4,5,5-trimethyltetrahydrofuran (**2g**), b.p. 87—89 °C/50 mmHg (Kugelrohr) (Found: C, 68.6; H, 11.65. $C_9H_{18}O_2$ requires C, 68.31; H, 11.47%); $\nu_{max.}$(neat) 1 130 and 1 080 cm^{-1}; $\delta_H(CDCl_3)$ 0.50—0.70 (15 H, m), 3.20—4.00 (2 H, m), and 4.90—5.10 (1 H, m).

5-Allyl-2-ethoxy-4-methyltetrahydrofuran (**2h**), b.p. 54—58 °C/22 mmHg (Kugelrohr) (no elemental analysis), $\nu_{max.}$(neat) 2 995, 1 110, 1 040, 885 cm^{-1}; $\delta_H(CDCl_3)$ 0.75—2.50 (11 H, m), 3.25—4.00 (3 H, m), 4.85–5.35 (3 H, m), and 5.50—6.30 (1 H, m).

2-Ethoxy-4,5-dimethyltetrahydrofuran (**2i**), b.p. 78—80 °C/53 mmHg (Kugelrohr) (Found: C, 66.95; H, 11.3. $C_8H_{16}O_2$ requires C, 66.63; H, 11.18%); $\nu_{max.}$(neat) 1 150 and 1 050 cm^{-1}; $\delta_H(CDCl_3)$ 0.90—2.10 (12 H, m), 3.20—3.90 (3 H, m), and 5.05 (1 H, m).

2-Ethoxy-5-ethyl-4-methyltetrahydrofuran (**2j**), b.p. 82—84.5 °C/50 mmHg (Kugelrohr) (Found: C, 68.5; H, 11.6. $C_9H_{18}O_2$ requires C, 68.31; H, 11.47%); $\nu_{max.}$(neat) 1 100 and 980 cm^{-1}; $\delta_H(CDCl_3)$ 0.75—2.27 (14 H, m), 3.80—4.30 (3 H, m), and 5.13 (1 H, m).

2-Ethoxy-5-isopropyl-4-methyltetrahydrofuran (**2k**), b.p. 83—85 °C/35 mmHg (Kugelrohr) (Found: C, 75.15; H, 9.7. $C_{13}H_{20}O_2$ requires C, 74.96; H, 9.68%); $\nu_{max.}$(neat) 1 165 and

1 050 cm^{-1}; $\delta_H(CDCl_3)$ 0.63—2.50 (16 H, m), 3.15—4.00 (3 H, m), and 5.05 (1 H, m).

General Procedure for the Oxidation of 2-Alkoxytetrahydrofurans (**2**).—To an ice-cooled solution of tetrahydrofuran (**2a**) (0.16 g, 1 mmol) in acetone (5 ml), Jones reagent (1.1 ml, 2.2 equiv.) was added slowly. After the complete addition, excess of isopropyl alcohol was added. The resulting solution was poured into water (50 ml) by decantation and the residual greenish precipitates were washed with acetone several times. The combined aqueous solution was neutralized with powdered $NaHCO_3$ and then extracted with chloroform. The extract was washed with brine and dried ($MgSO_4$). Work-up gave the γ-butyrolactone (**3a**) (0.087 g, 87%), b.p. 94 °C/13 mmHg (Kugelrohr), $\nu_{max.}$(neat) 1 782 cm^{-1}; $\delta_H(CDCl_3)$ 1.13 (3 H, d, *J* 6.4 Hz), 1.80—2.80 (3 H, m), 3.87 (1 H, dd, *J* 8.6, 6.3 Hz), and 4.42 (1 H, dd, *J* 8.6, 6.8 Hz).

3-Ethyl-γ-butyrolactone (**3b**), b.p. 105—108 °C/13 mmHg (Kugelrohr), $\nu_{max.}$(neat) 1 775 cm^{-1}; $\delta_H(CDCl_3)$ 0.98 (3 H, t, *J* 6.6 Hz), 1.40—1.80 (2 H, m), 2.00—2.80 (3 H, m), 3.94 (1 H, dd, *J* 8.5, 6.4 Hz), and 4.44 (1 H, dd, *J* 8.5, 6.6 Hz).

3-Butyl-γ-butyrolactone (**3c**), b.p. 135—137 °C/12 mmHg (Kugelrohr) (Found: C, 67.45; H, 10.35. $C_8H_{14}O_2$ requires C, 67.57; H, 9.93%); $\nu_{max.}$(neat) 1 780 cm^{-1}; $\delta_H(CDCl_3)$ 0.90—1.60 (9 H, m), 2.00—2.80 (3 H, m), 3.89 (1 H, dd, *J* 8.5, 7.1 Hz), and 4.40 (1 H, dd, *J* 8.5, 7.2 Hz).

4'-Methylcyclohexanespiro-3'-(tetrahydrofuran)-2'-one (**3d**), b.p. 129—132 °C/5 mmHg (Kugelrohr) (Found: C, 71.1; H, 9.95. $C_{10}H_{16}O_2$ requires C, 71.39; H, 9.59%); $\nu_{max.}$(neat) 1 747 cm^{-1}; $\delta_H(CDCl_3)$ 1.07 (3 H, d, *J* 7.4 Hz), 1.20—2.70 (11 H, m), 3.84 (1 H, dd, *J* 8.6, 5.0 Hz), and 4.37 (1 H, dd, *J* 8.6, 6.1 Hz).

4-Vinyl-γ-butyrolactone (**3e**), b.p. 114—115 °C/13 mmHg (Kugelrohr) (Found: C, 64.55; H, 6.8. $C_6H_8O_2$ requires C, 64.27; H, 7.19%); $\nu_{max.}$(neat) 1 773 cm^{-1}; $\delta_H(CDCl_3)$ 2.10—2.90 (2 H, m), 2.90—3.50 (1 H, m), 3.98 (1 H, dd, *J* 9.0, 8.1 Hz), 4.42 (1 H, dd, *J* 8.1, 8.1 Hz), 5.11 (1 H, d, *J* 17.2 Hz), 5.13 (1 H, d, *J* 9.2 Hz), and 5.50—6.10 (1 H, m).

2-Carboxyethyl-3-methyl-γ-butyrolactone (**3f**), b.p. >150 °C/5 mmHg (Kugelrohr) (Found: C, 55.55; H, 7.4. $C_8H_{12}O_4$ requires C, 55.80; H, 7.03%); $\nu_{max.}$(neat) 3 200 and 1 760 cm^{-1}; $\delta_H(CDCl_3)$ 1.06 (3 H, d, *J* 6.4 Hz), 1.50—2.10 (3 H, m), 2.50—2.90 (3 H, m), 3.98 (1 H, dd, *J* 8.6, 8.4 Hz), 4.32 (1 H, dd, *J* 8.6, 8.6 Hz), and 10.64 (1 H, s).

3,4,4-Trimethyl-γ-butyrolactone (**3g**), b.p. 95—97 °C/13 mmHg (Kugelrohr) (lit.,[12] 97 °C/12 mmHg), $\nu_{max.}$(neat) 1 770 cm^{-1}; $\delta_H(CCl_4)$ 1.00—1.70 (9 H, m) and 2.00—2.80 (3 H, m).

4-Allyl-3-methyl-γ-butyrolactone (**3h**), b.p. 140—142 °C/5 mmHg (Kugelrohr) (Found: C, 68.25; H, 8.25. $C_8H_{12}O_2$ requires C, 68.57; H, 8.57%); $\nu_{max.}$(neat) 1 780 cm^{-1}; $\delta_H(CDCl_3)$ 1.15 (3 H, d, *J* 12 Hz), 3.00 (5 H, m), 3.90—4.25 (1 H, m), 5.16 (2 H, m), and 5.51—6.25 (1 H, m).

3,4-Dimethyl-γ-butyrolactone (**3i**), b.p. 87—90 °C/10 mmHg (Kugelrohr), $\nu_{max.}$(neat) 1 782 cm^{-1}; $\delta_H(CCl_4)$ 1.12 (3 H, d, *J* 6.5 Hz), 1.37 (3 H, d, *J* 6.5 Hz), 1.80—2.30 (2 H, m), 2.50 (1 H, m), and 4.01 and 4.50 (1 H, m, CH_3CH–O), [lit.,[12] 4.03 (seq. *trans* CH_3CH–O), 4.56 (seq. *cis* CH_3CH–O)].

4-Ethyl-3-methyl-γ-butyrolactone (**3j**), b.p. 103—106 °C/11 mmHg (Kugelrohr), $\nu_{max.}$(neat) 1 800 cm^{-1}; $\delta_H(CCl_4)$ 1.04 (3 H, t, *J* 6.5 Hz), 1.14 (3 H, d), 1.44—2.76 (3 H, m), 3.90 and 4.28 (1 H, m, CH_3CH–O), [lit.,[12] 4.20 (m, *cis* CH_3CH–O), and 3.87 (m, *trans* CH_3CH–O)].

4-Isopropyl-3-methyl-γ-butyrolactone (**3k**), b.p. 113—115 °C/11 mmHg (Kugelrohr), $\nu_{max.}$(neat) 1 770 cm^{-1}; $\delta_H(CCl_4)$ 0.98—1.02 (6 H, dd, *J* 9.77, 9.77 Hz), 1.16 (3 H, d, *J* 6.7 Hz), 1.85—1.90 (1 H, m), 2.17 (1 H, dd, *J* 17.7, 17.4 Hz), 2.33—2.40 (1 H, m), 2.70 (1 H, dd, *J* 17.7, 17.4 Hz), 3.85 and 3.96 (1 H, m, CH_3CH–O) [lit.,[14] 3.85 (dd, CH_3CH–O), and 3.94 (dd, 1 H, CH_3CH–O)].

3-Methyl-4-phenyl-γ-butyrolactone (**31**) was obtained from (**11**) by Method C and successive Jones oxidation without isolation of the tetrahydrofuran intermediate in 73% yield; b.p. 127—130 °C/3 mmHg (Kugelrohr) (lit.,[13] 128—130 °C/2.5 mmHg), $\nu_{max.}$(neat) 1 785 cm^{-1}; $\delta_H(CCl_4)$ 0.82 and 1.15 [3 H, d, *J* 6.5 Hz (*cis*); 6.0 Hz (*trans*)], 2.15—2.80 (3 H, m), 4.85 (1 H, d, *J* 8.0 Hz), 7.20 (5 H, s) [lit.,[12] 0.65 (d, *J* 7.0 Hz, *cis* CH_3), and 1.15 (d, *J* 6.0 Hz, *trans* CH_3)].

3-Methyl-2-phenyl-γ-butyrolactone (**3m**)[15] was obtained from (**1m**) by the method used for the preparation of (**3l**) in 60% yield; b.p. 90—93 °C/3 mmHg (Kugelrohr), $\nu_{max.}$(neat) 1 775 cm^{-1}; $\delta_H(CCl_4)$ 0.78 and 1.16 [3 H, d, *J* 7.5 Hz (*cis*); d, *J* 7.5 Hz (*trans*)], 2.50—2.90 (1 H, m), 3.30 (d, 1 H, *J* 11.0 Hz), 3.80 (1 H, t, *J* 9.0 Hz), 4.50 (1 H, t, *J* 9.0 Hz), and 7.30 (5 H, s).

Preparation of Dibutylchlorostannylpropanol (**4**).—To a solution of dibutyldichlorotin (16.6 g, 54.0 mmol) and AIBN (0.089 g, 0.54 mmol) in allyl alcohol (30 ml) cooled in an ice-bath was added dibutylstannane (12.7 g, 54.0 mmol). After 15 min, the reaction mixture was warmed to 40 °C and stirred for 10 h. The excess of allyl alcohol was evaporated off and the residue was chromatographed on silica gel. Elution with chloroform gave (**4**) (25.56 g, 86%), b.p. 147—150 °C/0.03 mmHg (Found: C, 40.35; H, 7.75; Cl, 11.7. $C_{11}H_{25}ClOSn$ requires C, 40.35; H, 7.70; Cl, 10.83%); $\nu_{max.}$(neat) 3 345 cm^{-1}; $\delta_H(CDCl_3)$ 0.67—2.00 (22 H, m), 3.60 (2 H, t, *J* 5.4 Hz), and 4.28 (1 H, s).

Preparation of (Dibutylchlorostannyl)propylmethacrylate (**5**).—Methacrloyl chloride (1.92 g, 18.3 mmol) was added dropwise over 20 min to an ice-cooled solution of (**4**) (3.0 g, 9.16 mmol) and 4-dimethylaminopyridine (2.24 g, 18.3 mmol) in dichloromethane (20 ml). The mixture was warmed to room temperature and stirred for 5 h. The resulting solution was poured into water (150 ml) and extracted with ether. The extract was dried ($MgSO_4$) and evaporated to give (**5**) (2.73 g, 75%); $\nu_{max.}$(neat) 1 720—1 740 and 1 160 cm^{-1}; $\delta_H(CDCl_3)$ 0.67—2.17 (22 H, m), 1.93 (3 H, s), 4.15 (2 H, t, *J* 6.0 Hz), 5.56 (1 H, s), and 6.08 (1 H, s).

Preparation of the Polymeric Tin Compound (**6**).—Styrene (1.05 g, 10.1 mmol) and (**5**) (1.0 g, 2.53 mmol) were copolymerized in the presence of divinylbenzene (0.082 g, 0.63 mmol) and AIBN (0.022 g, 0.13 mmol) in benzene (5 ml) at 70 °C for 96 h in a sealed tube. The resulting gelatinous material was washed with methanol to afford (**6**) (1.32 g, 64.4 wt%); $\nu_{max.}$(film) 1 780 and 1 180 cm^{-1}. The content of the tin moiety was estimated by elemental analysis [Found: C, 72.59; H, 7.42; Sn, 3.41% (styrene unit/Sn = 84.7/15.3)].

Acknowledgements

We thank Professor P. Moland (University of Ottawa) for the n.m.r. data for compound (**3m**).

References

1 J-M. Surzur, 'Reaction Intermediates,' ed. R. A. Abramovitch, Plenum, New York, 1979, vol. 2, p. 204.
2 C. Walling and A. J. Cioffali, *J. Am. Chem. Soc.*, 1972, **94**, 6059; D. J. Edge and J. K. Kochi, *ibid.*, 1972, **94**, 7695; T. W. Smith and G. B. Butller, *J. Org. Chem.*, 1978, **43**, 6; D. H. R. Burton, A. L. J. Beckwith, and A. J. Goosen, *J. Chem. Soc.*, 1965, 181; M. Julia, C. Descoins, M. Billarge, B. Jaquet, D. Uguen, and F. Groeger, *Tetrahedron Lett.*, 1975, 1737.
3 A. L. J. Beckwith and K. U. Ingold, 'Rearrangement in Ground and Excited States,' ed. P. de Mayo, Academic Press, New York, 1980, vol. 1, p. 182; A. L. J. Beckwith, *Tetrahedron*, 1981, **37**, 3073 and references cited therein.

4 For recent examples see; R. Scheffold, M. Dike, S. Dike, T. Herold, and L. Walder, *J. Am. Chem. Soc.*, 1980, **102**, 3642; M. D. Bachi, F. Frolow, and C. Hoornaert, *J. Org. Chem.*, 1983, **48**, 1841; S. Danishefsky, S. Chackalamannil, and B. J. Uang, *J. Org. Chem.*, 1982, **47**, 2231; D. J. Hart and C. Chuang, *J. Org. Chem.*, 1983, **48**, 1784; A. L. J. Beckwith and D. R. Boate, *Tetrahedron Lett.*, 1985, 1761; M. Okabe, M. Abe, and M. Tada, *J. Org. Chem.*, 1982, **47**, 1775, 5382; D. L. J. Clive, P. L. Beaulieu, and Lu Set, *J. Org. Chem.*, 1984, **49**, 1313; N. N. Marinovic and H. Ramanathan, *Tetrahedron Lett.*, 1983, 1871; J. Barluenga, J. L. Prado, P. J. Campos, and G. Asensio, *Tetrahedron*, 1983, **39**, 2863; E. J. Coley and S. G. Pyne, *Tetrahedron Lett.*, 1983, 2821; M. Ladlow and G. Pattenden, *ibid.*, 1984, 4317; G. A. Kraws and K. Landgrebe, *ibid.*, 1984, 3939; R. Grigg, J. F. Malone, T. R. Mitchell, A. Ramasubbu, and R. M. Scott, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1754; C. S. Wilcox and L. M. Thomasco, *J. Org. Chem.*, 1985, **50**, 546; A. Padwa, H. Nimmesgern, and G. S. K. Wong, *Tetrahedron Lett.*, 1985, 957; N. Ono, H. Miyake, and A. Kaji, *Chem. Lett.*, 1985, 635.

5 (*a*) Y. Ueno, K. Chino, and M. Okawara, *Tetrahedron Lett.*, 1982, 2575; (*b*) Y. Ueno, R. K. Khare, and M. Okawara, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2637; (*c*) Y. Ueno, C. Tanaka, and M. Okawara, *Chem. Lett.*, 1983, 795; (*d*) O. Moriya, Y. Ueno, and M. Okawara, *Chem. Lett.*, 1984, 1437.

6 G. Stork and N. H. Baine, *J. Am. Chem. Soc.*, 1982, **104**, 2321; G. Stork and R. Mook, Jr., *ibid.*, **105**, 3741; G. Stork and P. M. Sher, *ibid.*, 1983, **105**, 6765; G. Stork and M. Kahn, *ibid.*, 1985, **107**, 500.

7 J. C. Craig and E. C. Horning, *J. Org. Chem.*, 1960, **25**, 2098.

8 N. M. Weinshenker, G. A. Grosby, and J. Y. Wong, *J. Org. Chem.*, 1975, **40**, 1966. H. Schumann and B. Pachaly, *Angew. Chem., Int. Ed. Engl.*, 1981, 1043.

9 E. J. Corley and J. W. Suggs, *J. Org. Chem.*, 1975, **40**, 2554.

10 K. Saigo, M. Morikawa, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 1656; J. M. Berge and S. M. Roberts, *Synthesis*, 1979, 471.

11 T. L. Crowley and H. Rapoport, *Acc. Chem. Res.*, 1976, **9**, 135.

12 S. Byström, H. E. Högberg, and T. Norim, *Tetrahedron*, 1981, **37**, 2249.

13 M. Tokuda, Y. Yokoyama, T. Taguchi, A. Suzuki, and M. Itoh, *J. Org. Chem.*, 1972, **37**, 1859.

14 H. Nagashima, H. Wakamatsu, K. Itoh, Y. Tomo, and J. Tsuji, *Tetrahedron Lett.*, 1983, 2395.

15 A. L. J. Beckwith, T. Lawrence, and A. K. Serelis, *J. Chem. Soc., Chem. Commun.*, 1980, 484.

16 M. M. Kayser and P. Moland, *Tetrahedron Lett.*, 1979, 695.

17 H. House, J. Lubinowski, and J. J. Good, *J. Org. Chem.*, 1975, **40**, 86.

18 J. E. Baldwin and L. E. Walker, *J. Org. Chem.*, 1966, **31**, 3985.

Received 15*th July* 1985; *Paper* 5/1194