

Synthesis and Reaction of 3-Hydroxytetrahydro-4H-pyran-4-one

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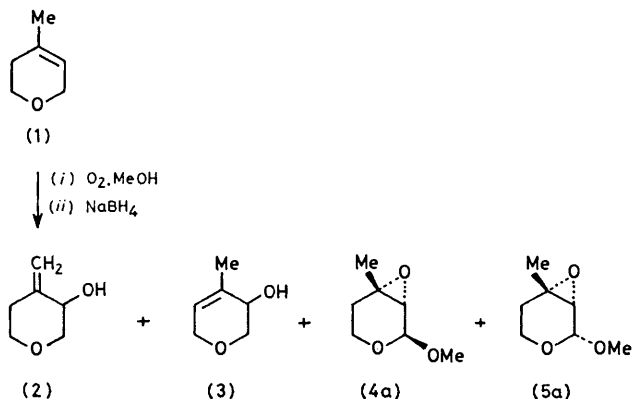
Photosensitized oxygenation of 5,6-dihydro-4-methyl-2H-pyran (1) in methanol followed by reduction gave two kinds of allyl alcohols [(2) and (3)] together with the epoxy-ethers (4) and (5). When the reaction was carried out in solvents other than alcohols it gave (2) and (3) exclusively. Ozonization of 4-methylenepyrans (2) and (13) followed by reduction with zinc powder-acetic acid afforded 3-hydroxytetrahydropyrans (11) and (14). Bromination of (14) gave the dibromide (16), which yielded bromopyran (17) and 3-acetoxy-4H-pyran-4-one (18) on treatment with 1,8-diazabicyclo[5.4.0]undecene. However, the reaction of (16) with silver acetate in acetic acid predominantly afforded (17) in excellent yield. Other allied reactions and mechanisms of these reactions are described.

We have previously reported the synthesis of tetrahydro-4H-pyran-3,4-diones and their derivatives,¹ and in this paper we describe the formation of 3-hydroxytetrahydro-4H-pyran-4-one from 5,6-dihydro-4-methyl-2H-pyran (1) and its chemistry.

The photosensitized oxygenation of allyl methyl ethers have been studied,² but that of dihydropyrans has received little attention. Photosensitized oxygenation of 1-methylcyclohexene has been shown³ to give two secondary alcohols and tertiary allyl alcohol, and we therefore felt that for compound (1) which possesses an allylic oxygen the behaviour of corresponding tertiary hydroperoxide (generated *in situ*) would be of interest.

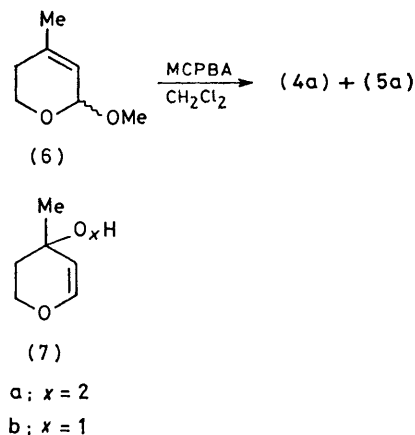
RESULTS AND DISCUSSION

Rose Bengal-sensitized photo-oxidation (see Experimental section) of (1) in methanol at 20 °C for 45 h, followed by treatment with sodium borohydride, gave two allyl alcohols [(2) and (3)] and a mixture of epoxy-ethers [(4a) and (5a)] along with recovered (1) (68.2%).



The structures of the compounds (2)—(5a) were assigned on the basis of their i.r., n.m.r., and mass spectra, and by elemental analysis. The ¹H n.m.r. spectrum of (4a) exhibits singlets at δ 2.67 (C-3 proton) and 4.59 (C-2 proton); (5a), however, exhibits doublets at δ 2.94 (*J* 3.0 Hz) and 4.65 (*J* 3.0 Hz). From these results, (4a) is assigned the *trans* configuration and (5a) the *cis* configuration. The observed coupling constant

of 3.0 Hz is consistent with the *cis* conformation, in accordance with the Karplus relationship.⁴ In order to confirm the stereochemistry of the epoxy-ether, the epoxidation of 5,6-dihydro-2-methoxy-4-methyl-2H-pyran (6)⁵ was examined. Epoxidation of (6) with *m*-



chloroperbenzoic acid (MCPBA) afforded a mixture of (4a) and (5a), ratio 84 : 16, in 56% yield. This ratio is in accordance with reported results and is due to steric hindrance of the methoxy-group.⁶

In the photo-oxidation of (1) it is suggested that products (2) and (3) arose from a normal 'ene'-type reaction followed by reduction. Products (4a) and (5a) may have arisen from the tertiary hydroperoxide (7a). None of the possible tertiary alcohol (7b) was isolated from the reaction. To find support for the possible intermediacy of hydroperoxide in the formation of (4a) and (5a) the following experiments were carried out.

Bubbling oxygen through a solution of (1) in various alcohols in the presence of 2,2'-azobis-(2-methylpropionitrile) (AIBN), followed by treatment with sodium borohydride, afforded the expected epoxy-ethers [(4) and (5)] along with the radical oxidation products (8) and (9) (Table 1).

We also examined the oxidation of 2,3-dihydro-4-methyl-4H-pyran (10).⁷ Photo-oxygenation of (10) in methanol, followed by reduction with sodium borohydride, gave the 'ene'-mode product (9) and the

TABLE 1
Radical oxidation of (1) in alcohols^a

R	Temperature (°C)	Time/h	Products (%) ^b
Me	63–65	20	(4a) (2.0), (5a) (6.1), (8) (2.6), (9) (20.0)
CHMe ₂	70–73	21	(4b) (3.3), (5b) (7.7), (9) (10.0)
CH ₂ Ph	70–73	26	(4c) (3.6), (5c) (10.4), (9) (16.0)

^a Under the conditions, a large amount of (1) was recovered.

^b Isolated yield.

TABLE 2
Sensitized photo-oxygenation of (1)

Concentration/mol dm ⁻³	Solvent	Sensitizing dye ^a	Temperature (°C)	Time/h	Yield (%)	Ratio (%) ^b
0.4	MeOH	RB	20	45	23.1 ^c	68 : 32
0.4	MeCN	RB	20	35	40.8	70 : 30
0.4	CH ₂ Cl ₂	HP	20	35	38.1	68 : 32
0.5	MeCN	RB	20	40	45.4	70 : 30
1.1	MeCN	RB	18	25	39.7	70 : 30

^a RB, Rose Bengal; HP, hematoporphyrin. ^b Determined by g.l.c. ^c Epoxy-ethers (4a) and (5a) were also obtained.

'dioxetan'-mode product⁸ (polymerized). In this reaction no epoxy-ethers were detected, but the radical oxidation of (10) in methanol afforded a mixture of (4a) and (5a).

Thus in the sensitized photo-oxygenation of (1) it is reasonable to postulate that the putative tertiary hydro-

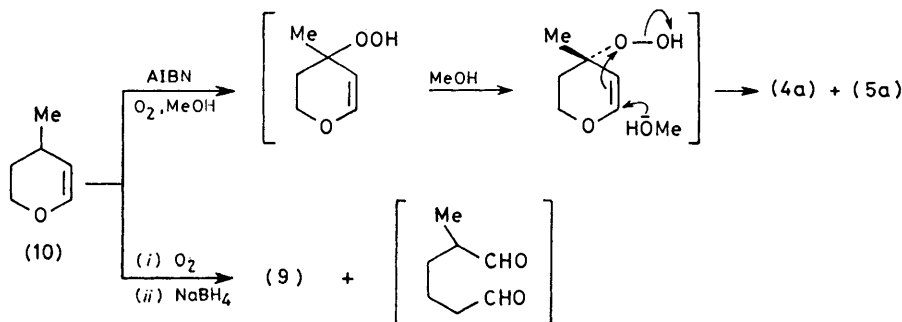
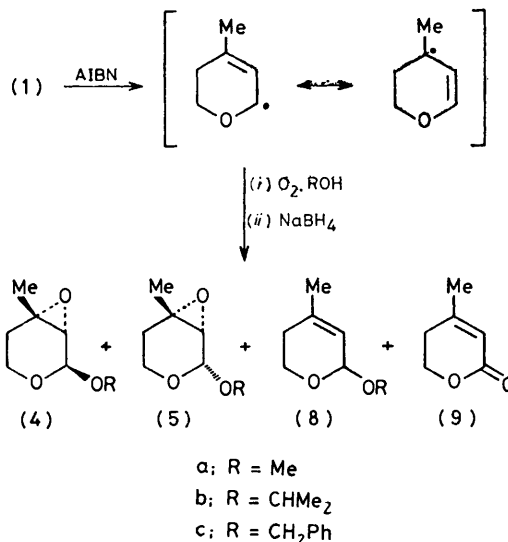
peroxide formed in the first stage was decomposed by the reaction with alcohol to give the epoxy-ethers (4) and (5). We therefore examined photo-oxygenation of (1) in various solvents, and the results are summarized in Table 2.

When (1) in acetonitrile was photo-oxidized for 40 h and subsequently reduced with sodium borohydride, a mixture of (2) and (3) was obtained, in the ratio 7 : 3, in 45.4% yield. Although compounds (2) and (3) were separable by preparative g.l.c., 3-hydroxytetrahydro-4H-pyran-4-one (11) was expected to be easily isolable by the oxidation used in the next step, and thus the mixture of (2) and (3) was used without further purification.

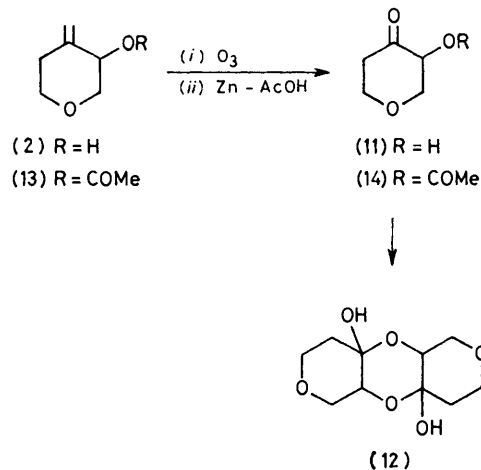
A solution of (2) in methylene chloride was ozonized at -50 °C and after decomposition of the ozonide with zinc powder-acetic acid, (11) was isolated in a pure state in 80% yield.

Compound (11) was converted to the stable acetoxy-derivative (14) by treatment with acetic anhydride in

the presence of sodium acetate. When set aside for several weeks, the mobile liquid (11) dimerized⁹ to the crystalline hemiacetal (12).



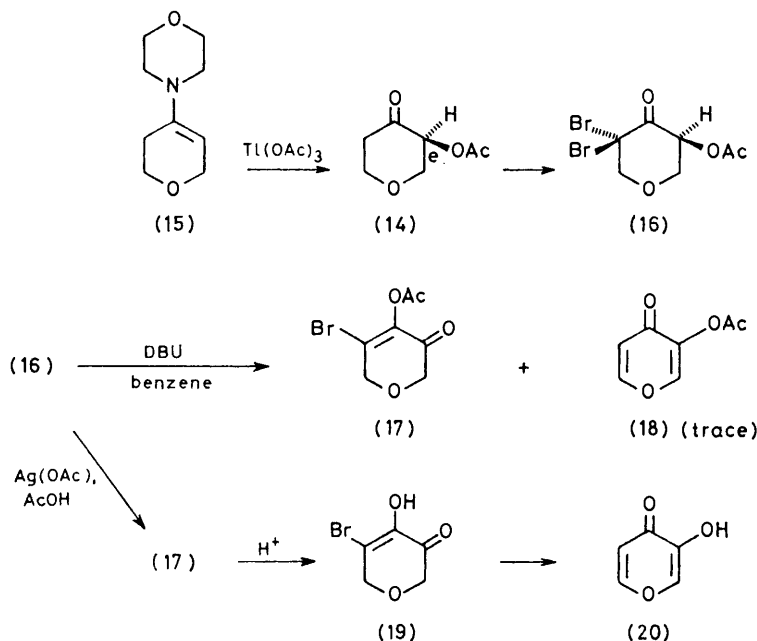
zinc powder-acetic acid. The structure of (14) was assigned by i.r. and n.m.r. spectra, elemental analysis, and comparison with a sample prepared by the reaction



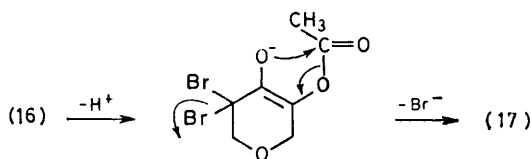
of 2,3-dihydro-4-morpholino-2H-pyran (15) with thallic acetate¹⁰ in acetic acid.

The acetoxy-group in compound (14) was in the equatorial orientation, on the basis of n.m.r. spectroscopy. Dioxan dibromide dibromination of (14) resulted in the formation of (16) as a white, crystalline material.

The reaction of (16) with 1,8-diazabicyclo[5.4.0]-undecene (DBU) in benzene at 5 °C gave (17) and a trace of 3-acetoxypyromeconic acid (18). The formation of (17) indicated that 1,3-elimination of hydrogen bromide accompanied by intramolecular migration of the acetyl group¹¹ had occurred.



Treatment of 3,3,5-tribromotetrahydro-4H-pyran-4-one with silver acetate in acetic acid at room temperature for 3 h has been shown¹ to afford the hydroxypyryone (19) and the enol acetate (17) (ratio 2 : 1) in excellent yield. Under similar conditions, (16) was unchanged; however, reaction of (16) with silver acetate at 115–120 °C for 10 h predominantly provided (17) in 80%



yield; no hydroxypyryone (19) was isolated. These results suggest that (16) is not an intermediate in the reaction starting from 3,3,5-tribromotetrahydro-4H-pyran-4-one. Hydrolysis of (17) afforded (19), which has been shown to give pyromeconic acid (20) by dehydrobromination.¹

EXPERIMENTAL

N.m.r. spectra were recorded on a JEOL C-60 spectrophotometer; i.r. spectra were taken on a Hitachi model

215 spectrophotometer; mass spectra were determined on a Hitachi RMU-6E spectrometer. For column chromatography Wakogel C-200 was used. G.l.c. was performed with a Shimadzu GC-4A instrument using 15% PEGS on 60–80 mesh Cerite, on a 3 m × 3 mm column.

Photosensitized Oxidation of 5,6-Dihydro-4-methyl-2H-pyran (1).—The following results were typical, and individual conditions are listed in Table 2. Dihydropyran (1) (2.0 g) in absolute methanol (50 ml) containing Rose Bengal (0.05 g) was irradiated (five 30 W fluorescent tubes) and oxygenated at 20 °C for 45 h (collapse of the red colour was observed). The reaction mixture was then added to a solution of sodium borohydride (0.45 g) in 1.2N sodium

hydroxide (10 ml) and stirred for 2 h. Excess of sodium borohydride was destroyed by addition of saturated ammonium chloride solution, and the mixture was then poured into water and extracted with ether–methylene chloride. The extract was dried and distilled to give recovered (1) (68.2%), and a residual oil which was chromatographed on a silica gel column. Elution with n-hexane–isopropyl ether (1 : 1) gave a mixture (68 : 32 by g.l.c.) of the allyl alcohols (2) and (3) (0.527 g, 23.1%) and a mixture (41 : 59 by g.l.c.) of (4a) and (5a) (0.187 g, 6.5%). The products were separated by preparative g.l.c. (PEGS, 3 m × 3 mm; 145 °C, He). 3-Hydroxy-4-methylenetetrahydropyran (2) had b.p. 78–79 °C at 20 mmHg; ν_{max} (neat) 3 400 (O–H), 1 655 (C=C), 1 100 (C–O–C), and 900 cm^{-1} (C=CH₂); $\delta(CCl_4)$ 2.30 (2 H, m), 3.0–4.1 (6 H, m), 4.77 (1 H, s), and 4.91 (1 H, s); m/e 114 (M^+) (Found: C, 63.05; H, 8.9. C₆H₁₀O₂ requires C, 63.15; H, 8.85%). 5,6-Dihydro-5-hydroxy-4-methyl-2H-pyran (3) had b.p. 95–96 °C at 22 mmHg; ν_{max} (neat) 3 400 (O–H), 1 650 (C=C), and 1 100 cm^{-1} (C–O–C); $\delta(CCl_4)$ 1.80 (3 H, br s), 2.85 (1 H, s), 3.93 (2 H, m), 3.3–3.8 (3 H, m), and 5.42 (1 H, m); m/e 114 (M^+) (Found: C, 62.9; H, 8.7. C₆H₁₀O₂ requires C, 63.15; H, 8.85%). Except for methanol as reaction solvent, the resulting oil was directly distilled to give a mixture of (2) and (3) (b.p. 92–97 °C at 23 mmHg). trans-2-Methoxy-3,4-epoxy-4-methyltetrahydro-4H-pyran-4-one (4a) had b.p. 78–

79 °C at 20 mmHg; ν_{\max} (neat) 2 820 (OMe), 1 270, 1 070, 1 040, 965, 925, 890, and 835 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.35 (3 H, s), 1.6—1.9 (2 H, m), 2.67 (1 H, s), 3.38 (3 H, s), 3.1—3.8 (2 H, m), and 4.59 (1 H, s); m/e (%) 113 (5, $[M - \text{OMe}]^+$), 84 (46), 55 (81), and 41 (100) (Found: C, 58.25; H, 8.7. $\text{C}_7\text{H}_{12}\text{O}_3$ requires C, 58.3; H, 8.4%). *cis*-2-Methoxy-3,4-epoxy-4-methyltetrahydro-4H-pyran-4-one (5a) had b.p. 93—94 °C at 22 mmHg; ν_{\max} (neat) 2 845 (OMe), 1 265, 1 070, 1 040, 960, 870, and 840 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.32 (3 H, s), 1.6—1.9 (2 H, m), 2.94 (1 H, d, J 3.0 Hz), 3.33 (3 H, s), 3.1—3.8 (2 H, m), and 4.65 (1 H, d, J 3.0 Hz); m/e (%) 113 (9, $[M - \text{OMe}]^+$), 84 (38), 55 (79), and 43 (100) (Found: C, 57.95; H, 8.4. $\text{C}_7\text{H}_{12}\text{O}_3$ requires C, 58.3; H, 8.4%).

Epoxidation of 5,6-Dihydro-2-methoxy-4-methyl-2H-pyran (6).—To a mixture of (6) (1.30 g, 0.01 mol) in methylene chloride (100 ml) and 0.5M aqueous sodium hydrogen-carbonate (30 ml) was added 70% *m*-chloroperbenzoic acid (2.50 g, 0.01 mol) with stirring. After stirring at room temperature for 6 h, the organic layer was washed with 1N sodium hydroxide solution and water, and then dried. Removal of methylene chloride left a clear oil, which was distilled to yield a mixture (0.80 g, 56%) of the *trans*- (4a) and *cis*-epoxy-ether (5a) [(4a):(5a) = 84:16 by g.l.c.], b.p. 78—79.5 °C at 20 mmHg.

Free-radical Oxidation of (1) in Various Alcohols.—The following results were typical, and individual conditions are listed in Table 1. Through a refluxing mixture of (1) (13.7 g, 0.14 mol), methanol (5.5 g, 0.17 mol), and AIBN (0.1 g, 0.006 mol) oxygen was bubbled for 20 h. The reaction mixture was then treated with sodium borohydride (3.2 g, 0.084 mol) in 2N sodium hydroxide (42 ml). After the usual work-up, the resulting oil from the organic layer was chromatographed on a silica gel column and eluted with *n*-hexane-isopropyl ether (1:1) to give 5,6-dihydro-2-methoxy-4-methyl-2H-pyran (8) (0.44 g, 2.6%) and a mixture of (4a) and (5a) (1.59 g, 8.1%) [(4a):(5a) = 24:76 by g.l.c.], b.p. 82—96 °C at 18 mmHg. The aqueous layer was then acidified with hydrochloric acid and extracted with chloroform. The extract was dried, evaporated, and distilled to give 5,6-dihydro-4-methyl-2H-pyran-2-one (9) (3.41 g, 20%). (8), b.p. 40 °C at 21 mmHg; ν_{\max} (neat) 2 820 (OMe), 1 670 (C=C), and 1 060 cm^{-1} (C—O—C); $\delta(\text{CCl}_4)$ 1.74 (3 H, br s), 1.9 (2 H, m), 3.32 (3 H, s), 3.7 (2 H, m), 4.66 (1 H, br s), and 5.34 (1 H, br s); m/e (%) 128 (1, M^+), 97 (34, $[M - \text{OMe}]^+$), 53 (69), and 41 (100). (9), b.p. 81—82 °C at 0.3 mmHg; ν_{\max} (neat) 1 725 (C=O) and 1 645 cm^{-1} (C=C); $\delta(\text{CCl}_4)$ 1.99 (3 H, m), 2.36 (2 H, t, J 6.0 Hz), 4.30 (2 H, t, J 6.0 Hz), and 5.67 (1 H, m); m/e (%) 112 (14, M^+), 82 (100, $[M - \text{CH}_2\text{O}]^+$), and 54 (66).

The epoxy-ethers (4b, c) and (5b, c) and the δ -lactone (9) were similarly obtained, and pure samples were isolated by preparative g.l.c. (4b), n_D^{20} 1.443 2; ν_{\max} (neat) 1 270, 1 050 (C—O—C), 1 205, 920, and 780 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.14 (3 H, d, J 6.0 Hz), 1.18 (3 H, d, J 6.0 Hz), 1.32 (3 H, s), 1.77 (2 H, m), 2.62 (1 H, s), 3.40 (2 H, m), 3.88 (1 H, heptet, J 7.0 Hz), and 4.78 (1 H, s). (5b), n_D^{20} 1.4572; ν_{\max} (neat) 1 265, 1 035 (C—O—C), 1 135, 1 050, and 870 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.15 (3 H, d, J 6.0 Hz), 1.20 (3 H, d, J 6.0 Hz), 1.34 (3 H, s), 1.70 (2 H, m), 2.87 (1 H, d, J 4.0 Hz), 3.45 (2 H, m), 3.72 (1 H, heptet, J 7.0 Hz), and 4.86 (1 H, d, J 4.0 Hz). (4c), n_D^{20} 1.515 0; ν_{\max} (neat) 3 060, 3 020, 1 495 (phenyl), 1 270, 1 045 (C—O—C), 925, 735, and 695 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.33 (3 H, s), 1.77 (2 H, m), 2.72 (1 H, s), 3.42 (2 H, m), 4.50 (1 H, d, J 12.0 Hz), 4.65 (1 H, d, J 12.0 Hz), 4.78 (1 H, s), and 7.23 (5 H, s) (Found: C, 70.8; H, 7.3. $\text{C}_{13}\text{H}_{16}\text{O}_3$

requires C, 70.9; H, 7.3%). (5c), m.p. 29.5—30 °C; ν_{\max} (KBr) 3 060, 3 030, 1 605, 1 500 (phenyl), 1 270, 1 050 (C—O—C), 860, 730, and 690 cm^{-1} ; $\delta(\text{CCl}_4)$ 1.34 (3 H, s), 1.72 (2 H, m), 2.89 (1 H, d, J 4.0 Hz), 3.50 (2 H, m), 4.50 (1 H, d, J 12.0 Hz), 4.65 (1 H, d, J 12.0 Hz), 4.80 (1 H, d, J 4.0 Hz), and 7.23 (5 H, s).

Oxidation of 3,4-Dihydro-4-methyl-2H-pyran (10).—(a) A mixture of the dihydropyran (10) (2.0 g) in methanol (50 ml) and Rose Bengal (0.05 g) was photo-oxygenated at 20 °C for 45 h. Sodium borohydride (0.45 g) in 1.2N sodium hydroxide (10 ml) was then added, and after 2 h excess of sodium borohydride was destroyed by the addition of ammonium chloride. After normal work-up, the resulting oil was distilled to give (9) (0.40 g); further (9) (0.36 g) was obtained from acidification of the aqueous layer; combined yield of (9), 0.76 g (34%), b.p. 110—114 °C at 25 mmHg. It was identical (i.r. and n.m.r. spectra) with a sample of (9) prepared by free-radical oxidation of (1).

(b) Into a refluxing solution of (10) (1.2 g) in methanol (30 ml) containing AIBN (0.03 g), oxygen was bubbled for 20 h. After treatment with sodium borohydride in sodium hydroxide and work-up, the resulting mixture was concentrated to give a residual oil, g.l.c. analysis (15% PEGS, 145 °C) of which indicated that it was primarily starting material (10), with small amounts of the epoxy-ethers (4a) (0.8%) and (5a) (1.1%).

3-Hydroxytetrahydro-4H-pyran-4-one (11).—A 7:3 mixture of (2) and (3) (11.8 g) in methylene chloride (150 ml) was placed in a 500-ml flask equipped with an ozone inlet, and a gas outlet. Ozone was produced by electric discharge from an ozonator and bubbled through the solution at -50 °C for 3 h; excess of O_3 was then removed by flushing with oxygen. Acetic acid (60 ml), water (2 ml), ether (60 ml), and zinc powder (20 g) were then added to the ozonolysis mixture, which was stirred under reflux (46 °C) for 1 h. When the ozonide had been completely decomposed, the inorganic materials were filtered off and the filtrate was dried (MgSO_4). The solvent was removed under reduced pressure, and the residue distilled to give (11) (3.40 g, 43%), b.p. 50—54 °C at 0.15 mmHg; ν_{\max} (neat) 3 390 (O—H) and 1 720 cm^{-1} (C=O); $\delta(\text{CDCl}_3)$ 2.5—2.9 (2 H, m), 3.2—4.0 (4 H, m), and 4.0—4.5 (2 H, m). This compound dimerised to give crystals of (12) when set aside for a few weeks in an ice box; (12), m.p. 125—127 °C; ν_{\max} (KBr) 3 380 cm^{-1} (O—H); m/e 116 ($[M/2]^+$) (Found: C, 51.2; H, 6.8. $\text{C}_{10}\text{H}_{16}\text{O}_6$ requires C, 51.7; H, 6.9%). *3-Acetoxytetrahydro-4H-pyran-4-one* (14) had m.p. 85—86 °C, ν_{\max} (KBr) 1 740 and 1 720 cm^{-1} (C=O); $\delta(\text{CDCl}_3)$ 2.15 (3 H, s), 2.62 (2 H, m), 3.58 (2 H, m), 4.23 (2 H, m), 6.37 (1 H, dd, J 7.0 and 11.0 Hz, 3-axial proton) (Found: C, 53.3; H, 6.55. $\text{C}_7\text{H}_{10}\text{O}_4$ requires C, 53.15; H, 6.35%).

3-Acetoxy-4-methylenetetrahydropyran (13).—Acetylation of a 7:3 mixture of (2) and (3) (10.5 g), with acetic anhydride (70 ml) and sodium acetate (1.2 g) at 60 °C for 7 h and distillation gave 12.2 g (87%) of a mixture of the corresponding acetates, b.p. 46—50 °C at 0.8 mmHg.

2,3-Dihydro-4-morpholino-2H-pyran (15).—A mixture of tetrahydro-4H-pyran-4-one (2.0 g, 0.02 mol),¹² morpholine (1.7 g, 0.04 mol), and toluene (5 ml) was refluxed, while the water was removed with a Dean and Stark trap, for 3 h. Removal of the solvent and distillation of the residue gave 3.30 g (97%) of (15), b.p. 62—64 °C at 0.1 mmHg; ν_{\max} (neat) 1 650 cm^{-1} (C=O); $\delta(\text{CCl}_4)$ 2.21 (2 H, m), 2.85 (4 H, m), 3.79 (4 H, m), 3.91 (2 H, m), 4.24 (2 H, m), and 4.60 (1 H, m).

3-Acetoxytetrahydro-4H-pyran-4-one (14).—(a) Preparation of (14) was carried out according to the procedure for (11) described above, but using, instead of (2), compound (13) (15.6 g, 70% purity) prepared as above; the crystalline product was recrystallized from benzene–hexane to yield (14) (8.9 g, 80%), m.p. 85–86 °C.

(b) A mixture of (15) (2.7 g, 0.016 mol), acetic acid (20 ml), and thallic acetate (6.2 g, 0.016 mol)¹⁰ was stirred under a nitrogen atmosphere at 40 °C for 45 h. The thallium was filtered off, acetic acid was removed under reduced pressure, water (15 ml) was added, and the solution was extracted with chloroform. The chloroform extract was washed successively with 10% sodium hydrogencarbonate solution, 10% hydrochloric acid, and water, and dried over magnesium sulphate. Removal of the solvent gave a solid which was recrystallized from benzene–hexane to give pure (14) (1.38 g, 55%), m.p. 85–86 °C, which was identical with a sample prepared by acetylation of (11) as described above.

3-Acetoxy-5,5-dibromotetrahydro-4H-pyran-4-one (16).—Bromine (4.6 g, 0.029 mol) was added dropwise to dioxan (3 ml) with stirring at room temperature. The acetoxy-pyran (14) (1.9 g, 0.012 mol) in ether (10 ml) was added to the mixture at 20 °C, and the mixture was stirred for 12 h and then poured into ice–water. The organic layer was separated, the aqueous layer was extracted with ether, and the combined ethereal solution was well washed with water and then dried over magnesium sulphate. Removal of the solvent and chromatography of the residue (silica gel, benzene as eluant) gave (16) (2.0 g, 51%), m.p. 59–61 °C; ν_{\max} (KBr) 1 740 and 1 720 cm^{-1} (C=O); $\delta(\text{CCl}_4)$ 2.16 (3 H, s), 3.65 (2 H, m), 4.33 (2 H, m), and 6.08 (1 H, dd, J 7.0 and 11.0 Hz) (Found: C, 26.6; H, 2.55; Br, 50.6. $\text{C}_7\text{H}_8\text{Br}_2\text{O}_4$ requires C, 26.6; H, 2.55; Br, 50.6%).

The Reaction of (16) with DBU.—To a mixture of (16) (1.0 g) in benzene (8 ml) was added DBU (1.0 g) at 0 °C, and the reaction was stirred at 6–8 °C for 20 h; the mixture was then neutralized with hydrochloric acid, the precipitated mass was filtered off, and the filtrate was dried (MgSO_4) and evaporated. Chromatography of the residue [a trace of the acetoxypropaneconic acid (18)¹³ was detected by t.l.c.] on a silica gel column using benzene–ethyl acetate (10 : 1) gave (17) (52 mg, 8%), m.p. 50–51 °C (lit.,¹ m.p.

50–51 °C); $\delta(\text{CCl}_4)$ 2.25 (3 H, s), 4.21 (2 H, s), and 4.61 (2 H, s); m/e (%) 236/234 (M^+) and 43 (100).

The Reaction of (16) with Silver Acetate.—A mixture of (16) (3.16 g, 0.01 mol) and silver acetate (3.0 g, 0.02 mol) in acetic acid (25 ml) was stirred at 115–120 °C for 10 h. The precipitated silver bromide was filtered off, acetic acid was removed *in vacuo*, and the residue was chromatographed on silica gel (eluant benzene) to give (17) (1.89 g, 80%), b.p. 91–93 °C at 0.15 mmHg, m.p. 50–51 °C.

5-Bromo-4-hydroxy-2H-pyran-3(6H)-one (19).—A mixture of (17) (30 mg) and 2M hydrochloric acid (5 ml) was heated at 100 °C for 1 h. The cooled mixture was concentrated, diluted with chloroform, dried (MgSO_4), and evaporated to leave an oil, which was chromatographed on silica gel to afford (19) (15 mg, 61%), m.p. 77–78 °C. The i.r. and n.m.r. spectra were identical with those of an authentic sample.¹

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