Some reactions of 2,4-dimethoxytetrahydropyrans[1]

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Acid-catalyzed elimination of methanol from 2,4-dimethoxytetrahydropyran (**1**) produces 2-methoxy-5,6-dihydro-2*H*-pyran (**3**) rather than the expected olefin 4-methoxy-3,4-dihydro-2*H*-pyran (**2**).

The reaction of 1,3-dibromo-5,5-dimethylhydantoin with **3** in ether – methanol gives a 2:1 mixture of the isomers 3β-bromo-2α,4α-dimethoxytetrahydropyran (**5***a*) and 3α-bromo-2α,4β-dimethoxytetrahydropyran (**5***b*) respectively. A rationale is given to explain the preponderance of **5***a* over **5***b* and the highly selective attack of the bromine of the hydantoin and the methanol on C-3 and C-4 respectively of the double bond of **3**. Reduction of **5***ab* with zinc in ethanol provides only compound **3**.

The room temperature reaction of **1** in a mixture of water and 1,2-dimethoxyethane containing Amberlite IR-120, produces 2-hydroxy-4-methoxytetrahydropyran (**6**) as an equilibrium mixture of *cis* and *trans* isomers in the ratio 1:1. This gave a value of 0.9 kcal/mole for the anomeric effect in **6**. Pyrolysis of the derivative, 2-acetoxy-4-methoxytetrahydropyran failed to produce the olefin **2** and resulted only in extensive decomposition.

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Introduction

A recent communication from this laboratory described the preparation of *cis*- and *trans*-2,4-dimethoxytetrahydropyran (1). Since then, we have explored the utility of these isomers as intermediates for the preparation of 3-alkyl (or aryl) thio-2,4-dimethoxytetrahydropyrans. Although in our hands the 2,4-dimethoxytetrahydropyrans could not be converted to 3-alkyl (or aryl) thio-2,4-dimethoxytetrahydropyrans, a number of interesting reactions and properties of the dimethoxy compounds was discovered. This paper describes the results of these findings.

Results and Discussion

Since it has been shown that 3,4-dihydro-2*H*-pyran reacts with ethanesulfenyl chloride and then with methanol to produce 3-ethylthio-2-methoxytetrahydropyran (2, 3), it is quite possible that 4-methoxy-3,4-dihydro-2*H*-pyran (**2**, Scheme 1) might react in the same manner to provide the 3 - alkylthio - 2,4 - dimethoxytetrahydropyran. Accordingly, attempts were made to convert 2,4-dimethoxytetrahydropyran, (**1**), into **2**. This appeared to be feasible since both 2-*n*-butoxy-4-methyltetrahydropyran (4) and the 2-ethoxy homologue (5) have been successfully converted to 4-methyl-3,4-dihydro-2*H*-pyran by treatment with phosphorus pentoxide and *p*-toluenesulfonic acid respectively.

A *cis–trans* mixture of 2,4-dimethoxytetrahydropyran (**1**) (1) was heated at 180° with a catalytic amount of phosphorus pentoxide (4). Only extensive decomposition occurred. At a lower temperature (130° for 1.5 h), only unchanged **1** was obtained in an 88% yield (by distillation). When **1** was heated at 150° with a catalytic amount of *p*-toluenesulfonic acid (5), only 2-methoxy-5,6-dihydro-2*H*-pyran (**3**, Scheme 1) was obtained in an 86% yield. This product was identical in all respects with an authentic sample (6).

The formation of **3** is somewhat surprising since of the two methoxy groups in **1**, that at the anomeric carbon (C-2) is undoubtedly the more readily removed by acid catalysts because it is part of an acetal structure. It is quite likely that compound **3** was formed by a route such as the reverse of eq. *a*, Scheme 2 in the previous report (1).

A second route to 4-methoxy-3,4-dihydro-2*H*-pyran (**2**) was attempted, based upon the knowledge that reductive removal of halogen and an alkoxy group from a β-haloether leads to the formation of an olefin (7). The necessary intermediate, 3 - bromo - 2,4 - dimethoxytetrahydropyran was prepared by the reaction of 1,3-dibromo-5,5-dimethylhydantoin with 2-methoxy-5,6-dihydro-2*H*-pyran (**3**) in the solvent ether – methanol, a technique for bromomethoxylation of olefins employed by van de Sande and Kopecky (8). This route provided in a

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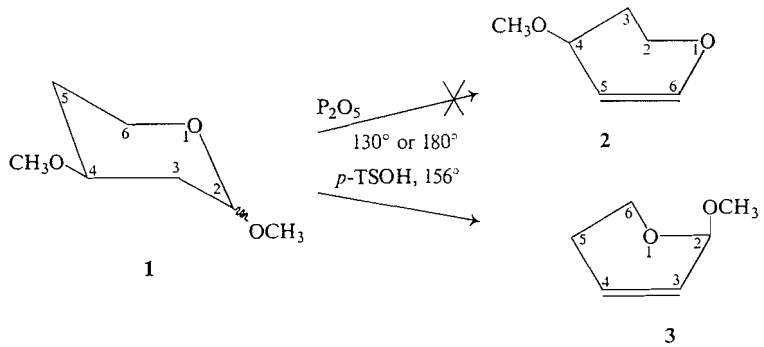


(p-TSOH = p-$CH_3C_6H_4SO_3H$)

SCHEME 1

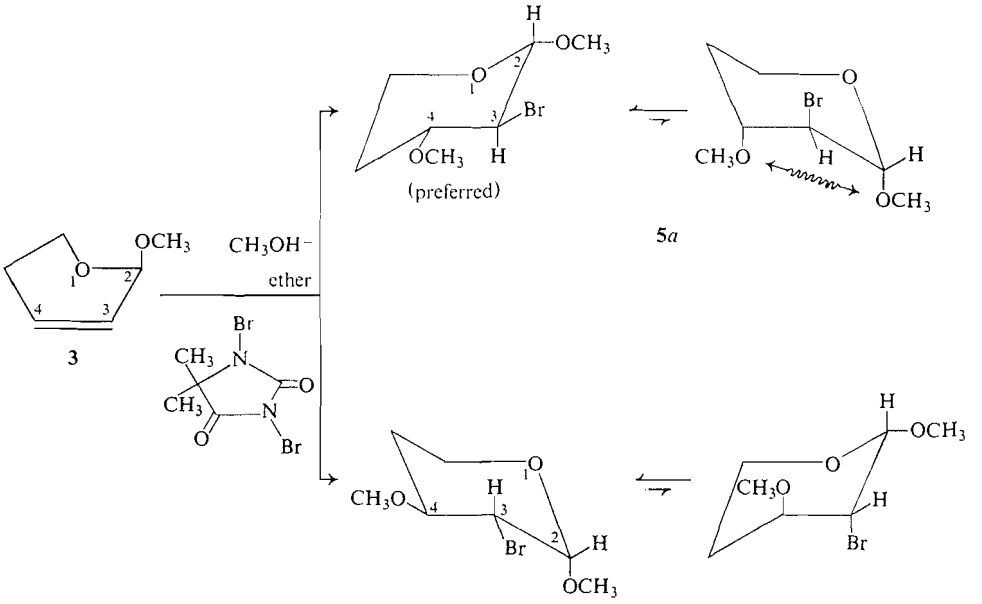
72% yield an isomeric mixture which was composed essentially of the two compounds, 3β-bromo - 2α,4α - dimethoxytetrahydropyran (**5***a* in Scheme 2) and 3α-bromo-2α,4β-dimethoxytetrahydropyran (**5***b*), in the proportion 2:1 respectively.

That the 2:1 mixture of **5***a* and **5***b* did not arise from an equilibration process stemming from acid catalyzed isomerization of the acetal linkage during the bromomethoxylation reaction, is strongly supported by the finding (9) that 2α-ethoxy - 3α,4β - dibromotetrahydropyran and 2α - ethoxy - 3β,4α - dibromotetrahydropyran, heated separately for 12 h in refluxing absolute ethanol containing some *p*-toluenesulfonic acid, failed to show evidence of isomerization. It is well-known that electron-withdrawing groups attached to the carbon adjacent to the anomeric center of an acetal, strongly retard hydrolysis of the acetal. Since both **5***a* and **5***b* are closely similar to the 2-ethoxy-3,4-dibromotetrahydropyrans both in structure and nature of the substituents, it can be concluded that under the low temperature conditions of bromomethoxylation (−50°), and during the short time required for the reaction, no significant isomerization would have occurred.

The structures and preferred conformations of the isomers **5***a* and **5***b* were determined by the following methods. Catalytic hydrogenation of this mixture, with palladium, gave a 2:1 mixture of *cis*- and *trans*-2,4-dimethoxytetrahydropyran whose nuclear magnetic resonance (n.m.r.) spectrum, refractive index, and infrared (i.r.) spectrum were identical to those of an authentic 2:1 mixture of these compounds (1). Thus, bromomethoxylation of **3** has occurred with highly selective attack of the methanol and bromine on C-4 and C-3 respectively of the double bond in **3**. The 100 MHz n.m.r. spectrum of the isomeric mixture (**5***a* and **5***b*) in $CDCl_3$ showed two doublets in the anomeric proton region, at τ 5.21 ($J_{2,3}$ = 2.6 Hz) and at τ 5.62 $J_{2,3}$ = 7.5 Hz). The magnitudes of the couplings permit the assignment of the former signal (τ 5.21) to the C-2 proton in a structure in which the C-3 bromine and C-2 methoxy groups are either *cis* to each other (axial–equatorial) or *trans* diaxial, while the latter signal (at τ 5.62) can be assigned to the C-2 proton of a structure in which these two groups are *trans* diequatorial (10).

Experience has shown that bromomethoxylation of olefins occurs such that the bromine and methoxy groups attack the double bond *trans* to each other (11). As well, in the absence of strong 1,3-diaxial interaction, the anomeric effect (12) favors that conformer in the 2-alkoxytetrahydropyrans in which the alkoxy group is axial. On the basis of these two observations and the information given above, a definite structural and preferred conformational assignment of **5***a* and **5***b* can be made. These are shown in Scheme 2.

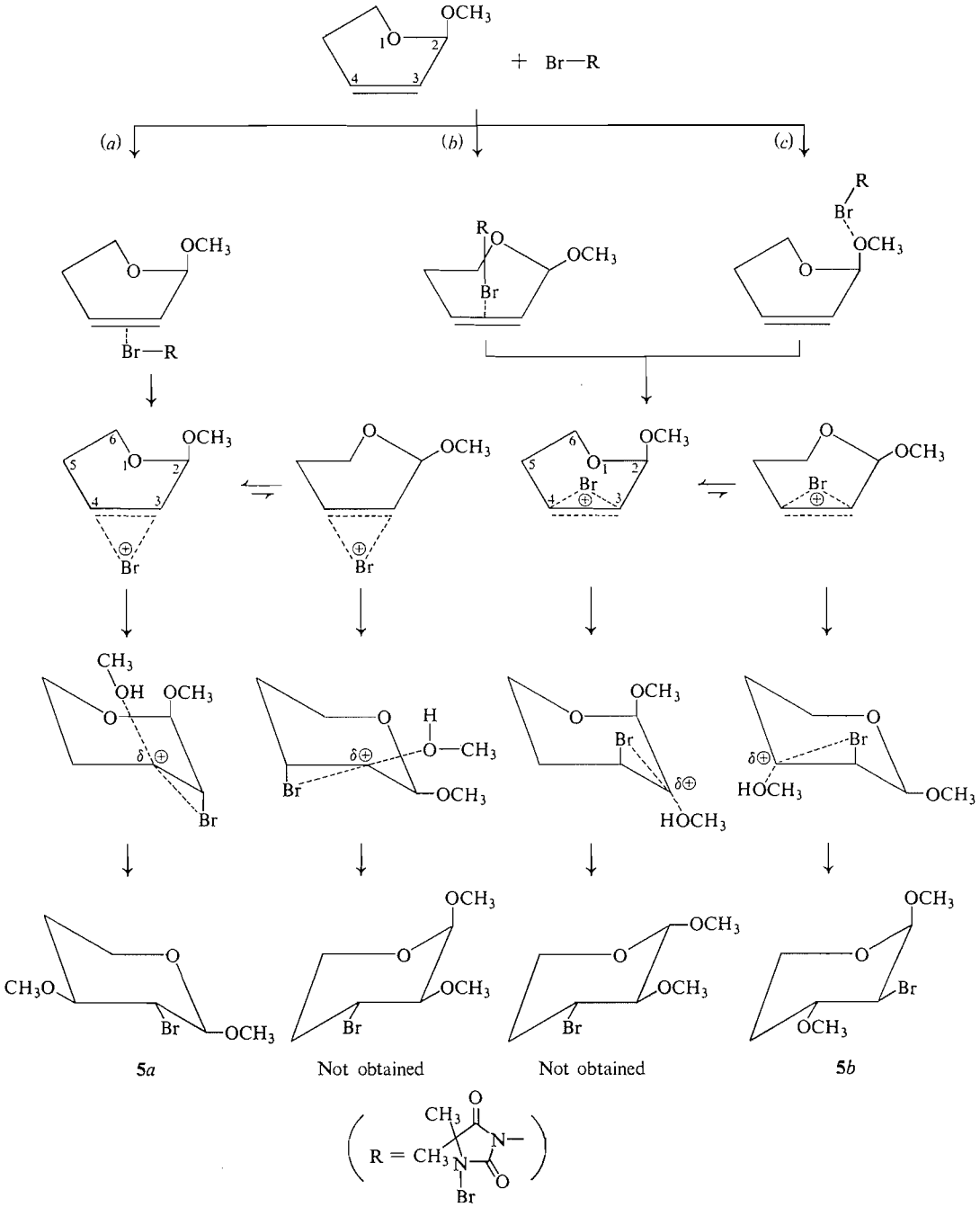
The following rationale is given to explain both the 2:1 predominance of isomer **5***a* in which the C-3 bromine and C-2 methoxy groups are *trans* to each other, and the highly selective attack of the bromine atom on C-3 of compound **3**. Because of the anomeric effect (12), the preferred conformation of compound **3** is no doubt that in which the anomeric methoxy group is *quasi* axial (9). Accordingly, attack by the bulky



SCHEME 2

1,3-dibromo-5,5-dimethylhydantoin then must be preferably by a route *trans* to the C-2 methoxy group of **3** to avoid its bulk steric opposition (route (*a*), Scheme 3). However, the formation of a substantial amount of isomer **5***b* in which the C-3 bromine is *cis* to the C-2 methoxy group, clearly shows that the double bond is reasonably accessible from the side on which the C-2 methoxy group is located. This could occur by way of the alternative conformer of **3** in which the C-2 methoxy group is *quasi* equatorial (route (*b*), Scheme 3), since in such a position it would offer less steric resistance. However, previous work (9) has indicated that compound **3** exists to the extent of 80% in the conformation in which the anomeric methoxy group is *quasi* axial. In view of this, and the fact that there is no hindrance to approach by the brominating agent via route (*a*) *trans* to the anomeric methoxy group, one should expect an even greater proportion of **5***a* to **5***b* than 2:1. It appears then that there is some other factor which promotes attack by the *N*-bromohydantoin from the same side as the *quasi* axial anomeric methoxy group. Our recent work (9), concerning the preferred attack of bromine on the C-3 position of compound **3** and also *cis* to the C-2 methoxy group, has suggested the possibility that the brominating agent could transfer the species $Br^{\oplus}$ to the double bond by association of the bromine with the anomeric methoxy group's oxygen atom. In the present case, the extent to which such association (route (*c*), Scheme 3) is involved in the bromination reaction would depend upon the ability of the oxygen atom to compete for the $Br^{\oplus}$ with the resonance stabilized hydantoin anion which liberates the $Br^{\oplus}$. Such a directive effect of the anomeric methoxy group, possibly assisted to some extent by a similar association with the ring oxygen when the *quasi* equatorial conformer is attacked, might well play a part in this reaction and thus account at least in part for the 33% proportion of isomer **5***b*.

Both the above mentioned directions of attack on the double bond of **3** by the brominating agent would lead to the transient formation of the 3-membered ring bromonium ion (Scheme 3), which is then attacked by the methanol from the side *trans* to the bromine atom (13, 14). The factors which determine the direction of opening of such 3-membered halonium rings have been discussed previously (13, 14). It is clear that the reaction of the *trans* bromonium ion (obtained by route (*a*)) with methanol should (*and does*)



SCHEME 3

occur preferentially at C-4, since by this path, the bulk steric and the polar repulsion of the C-2 methoxy group is minimal. As well, C-4 — Br bond breaking to form an incipient carbonium ion at C-4 is less inhibited by the electron-withdrawing effect of the geminal dioxy group on C-2, than is carbonium ion formation at C-3 (9, 15). Attack at C-4 would also permit the opening of the 3-membered ring so that the substituents at C-3 and C-4 are *trans* diaxial, with the tetrahydropyran ring in the favored chair form (16). For this same type of favored ring opening to occur by attack of methanol at C-3, a conformational change in the bromonium ion structure must occur in opposition to the anomeric effect.

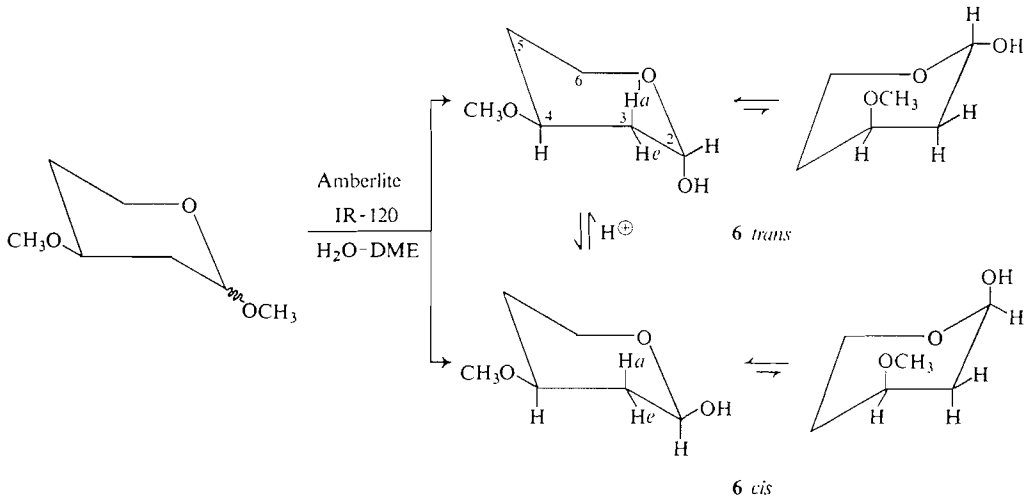
With respect to the *cis* bromonium ion obtainable via route (*b*) and/or (*c*) (Scheme 3), the experimental evidence shows that attack by methanol is essentially at C-4. For this to occur in agreement with the view that preference is given to the pathway in which the entering and "leaving" groups of the 3-membered ring are *trans* diaxial and the 6-membered ring is in the chair form (16), a conformational change must also take place in the bromonium ion structure so that the C-2 methoxy group is *quasi* equatorial. This must occur in opposition to the anomeric effect and hence such a reaction should be retarded. It is not sufficient to say that a reaction involving the less favored conformation would occur because the alternative route (attack of methanol at C-3, with attendant *trans* diaxial opening and maintenance of chair form) would have all three substituents axially disposed, hence resulting in sufficient 1,3-diaxial repulsion to prevent this alternative route, since similar 1,3-diaxial repulsion of all three substituents was not prohibitive in route (*a*). A factor which may be very important in promoting C-4 — Br bond breaking and successful attack by the methanol at C-4 is the electronic effect of the C-2 geminal dioxy group, which would retard incipient carbonium ion formation less at C-4 than at C-3. This factor is present in both the *trans* (route (*a*)) and the *cis* (route (*b*), (*c*)) species and hence may be the dominant factor which determines that **5***a* and **5***b* be formed.

Separation of the isomers **5***a* and **5***b* was not attempted. When this 2:1 mixture was treated with zinc in refluxing ethanol according to Boord's method (7), there was obtained only unchanged starting material (~50%) and 2-methoxy-5,6-dihydro-2*H*-pyran, (**3**) (in a 44% yield). None of the expected olefin, **2**, was detected.

A final attempt to synthesize 4-methoxy-3,4-dihydro-2*H*-pyran (**2**) was made using the method of ester pyrolysis to produce olefins. The advantage of such a method is that it provides a product free from isomers (17). The pyrolysis of carbonate esters (18) has the added advantage that they decompose at lower temperatures than do the acetate esters, and produce the innocuous products carbon dioxide and an alcohol rather than acetic acid.

For the preparation of such esters, the compound 2 - hydroxy - 4 - methoxytetrahydropyran (**6**) was required. This was readily made in a 74% yield by treatment of a solution of 2,4-dimethoxytetrahydropyran (**1**) in the mixed solvent, water, and 1,2-dimethoxyethane (DME), with Amberlite IR-120 (Scheme 4). This distillable material was found to be a 1:1 equilibrium mixture of the *cis* and *trans* isomers as shown by the 100 MHz n.m.r. spectrum in D_2O. The signals for the anomeric protons were at τ 4.80 (triplet, $J_{2,3a} = J_{2,3e} = 3.7$ Hz) and at τ 5.28 (quartet, $J_{2,3a} = 7.5$ Hz, $J_{2,3e} = 2.0$ Hz).

It has been shown that in the compounds *cis*- and *trans*-2,4-dimethoxytetrahydropyran, the C-4 methoxy group prefers to adopt the equatorial position (1). Accordingly, the *cis*- and *trans*-2-hydroxy - 4 - methoxytetrahydropyrans most likely exhibit the same preference in conformation. On this basis, the magnitudes of the couplings stated above permit the indentification of the *cis* and *trans* isomers. These isomers, **6**, and their preferred conformations are shown in Scheme 4. From the integrated area of the anomeric proton signals we know that the ratio of *cis*:*trans* is 1:1, and since this is an acid catalyzed equilibrium mixture, it is clear that in D_2O the free energy difference between the two isomers is ~0 kcal/mole. Inspection of the preferred conformers of *cis*- and *trans*-2-hydroxy-4-methoxytetrahydropyran (Scheme 4) suggests that the *cis* isomer, possessing an equatorial hydroxyl group at C-2, should be preferred over the *trans* isomer with the axial hydroxyl group at C-2 by ~0.9 kcal/mole as a result of the interaction of the axial hydroxyl group in the latter isomer with the two *syn*- axial hydrogen atoms at C-4 and C-6 (19). The equilibrium composition of 1:1 for



SCHEME 4

the two isomers shows that the magnitude of the anomeric effect present in 2-hydroxy-4-methoxytetrahydropyran in D_2O must then be ~0.9 kcal/mole. The anomeric effect for the compounds *cis*- and *trans* - 2,4 - dimethoxytetrahydropyran, on the basis of their spectra in $CDCl_3$, has been calculated to be ~1.4 kcal/mole (1). The smaller value (0.9 kcal/mole) observed for 2 - hydroxy - 4 - methoxytetrahydropyran is not surprising since it is known that the anomeric effect decreases as the solvent becomes more polar (19, 20).

Treatment of the isomeric mixture of **6** with acetic anhydride in pyridine provided a 61% yield of a mixture of *cis*- and *trans*-2-acetoxy-4-methoxytetrahydropyran in the expected 1:1 ratio, as shown by the 60 MHz n.m.r. spectrum in $CDCl_3$. The magnitude of the couplings agrees with the preferred conformation in which the C-4 methoxy group is equatorial. The signals at τ 3.88 (triplet, $J_{2,3a} = J_{2,3e} = 3.0$ Hz) and at τ 4.34 (quartet, $J_{2,3a} = 7.5$ Hz, $J_{2,3e} = 3.0$ Hz were assigned to the anomeric protons of the *trans* and *cis* isomers respectively.

Room temperature treatment of the 1:1 mixture of 2-acetoxy-4-methoxytetrahydropyran in glacial acetic acid, with a catalytic amount of *p*-toluenesulfonic acid, in an attempt to achieve equilibrium, as had been done by Anderson and Sepp (21) with 2-acetoxy-4-methyltetrahydropyran, in order to determine the influence of the acetoxy group in determining the magnitude of the anomeric effect, was unsuccessful. Within 1 h the solution had darkened, and an n.m.r. analysis of the crude reaction product in $CDCl_3$ showed complete absence of the signals at τ 3.88 and τ 4.34 due to the anomeric protons of the two isomers. Apparently, a simple anomerization had not occurred. The nature of this change was not investigated further.

Pyrolysis of 2-acetoxy-4-methoxytetrahydropyran at either 180° or 290° gave only extensive decomposition. No evidence was found for the formation of either 4-methoxy-3,4-dihydro-2*H*-pyran (**2**) or its isomer 2-methoxy-5,6-dihydro-2*H*-pyran (**3**).

Attempts to prepare the carbonate ester of **6** by treatment with methyl chloroformate in pyridine (18) gave only unchanged **6** in high yield.

Experimental

All boiling points and melting points are uncorrected.

Infrared spectra were recorded on Perkin–Elmer instruments, models 21 and 421.

The n.m.r. spectra were obtained with a Varian Associates model A-60 (60 MHz) spectrometer or a Varian Associates HA-100 (100 MHz) spectrometer. Unless otherwise stated, the n.m.r. spectra were obtained from samples dissolved in $CDCl_3$. Tetramethylsilane was used as internal reference.

Solvents were removed by a rotary evaporator under reduced pressure unless otherwise stated.

Elemental analyses and molecular weight determinations were carried out by Mrs. Darlene Mahlow of the Chemistry Department of the University of Alberta, Edmonton, Alberta.

2-Methoxy-5,6-dihydro-2H-pyran (3)

It was prepared by a modification of the procedure of Woods and Sanders (6). To a stirred solution of sodium methoxide (29.7 g, 0.55 mole) in 300 ml of anhydrous dimethylsulfoxide was added dropwise 97 g (0.5 mole) of 3-bromo-2-methoxytetrahydropyran (15). An exothermic reaction ensued and the rate of addition was controlled so that the reaction temperature did not exceed 60°. When the addition was completed, the mixture was stirred for a further 15 min, and then subjected to fractional distillation under reduced pressure. All material in the boiling range 62° at 700 mm to 90° at 23 mm was collected in a dry ice–acetone cooled receiver. This material was redistilled under reduced pressure in a Nestor–Faust spinning band column and afforded 44 g (77%) of 2-methoxy-5,6-dihydro-2*H*-pyran, b.p. 66° at 67 mm, n_D^{23} 1.4430 (lit. b.p., 136–138° at 700 mm, n_D^{25} 1.4425 (6)).

2,4-Dimethoxytetrahydropyran (1)

It was prepared according to published directions (1).

Attempted Acid Catalyzed Removal of Methanol from 1 to Produce 4-Methoxy-3,4-dihydro-2H-pyran (2)

The published procedure (5) provided no detailed directions. Accordingly, those employed here are described below. A solution of 100 mg of *p*-toluenesulfonic acid in 20 g (0.137 mole) of 2,4-dimethoxytetrahydropyran (1) was heated to 150° for 2 h. Distillation of the reaction mixture under reduced pressure afforded 13.5 g (86%) of 2-methoxy-5,6-dihydro-2*H*-pyran, boiling at 69° at 70 mm. This was identical to authentic material (6) as shown by its i.r. and n.m.r. spectra.

3-Bromo-2,4-dimethoxytetrahydropyran (5)

1,3-Dibromo-5,5-dimethylhydantoin (7.0 g, 0.025 mole) (Matheson, Coleman and Bell) was added in small portions to a cold (−50°) stirred solution of 2-methoxy-5,6-dihydro-2*H*-pyran (5.7 g, 0.05 mole) in a mixture of 10 ml of dry ether and 10 ml of dry methanol. When the addition was completed, the reaction mixture was allowed to warm to room temperature and then poured into ice-cold, saturated sodium bicarbonate solution. The resulting mixture was extracted with ether, and the ether extract washed with saturated aqueous sodium bisulfite solution and then with saturated aqueous sodium bicarbonate solution. The dried ($MgSO_4$) ether solution was separated from the drying agent and freed from ether. The residual oil was distilled under vacuum and provided 8.0 g (72%) of 3-bromo-2,4-dimethoxytetrahydropyran, b.p., 63° at 0.05 mm, n_D^{22} 1.4832.

Anal. Calcd. for $C_7H_{13}BrO_3$ (mol. wt. 225): C, 37.36; H, 5.82; Br, 35.50. Found (mol. wt. (mass spectrum) 225): C, 37.35; H, 5.77; Br, 35.78.

The n.m.r. spectrum was consistent with the structure. The significant details of the n.m.r. spectrum are given in the Discussion.

To 3-bromo-2,4-dimethoxytetrahydropyran (5.2 g, 0.023 mole) in 50 ml of anhydrous methanol containing 1.7 g (0.03 mole) of sodium methoxide, was added 500 mg of 5% palladium on charcoal. The resulting mixture was shaken for 24 h with hydrogen at 55 p.s.i. in a Parr hydrogenator. The solids were then separated by filtration and the solvent removed from the filtrate. An ether solution of the residual paste was washed with water, dried ($MgSO_4$), and freed from solvent by fractional distillation. The product (2.2 g, 67%) was 2,4-dimethoxytetrahydropyran whose refractive index, n.m.r., and i.r. spectra were identical with those of an authentic sample (1). The n.m.r. spectrum showed it to be a mixture of *cis* and *trans* isomers in the ratio 2:1 (integrated areas of the anomeric proton signals).

2-Hydroxy-4-methoxytetrahydropyran (6)

A solution of 2,4-dimethoxytetrahydropyran (1) (7 g, 0.454 mole) in 75 ml of water containing 25 ml of DME and 1.5 g of Amberlite IR-120 ion exchange resin, was stirred at room temperature for 24 h. The solution was then filtered and the filtrate freed from solvents. Toluene (10 ml) was added towards the end of the solvent removal to effect complete elimination of water by azeotropic distillation. Fractional distillation of the residual oil under reduced pressure gave 4.7 g (74%) of 2-hydroxy-4-methoxytetrahydropyran as a (1:1) mixture of *cis* and *trans* isomers, b.p., 65° at 0.1 mm; n_D^{23} 1.4573.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.61; H, 9.37.

The i.r. absorption spectrum in CCl_4 showed a broad absorption band at 3400 cm^{-1} (OH). The n.m.r. spectrum was consistent with the assigned structure and the analysis of its significant features is described in the Discussion.

2-Acetoxy-4-methoxytetrahydropyran

A solution of 2-hydroxy-4-methoxytetrahydropyran (8 g, 0.06 mole) and acetic anhydride (10.2 g, 0.1 mole) in 50 ml of dried (KOH) pyridine was heated under reflux for 15 min. The cooled reaction mixture was diluted with 125 ml of water and then treated with solid sodium bicarbonate until evolution of carbon dioxide ceased. An ether extract (3X) was washed successively with ice-cold 10% hydrochloric acid, with saturated aqueous sodium bicarbonate, and then with water. The dried ($MgSO_4$) ether solution was freed from solvent and the residue distilled under reduced pressure to give 6.4 g (61%) of 2-acetoxy-4-methoxytetrahydropyran. This was a 1:1 mixture of *cis* and *trans* isomers as shown by integration of the anomeric proton signal areas of the n.m.r. spectrum. The salient features of the n.m.r. spectrum are presented in the Discussion. It had b.p., 67° at 0.05 mm; n_D^{22} 1.4447.

Anal. Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.07; H, 7.91.

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