(CHPh), 5.20 (CH<sub>2</sub>NO<sub>2</sub>), 5.36 (t, H-1), 5.8 (m, H-5), 6.25 (m, H-4, H-6,  $J_{4,3} = 4$ ,  $J_{4,5} = 10$  Hz), 6.70 (OCH<sub>3</sub>), 6.83–7.05 (m, H-3), 7.96–8.10 (5 peaks, H-2a, H-2e). Irradiation at  $\tau$  8.0 (H-2) collapsed the H-1 signal to a singlet and altered the H-3 multiplet. Irradiation at  $\tau$  5.36 (H-1) collapsed the multiplet at  $\tau$  8.0 to three peaks. Irradiation at  $\tau$  7.0 (H-3) changed the multiplet at  $\tau$  8 to a broad singlet and altered the signals at  $\tau$  6.25 showing  $J_{4,5} = 10$  Hz.

Anal. Calcd. for  $C_{15}H_{19}NO_6$ : C, 58.2; H, 6.2; N, 4.5. Found: C, 58.18; H, 6.0; N, 4.35.

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# A Simple Synthesis of 2-Methoxy and 2-Ethoxytetrahydrofuran

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Ozonolysis of dihydropyran gives 4-formyloxybutyraldehyde which is then easily converted into 2-methoxy or 2-ethoxytetrahydrofuran.

L'ozonolyse du dihydropyranne conduit au formyloxy-4-butyraldehyde qui se transforme facilement en méthoxy-2- ou éthoxy-2-tétrahydrofuran.

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In connection with our recent investigation on the ozonolysis of acetals (1), we required a certain quantity of 2-methoxytetrahydrofuran (1*a*). A search in the chemical literature revealed that the standard method to prepare 2-alkoxytetrahydrofuran is the addition of alcohols to 2,3-dihydrofuran in presence of mineral acid (2). However, 2,3-dihydrofuran is not very readily available (2–5). The alternative synthesis of 2-alkoxytetrahydrofuran (6) from tetrahydrofuran and *t*-butyl perbenzoate in the presence of alcohols is not more convenient (2).

We wish to report a new two-step synthesis of 2-methoxytetrahydrofuran from a readily

available starting material while using simple experimental procedures.

Ozonolysis of dihydropyran in methanol at  $-78^{\circ}$  followed by the addition of methyl sulfide (7) gave 4-formyloxybutyraldehyde (2) in 95% yield (see Scheme 1). The next operation was to convert 2 into 2-methoxytetrahydrofuran (1*a*). One possible route for such a transformation was the hydrolysis of 2 to 3 and then the conversion 3 into 1*a*. We felt that such a two-step procedure should be avoided because we were expecting experimental difficulties in the isolation of the water-soluble 2-hydroxytetrahydrofuran (3) (8). Also, the use of methanol as solvent in the final step was not desirable since 2-methoxytetrahydrofuran (1*a*) has a low boiling

NOTES

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point. Consequently, we directed our effort in the development of a one-step procedure from 2.

Treatment of 2 with 1 mol-equiv of trimethyl orthoformate containing a drop of methanol and a catalytic amount of *p*-toluenesulfonic acid at room temperature gave 2-methoxytetrahydrofuran (1*a*) in 80% yield after distillation. During this reaction, 2 mol-equiv. of the low boiling methyl formate are formed. Using similar experimental conditions, and triethyl orthoformate, 2 was transformed into 2-ethoxytetrahydrofuran (1*b*) in 84% yield after distillation.

## Experimental

The i.r. spectra were taken on a Perkin-Elmer 257 Spectrophotometer. The n.m.r. spectra ( $\tau$  value) were recorded on a Varian A-60 Spectrometer in solvent indicated and with TMS as internal standard. The ozonized oxygen was produced by a Welsbach T-816 Laboratory Ozonator. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

### 4-Formyloxybutyraldehyde (2)

Dihydropyran (63 g, 0.75 mol) was dissolved in reagent grade methanol (100 ml) and cooled at  $-78^{\circ}$ . Ozonized oxygen (3.7%-O<sub>3</sub>/O<sub>2</sub>, 1.5 l/min) was passed through the solution and the end of the reaction was indicated by the appearance of the characteristic blue color of ozone. The excess ozone was swept away with a stream of nitrogen, methyl sulfide (80 ml) was added to the reaction mixture which was allowed to be warmed up at  $-10^{\circ}$  (bath temperature) for 1 h, then at 0° for 1 h, and finally at room temperature for 3 h. The solvent was removed in vacuo and water (300 ml) was added. The aqueous phase was extracted with ether  $(4 \times 50 \text{ ml})$  and with dichloromethane  $(4 \times 50 \text{ ml})$ ml). The combined organic phase was dried over magnesium sulfate, filtered, and evaporated to dryness yielding crude 2 (85.1 g, 97%). Distillation in vacuo (b.p. 55°, 2 mm) gave pure 4-formyloxybutyraldehyde (82.5 g, 95%). The i.r. v (max)  $1720 \text{ cm}^{-1}$ ; n.m.r.:  $\tau$  (CDCl<sub>3</sub>) 0.27 (1H, triplet, J = 1.0 Hz, CHO), 1.97 (1H, singlet, -OCHO), 5.82 (2H, triplet, J = 7.0 Hz, -CH<sub>2</sub>-OCHO), 7.24-7.64 (2H, multiplet, -CH<sub>2</sub>-CHO), and 7.79-8.27 (2H, multiplet, CH<sub>2</sub>-CH<sub>2</sub>-CHO).

Anal. Calcd. for  $C_5H_8O_3$ : C, 51.72; H, 6.94; O, 41.34. Found: C, 51.48; H, 7.20; O, 41.32.

#### 2-Methoxytetrahydrofuran (1a)

Trimethyl orthoformate (2.12 g, 0.02 mol) was slowly added (exothermic reaction) to a cooled mixture (0°) of 4-formyloxybutyraldehyde (2.32 g, 0.02 mol), p-toluenesulfonic acid (2 mg), and one drop of methanol. The reaction mixture was then left at room temperature for 36 h. Anhydrous sodium carbonate (100 mg) was added and the reaction mixture was magnetically stirred for 1 h. The inorganic salt was filtered and methyl formate was removed by distillation at normal pressure. Water (2 ml) was added to the reaction mixture which was extracted with ether  $(4 \times 50 \text{ ml})$ . Distillation of the dried (magnesium sulfate) organic phase gave pure 2-methoxytetrahydrofuran (1.63 g, 80%, b.p. 106-107°, lit. (8) b.p. 105-107°). The n.m.r.:  $\tau$  (CDCl<sub>3</sub>) 5.1 (1H, multiplet, CHOCH<sub>2</sub>), 6.00-6.65 (2H, multiplet, CH<sub>2</sub>O), 6.75 (3H, singlet, OCH<sub>3</sub>), and 7.85-8.40 (4H, multiplet).

Anal. Caled. for  $C_5H_{10}O_2$ : C, 58.80; H, 9.87; O, 31.33. Found: C, 58.90; H, 9.81; O, 31.29.

#### 2-Ethoxytetrahydrofuran (2b)

2-Ethoxytetrahydrofuran (2b, 1.95 g, 84%, b.p. 125°, lit. (9) b.p. 125°) was obtained by utilizing an identical experimental procedure as the one described above with the exception that trimethyl orthoformate was replaced by triethyl orthoformate (2.964 g, 0.02 mol) and methanol by ethanol (one drop). The n.m.r.:  $\tau$  (CDCl<sub>3</sub>) 4.92 (1H, multiplet, CHOC<sub>2</sub>H<sub>5</sub>), 5.95-6.80 (4H, multiplet, OCH<sub>2</sub> and OCH<sub>2</sub>CH<sub>3</sub>), 8.35-7.90 (4H, multiplet), and 8.85 (3H, triplet, J = 7.0 Hz, CH<sub>3</sub>CH<sub>2</sub>O).

Anal. Calcd. for  $C_6H_{12}O_2$ : C, 62.04; H, 10.41; O, 27.55. Found: C, 61.86; H, 10.41; O, 27.73.

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