is 2-oxo-5-acetoxymethylene-2,5-dihydrofuran; the yields of 8–9.7 g. of sublimed material represented 21–24%.

Anal. Calcd. for $C_7H_6O_4$: C, 54.55; H, 3.92. Found: C, 54.39, 54.65; H, 3.77, 4.07.

2-Oxo-5-methoxymethylene-2,5-dihydrofuran (VII. R = OCH_3). The addition of furfuryl methyl ether (VI. R_2 = H, OCH_3) (28 g., 0.25 mole) to a well stirred slurry of bromine (40 g., 0.25 mole) and potassium acetate (51.5 g., 0.52 mole) in acetic anhydride (150 ml.) at −17° produced instantaneous decolorization and a temperature rise to 4°. Stirring at 0° and 80° followed by salt and solvent removal, all as described above, gave a dark-brown viscous residue. Removal of salts precipitated by the addition of ether (100 ml.) and subsequent ether removal gave a black viscous residue which was distilled from a flask coated with potassium acetate. The high-boiling distillate (12.6 g., boiling-range 60–107°/2–3 mm.) was immediately washed with dilute aqueous cold carbonate and quickly extracted with ether. Fractional distillation of the ether extract yielded 2 g. (0.012 mole, 6.4%) of a colorless liquid, b.p. 51–52°/3 mm., n_D^{20} = 1.4743; microanalysis, the formation of a purple color with phosphoric acid and the immediate hydrolysis with sulfuric acid to a product which gives a dinitrophenylhydrazone derivative support the identification of this material as 2-oxo-5-methoxymethylene-2,5-dihydrofuran.

Anal. Calcd. for $C_6H_6O_3$: C, 57.20; H, 4.76. Found: C, 56.72, 56.97; H, 4.96, 4.71.

Repetition of this reaction sequence on a molar scale gave inconclusive results; unstable higher-boiling materials of nonanalytical purity were obtained.

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NOTRE DAME, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Reactions of Furan Compounds. XIX. Synthesis of 2-Methoxyfuran and its 5-Methyl- and 5-Methoxymethyl Derivatives[1]

G. FRANK D'ALELIO, CARL J. WILLIAMS, JR.,[2] AND CHRISTOPER L. WILSON

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Modification of the acid-catalyzed pyrolysis of 2,5-dimethoxy-2,5-dihydrofuran has given an improved yield of 2-methoxyfuran. Similar pyrolyses of 2,5-dimethoxy-2,5-dihydro-2-methylfuran and 2,5-dimethoxy-2,5-dihydro-2-furfuryl methyl ether have given 2-methoxy-5-methylfuran and 2-methoxy-5-furfuryl methyl ether, respectively. Diels-Alder adducts of these new substituted methoxyfurans with maleic anhydride are reported, as well as the synthesis of 3-methoxy-6-methyl phthalic anhydride by the aromatization of 3-methoxy-6-methyl-3,6-epoxy-Δ^4-tetrahydrophthalic anhydride.

The synthesis of 2-methoxyfuran (II. R = H) has been previously reported by two different routes: the reaction of 5-bromo-2-furoic ester with sodium methoxide followed by saponification and decarboxylation (10–36%),[3] and the acid-catalyzed pyrolysis of 2,5-dimethoxy-2,5-dihydrofuran (11%).[4]

The pyrolytic technique has been improved by the dropwise introduction of 2,5-dimethoxy-2,5-dihydrofuran (I. R = H) into a preheated (220–250°) mixture of β-naphthalenesulfonic acid and high-boiling diluent. Resinification was minimized by maintaining the rate of intermediate addition, as accurately as possible, equal to that of product distillation. Once this condition was established, the pyrolysis proceeded with relative smoothness, and 51% of 2-methoxyfuran (II. R = H) was obtained.

The general applicability of this acid-catalyzed elimination of methanol has now been demonstrated. The intermediates, 2,5-dimethoxy-2,5-dihydro-2-methylfuran (I. R = $-CH_3$) and 2,5-dimethoxy-2,5-dihydro-2-furfuryl methyl ether (I. R = $-CH_2OCH_3$), were prepared by electrolytic oxidation of 2-methyl furan and furfuryl methyl ether respectively.[5]

The dropwise introduction of 2,5-dimethoxy-2,5-dihydro-2-methylfuran into a mixture of β-naphthalenesulfonic acid and high-boiling diluent gave no elimination; the intermediate was recovered unchanged. The addition of a few drops of glacial acetic acid to the pyrolysis flask provided sufficient acidity for elimination, and 2-methoxy-5-methylfuran (II. R = $-CH_3$, 28%) was obtained. Analytical results indicated a sensitivity of 2-methoxy-5-methylfuran to atmospheric oxygen; redistillation and storage under nitrogen at 5° gave an analytically stable sample. Oxidation of 2-methoxy-5-methylfuran by potassium ferricyanide to recognizable products failed.

The pyrolysis of 2,5-dimethoxy-2,5-dihydro-2-furfuryl methyl ether (I. R = $-CH_2OCH_3$) required even more stringent acidic conditions. The intermediate was recovered in good yield from successive treatments with β-naphthalenesulfonic acid, glacial acetic acid, or *o*-phosphoric acid in the pyrolysis flask at 250°. Partially pyrolysis, induced by mixing *o*-phosphoric acid with the intermediate be-

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(1) Abstracted from a portion of the Ph.D. dissertation of C. J. Williams, University of Notre Dame, 1958.

(2) Present address: Research Laboratories, Eastman Kodak Co.

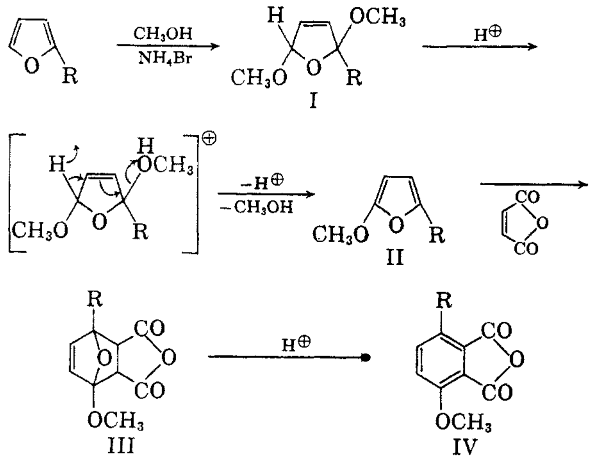
(3) E. K. Amstutz and R. J. Petfield, *J. Org. Chem.*, **19**, 1944 (1954).

(4) C. L. Wilson, M. P. Cava, and C. J. Williams, Jr., *Chem. and Ind.*, **1955**, 17.

(5) N. Clauson-Kaas *et al.*, *Acta Chem. Scand.*, **6**, 545, 556 (1952).

fore addition to the pyrolysis flask which also contained o-phosphoric acid, gave 2-methoxy-5-furfuryl methyl ether (II. R = $-CH_2OCH_3$, 23%).

The pyrolysis of dialkoxydihydrofurans seems clearly an acid-catalyzed process which may be denoted by the following equation, I → II,



The substituted dialkoxydihydrofurans exhibited greater stability to acid-catalyzed pyrolysis than the analogous substituted 2,5-diacetoxy-2,5-dihydrofurans, which defy isolation and purification in the presence of traces of acid impurities.[6]

The Diels-Alder reactivity of the two new furan ethers was exemplified by their addition to maleic anhydride. Thus 2-methoxy-5-methylfuran and 2-methoxy-5-methyl furfuryl ether gave 3-methoxy-6-methyl-3,6-epoxy-Δ^4-tetrahydrophthalic anhydride (III. R = $-CH_3$) and 3-methoxy-6-methoxymethyl-3,6-epoxy-Δ^4-tetrahydrophthalic anhydride (III. R = $-CH_2OCH_3$), respectively.

In a manner analogous to the facile aromatization of the furan-maleic anhydride adduct (3,6-epoxy-Δ^4-tetrahydrophthalic anhydride) by various dehydrating agents, a new positional isomer, 2-methyl-6-methoxyphthalic anhydride (IV. R = $-CH_3$, 20%) was synthesized by aromatization of 3-methoxy-6-methyl-3,6-epoxy-Δ^4-tetrahydrophthalic anhydride (III. R = $-CH_3$) in polyphosphoric acid. Simple recrystallization of the adduct (III. R = $-CH_3$) from warm methanol gave identical material (IV. R = $-CH_3$, 75%), demonstrating the ease of this aromatization.

EXPERIMENTAL[7]

2,5-Dimethoxy-2,5-dihydrofuran (I. R = H). A solution of ammonium bromide (1.2 g., 0.012 mole), furan (17.3 g., 0.25 mole), and methanol (60 ml., 1.87 moles) was placed in the electrolysis cell. The electrolysis cell employed in this and subsequent preparations consisted of a hollow brass cylindrical cathode (14 × 1.5 in.) and a hollow graphite cylindrical anode (16 × 0.5 in.) held longitudinally within and insulated by rubber stoppers. A thermometer was suspended inside the graphite cylinder which had numerous holes throughout its length to permit flow of the electrolytic mixture with the brass tube. Current was applied by a commercial battery-charger capable of an output of 6 amperes at 30 volts. The average current was 2.6 amperes; the average cell temperature, 12°.

The cell was placed in an ice bath and 19 amp. hr. (140% of theory) was passed through the mixture. Neutralization of the yellow mixture by pouring it into 20 ml. of methanol containing 1.0 g. of sodium, removal of methanol by distillation, and filtration of sodium bromide left a residue which on distillation gave 2,5-dimethoxy-2,5-dihydrofuran (23.4 g., 0.18 mole, 72%, b.p. 159–165°, $n_D^{20} = 1.4316$) (lit.,[8] b.p. 160–162°, $n_D^{25} = 1.4323$).

2-Methoxyfuran (II. R = H). To a mixture of dibutyl phthalate (25 ml.) and β-naphthalenesulfonic acid, preheated to 220–250°, was added 2,5-dimethoxy-2,5-dihydrofuran (99 g., 0.76 mole), dropwise, in such a manner as to minimize accumulation of material in the pyrolysis flask, which consisted of standard-taper dropping-funnel, flask, Claisen-head column, condensor, and receiving flask. The distillate (82.2 g., b.p. 60–140°) was washed with 100 ml. of saturated calcium chloride and extracted with two 75-ml. portions of ether. Distillation of the dried ether extract yielded 2-methoxyfuran (37.8 g., 0.385 mole, 50.8%, b.p. 92–110°, $n_D^{20} = 1.4522$) (lit.,[3] b.p. 108–109°).

2,5-Dimethoxy-2,5-dihydro-2-methylfuran (I. R = $-CH_3$). A solution of ammonium bromide (2.2 g., 0.022 mole), 2-methylfuran (29.5 g., 0.36 mole) and methanol (48 ml., 1.5 moles) was electrolyzed as described above by the passage of 16 amp.-hr. (80% of theory) at an average current of 3 amperes. Neutralization, removal of solvent and precipitated salt, and distillation gave 2,5-dimethoxy-2,5-dihydro-2-methylfuran (25.2 g., 0.175 mole, 49%), b.p. 86–91°/55 mm., $n_D^{20} = 1.4304$) (lit.,[4] $n_D^{25} = 1.4262$, 70%).

2-Methoxy-5-methylfuran (II. R—OCH_3). A mixture of 2,5-dimethoxy-2,5-dihydro-2-methylfuran (25 g., 0.175 mole), β-naphthalenesulfonic acid (0.100 g.), and acetic acid (0.2 g.) was added dropwise to dioctyl phthalate (25 ml.) in such a manner as to minimize accumulation of material in the pyrolysis flask (heated by an open flame). The distillate (22.2 g., b.p. 125°/750 mm.) was washed with 100 ml. of saturated calcium chloride and extracted with two 75-ml. portions of ether; the ether extracts were in turn washed with 100 ml. of dilute sodium carbonate, and dried. Ether removal and fractional distillation gave 2-methoxy-5-methylfuran (5.3 g., 0.48 mole, 28%, b.p. 137–144°, $n_D^{20} =$ 1.4600), and 2,5-dimethoxy-2,5-dihydro-2-methylfuran (7.2 g., 0.051 mole, $n_D^{20} = 1.4323$). The 2-methoxy-5-methylfuran appeared unstable to atmospheric oxygen.

Anal. Calcd. for $C_6H_8O_3$: C, 64.27; H, 7.19. Found: C, 64.50, 62.90, 60.23, 59.23; H, 7.66, 7.42, 7.14, 7.10.

Redistilled 2-methoxy-5-methylfuran, (b.p. 136–137/750 mm.) stored under nitrogen at 5°, remained clear and colorless.

Anal. Found C, 63.29, 63.27; H, 7.32, 7.27.

3-Methoxy-6-methyl-3,6-epoxy-Δ^4-tetrahydrophthalic anhydride (III. R = $-CH_3$). Maleic anhydride (0.5 g., 0.05 mole) was dissolved in 2-methoxy-5-methylfuran (0.6 g., 0.05 mole). Benzene (3 ml.) was added to the resulting warm, bright orange mixture, followed by petroleum ether until a slight turbidity was induced. Fine white needles of 3-methoxy-6-methyl-3,6-epoxy-Δ^4-tetrahydrophthalic anhydride were precipitated, which, when washed with benzene and filtered, gave 0.65 g., 62% 0.031 mole, m.p. 133–135°. This distinguished 2-methoxy-5-methylfuran from the isomeric furfuryl methyl ether (maleic anhydride adduct, m.p. 97°).[9]

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(6) N. Clauson-Kaas, *et al.*, *Acta. Chem. Scand.*, **2**, 109–116 (1948); **4**, 1233 (1952).

(7) Analyses were performed by Midwest Microlab., Inc., Indianapolis, Indiana.

(8) N. Clauson-Kaas *et al.*, *Acta. Chem. Scand.*, **6**, 531, 962 (1954).

(9) M. G. Van Campen, Jr., and J. R. Johnson, *J. Am. Chem. Soc.*, **55**, 430 (1933).

Anal. Calcd. for $C_{10}H_{10}O_6$: C, 5 7.14; H, 4.76. *Found:* C, 57.02, 57.23; H, 4.81, 4.72.

3-Methoxy-6-methylphthalic anhydride (IV. R = $-CH_3$). Methanol (2 ml.) was added to 3-methoxy-6-methyl-3,6-epoxy-Δ^4-tetrahydrophthalic anhydride (0.50 g., 0.024 mole) and the mixture was warmed gently for 15 min. to effect solution. On standing overnight at 5°, fine white needles of 3-methoxy-6-methylphthalic anhydride (0.34 g., 0.018 mole, 75%) were precipitated, m.p. 186–187° (closed-tube). The melting point was unchanged by sublimation, and could be duplicated by cooling and remelting the sample.

An alternate aromatization was performed by suspending 3-methoxy-6-methyl-3,6-epoxy-Δ^4-tetrahydrophthalic anhydride (0.10 g., 0.005 mole) in 3 ml. of *o*-phosphoric acid at 25° and stirring vigorously for 10 min. The white precipitate obtained on pouring this mixture into ice water (10 ml.), when filtered, washed with cold water, and dried, gave 3-methoxy-6-methylphthalic anhydride (0.02 g., 0.001 mole, 20%), m.p. 186–188°. A mixed melting-point with the above sample aromatized in methanol showed no depression.

Anal. Calcd. for $C_{10}H_8O_4$: C, 62.50; H, 4.20. *Found:* C, 62.72, 62.41; H, 4.31, 4.19.

2,5-Dimethoxy-2,5-dihydro-2-furfuryl methyl ether (I. R = $-CH_2OCH_3$). A solution of ammonium bromide (1.2 g., 0.012 mole), furfuryl methyl ether (28 g., 0.25 mole) and methanol (48 ml. 1.5 moles) was electrolyzed as above at an average current of 3 amp. for 16 amp.-hr. Neutralization, solvent and salt removal, and distillation gave 2,5-dimethoxy-2,5-dihydro-2-furfuryl methyl ether (31.4 g., 0.18 mole, 72%, b.p. 90–94°/9 mm., n_D^{18} = 1.4412) (Lit.,[4] n_D^{18} = 1.4384, 83%).

2-Methoxy-5-furfuryl methyl ether (II. R = $-CH_2OCH_3$). A mixture of 2,5-dimethoxy-2,5-dihydro-2-furfuryl methyl ether (23.3 g., 0.13 mole) and *o*-phosphoric acid (0.5 g.) was added dropwise to a preheated (230°) mixture of dioctyl phthalate (11 g.) and *o*-phosphoric acid (0.25 g.), the addition being such as to minimize accumulation of material in the pyrolysis flask. The distillate (17.1 g., b.p. 60–105°) was added to 100 ml. of saturated calcium chloride and the resulting mixture was extracted with two 75-ml. portions of ether. The combined ether extracts were washed with aqueous dilute bicarbonate and dried; ether removal and fractional distillation of the residue gave 2-methoxy-5-furfuryl methyl ether (4 g., 0.03 mole, 23%, b.p. 93–100°/60 mm., n_D^{21} = 1.4620).

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.01, 59.28; H, 6.77, 6.97.

3-Methoxy-6-methoxymethyl-3,6-epoxy-Δ^4-tetrahydrophthalic anhydride (III. R = $-CH_2OCH_3$). Maleic anhydride (0.5 g., 0.05 mole) was mixed with 2-methoxy-5-furfuryl methyl ether; gentle heating gave a deep purple solution. Benzene (3 ml.) was added followed by petroleum ether until a slight turbidity existed; on standing overnight at 5°, precipitation occurred. Filtration and washing with cold benzene yielded 3-methoxy-6-methoxymethyl-3,6-epoxy-Δ^4-tetrahydrophthalic anhydride (0.12 g., 0.005 mole, 14%, m.p. 95–97°).

Anal. Calcd. for $C_{11}H_{12}O_6$: C, 55.00; H, 5.04. Found: C, 54.90; H, 5.00.

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