Method E. The preceding procedure was followed. A mixture of 119 g. (0.64 mole) of 4-ethyl-4-methyloctanoic acid, 352 g. (4 moles) of *n*-butyric acid, 500 ml. of petroleum ether (b.p. 60–70°), 2 g. of sodium, dissolved in about 100 ml. of methanol, and sufficient methanol to bring the volume to 1900 ml., was electrolyzed at about 5 amp. for 21 hr. There was obtained 29 g. (25%) of an alkane which boiled at 101–103°/15 mm., n_D^{25} 1.4291.

The high-boiling residue was treated as above to give 4 g. of coupling product, b.p. 182–184°/15 mm., n_D^{25} 1.4480.

Anal. Calcd. for $C_{20}H_{42}$: C, 85.02, H, 14.98. Found: C, 85.31; H, 14.87.

Physical constants of 5-ethyl-5-methyldecane. In addition to the constants given above, the following values were determined for each of the five samples of the hydrocarbon: sp. gr. 20/4, 0.7705–0.7707; solidification point, −80°; viscosity in centistokes, 1.71 (100° F.) 1.10 (115° F.), and 0.77 (210° F.); and viscosity index 92.5.

COLUMBIA, MO.

[CONTRIBUTION FROM THE JOHN STUART RESEARCH LABORATORIES OF THE QUAKER OATS CO.]

2-Methoxy-5-methylfuran: Preparation, Properties, and Proof of Structure[1]

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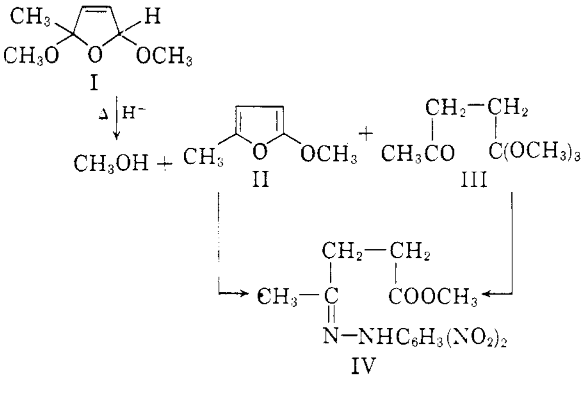
2-Methoxy-5-methylfuran (II) has been prepared in 68% yield by acid-catalyzed pyrolysis of 2,5-dimethoxy-2,5-dihydro-2-methylfuran. Other products obtained in the pyrolysis are methanol (64%), trimethyl ortholevulinate (III) (5–6%) and an unidentified polymer (*ca.* 10% by weight). The structure of II was confirmed by the following sequence of reactions: II + maleic anhydride ⟶ 3-methyl-6-methoxy-3,6-*endo*-oxo-1,2,3,6-tetrahydrophthalic anhydride (V) (84%) ⟶ 3-methyl-6-methoxyphthalic anhydride (VI) (48%) ⟶ the known 4-methoxybenzene-1,2,3-tricarboxylic acid (VII) (85%).

Samples of 2,5-dimethoxy-2,5-dihydro-2-methylfuran (I), prepared by electrolytic methoxylation of 2-methylfuran according to a modification of the method due to Clauson-Kaas *et al.*[2] (ammonium bromide electrolyte), have been found to contain traces of halogen (Beilstein test). Redistillation of stored specimens of I has invariably given rise to small amounts of methanol and a compound, boiling at *ca.* 130°, which from its physical properties and odor appeared to be methyl furfuryl ether.

Finding it practically impossible to explain the formation of methyl furfuryl ether from either methylfuran or I under the conditions of the aforementioned methoxylation or redistillation, we undertook to investigate the true structure of this substance. However, before tackling this problem, it seemed desirable to prepare deliberately the unknown compound in reasonable yield.

On the assumption that hydrogen halide, having its origin in the halogen contamination, was effecting the observed transformation of I, we tested catalytic amounts of strong acids (hydrogen chloride, *p*-toluenesulfonic acid, etc.) in a series of preliminary experiments. Subsequently, the unknown compound (II) was obtained in 68% yield together with a second product (III), by incremental addition of I to hot (*ca.* 250°) dimethyl phthalate containing a few drops of concentrated sulfuric acid, while removing the volatile products continuously by entraining in a gentle stream of nitrogen.

Analysis provided an empirical formula of $C_5H_5O(OCH_3)$, and the infrared spectrum revealed a furan structure for the compound. It was distinguished from the isomeric methyl furfuryl ether by facile formation of an adduct (V) with maleic anhydride, m.p. 111–112.5°, (84.3% yield). Methyl furfuryl ether sluggishly forms a maleic anhydride adduct melting at 97°.[3] From the orientation of substituents in the precursor (I), and the formation of methyl levulinate 2,4-dinitrophenylhydrazone (IV) on treatment with the hydrazine reagent, the structure of the compound was almost unequivocally established as 2-methoxy-5-methylfuran (II).



Further confirmation of the identity of II was achieved by the following sequence of reactions, culminating in 4-methoxybenzene-1,2,3-tricarboxylic acid (VII) which has been described.[4]

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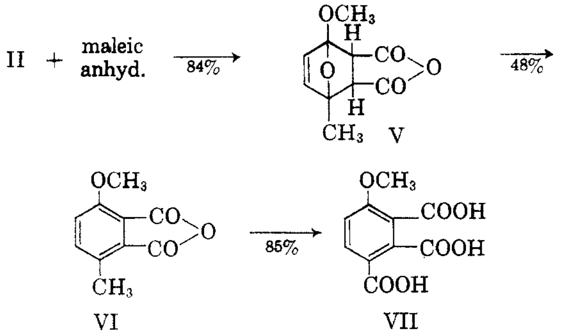
[1] This article, in its entirety, was presented as a portion of a paper of broader scope at the 127th National ACS Meeting in Cincinnati, Ohio, March 1955.

[2] N. Clauson-Kaas, F. Limborg, and P. Dietrich, *Acta Chem. Scand.*, **6**, 545 (1952).

[3] M. G. Van Campen and J. R. Johnson, *J. Am. Chem. Soc.*, **55**, 430 (1933).

[4] D. Gardner, J. F. Grove, and D. Ismay, *J. Chem. Soc.*, 1817 (1954).

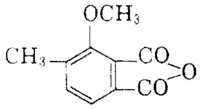


VI
m.p. 188.5–189°

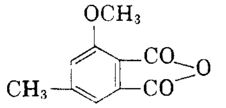
VII

The location of the methoxyl group at a bridgehead of bicyclic adduct (V) was indicated by its facile hydrolysis to a phenolic body.

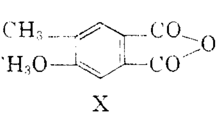
Structure VI is deduced from the following considerations. There are six isomeric x-methyl-y-methoxyphthalic anhydrides, of which four[5] (VIII–XI) have been described. The isomer (VI) obtained in this study melts much higher than any of these, and, on oxidation, gives a methoxybenzenetricarboxylic acid with the same melting point reported for VII (prepared[4] from 4-methoxy-2,3-dimethylacetophenone). While both VI (as assigned) and XII would give VII on oxidation, XII can be eliminated since it would necessitate a precursor adduct having structure XIIa which cannot give a phenol on *mild* hydrolysis.



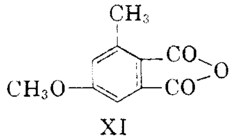
VIII
m.p. [illegible]°[8]



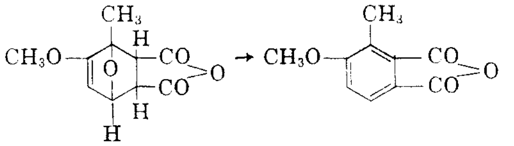
IX
m.p. 167°[9]



X
m.p. 158.5–159°[10]



XI
m.p. 139°[9]



XIIa XII

It will be recalled that in addition to II, a second compound (III) was isolated during the acid-catalyzed pyrolysis of I. Compound III has been better prepared by treating I with methanol containing a strong acid catalyst. Analysis indicated an empirical formula of $C_5H_7O(OCH_3)_3$ and infrared spectroscopy disclosed the presence of carbonyl and methyl ketone groups. Reaction with 2,4-dinitrophenylhydrazine reagent yielded IV. Whereas we are convinced that this compound is trimethyl ortholevulinate(III), unequivocal proof awaits its synthesis in an unambiguous manner (*e.g.*, from levulinonitrile). Its preparation from I may be accounted for by way of II as an intermediate.

EXPERIMENTAL[11]

2-Methoxy-5-methylfuran (II). To a 100-ml., three necked, round-bottomed flask, equipped with a dropping funnel, gas inlet capillary, and distilling head connected to a condenser, receiver (containing *ca.* 0.1 g. of anhydrous sodium carbonate), and Dry Ice traps, was added 25 ml. (*ca.* 30 g.) of dimethyl phthalate and 2–4 drops of concd. sulfuric acid. The flask was heated in an oil bath maintained at 250 ± 10° and a slow stream of dry nitrogen was started. 2,5-Dimethoxy-2,5-dihydro-2-methylfuran[2] (I) was added through the dropping funnel at a rate of about 5 sec. per drop until 130 g. (0.9 mole) had been added. The contents of the receiver and traps were combined (141 g.), 25 ml. of fresh dimethyl phthalate added, and fractionated, yielding: 20.4 g. (64%) of methanol, b.p. 63–70°, 68.4 g. (68%) of II, b.p. 120–136°, 8.5 g. (5.4%) of III, b.p. 94–100°/20 mm., and *ca.* 40 g. of dimethyl phthalate. The residue in the reaction vessel, a dark brown, viscous, polymeric material, weighed 13 g. (10% by weight based on I).

For analysis, a portion of the fraction of crude II was distilled once at 90 mm. (b.p. 75°) and again at atmospheric pressure, b.p., 131°; d_4^{25}, 1.0096; n_D^{25}, 1.4525; MR_D (calcd.), 30.06; MR_D (obsd.), 29.99. The infrared spectrum (0.1-cm. cell) indicated peaks at 6.29, 6.98, 7.36, 8.30, 9.86 and 13.70 μ, as compared to reference compounds furan[12] (peaks at 6.33, 6.71, 7.21, 8.41, 10.01 and 13.79 μ), and 2-methoxyfuran[13] (peaks at 6.5, 7.15 and 9.9 μ).

Anal. Calcd. for $C_6H_8O_2$: C, 64.27; H, 7.19; —OCH_3, 27.7. Found: C, 64.40; H, 7.19; —OCH_3, 27.0.

3-Methyl-6-methoxy-3,6-endo-oxo-1,2,3,6-tetrahydrophthalic anhydride (V). A solution of 11.2 g. (0.1 mole) of II, dissolved in 50 ml. of absolute ether, was added to a solution of 10.0 g. (0.1 mole) of maleic anhydride in 50 ml. of absolute ether. On standing at room temperature for 16 hr., there was deposited 15 g. (71.4%) of practically pure adduct (V), m.p. 110–112°. The mother liquor was then concentrated to *ca.* 25 ml. and on chilling yielded an additional 2.7 g. (12.9%) of adduct (after washing with ether).

For analysis, a sample was recrystallized twice from absolute ether, yielding transparent prisms, m.p. 111–112.5°.

Anal. Calcd. for $C_{10}H_{10}O_5$: C, 57.14; H, 4.80; neut. equiv., 105.1. Found: C, 57.32; H, 4.88; neut. equiv., 105.0.

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(5) Since the original presentation[1] of this paper, VI has been described[6] (m.p. 185–186°) with reasonable certainty. Isomer XII has also been reported,[6,7] but with some ambiguity.

(6) A. J. Birch and P. Hextall, *Australian J. Chem.*, **8**, 96 (1955); *Chem. Abstr.*, **50**, 884 (1956).

(7) W. Metlesics and F. Wessely, *Monatsh. Chem.*, **88**, 108 (1957); *Chem. Abstr.*, **51**, 12868 (1957).

(8) J. L. Simonsen and M. G. Rau, *J. Chem. Soc.*, 1339 (1921).

(9) A. N. Meldrum, *J. Chem. Soc.*, **99**, 1712 (1911).

(10) H. Raistrick and D. J. Ross, *Biochem. J.*, **50**, 635 (1952).

(11) All temperatures are uncorrected. Ultimate microanalyses were by the Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were obtained on a Perkin-Elmer, Model 21, double-beam instrument using sodium chloride sandwich cells.

(12) H. M. Randall, R. G. Fowler, N. Fuson, and J. R. Dangl, *Infrared Determinations of Organic Structures*, D. Van Nostrand Co., Inc., New York, 1949, pp. 46–65.

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

3-Methyl-6-methoxyphthalic anhydride (VI). A solution of 10.5 g. (0.05 mole) of V, dissolved in 75 ml. of warm glacial acetic acid, was added dropwise over a period of 30 min. to a solution of *ca.* 50 mg. of anhydrous zinc chloride in 20 ml. of boiling acetic anhydride contained in a 100-ml. flask equipped with reflux condenser and dropping funnel. The mixture was refluxed an additional 4.5 hr. and left to cool slowly to room temperature. After 16 hr., 3.6 g. (37.5%) of stout, pale yellow needles of practically pure VI, m.p. 188–189°, had deposited. The mother liquor was then concentrated to *ca.* 25 ml. and on chilling and filtering yielded an additional 1.0 g. (10.4%) of VI.

For analysis, a sample of VI was recrystallized twice from dry benzene; m.p. 188.5–189°.

Anal. Calcd. for $C_{10}H_8O_4$; C, 62.50; H, 4.19; neut. equiv., 96.1. Found: C, 62.60; H, 4.38; neut. equiv., 96.5.

The filtrate (obtained after concentrating and filtering, above) contains at least one more compound which has not been completely characterized. This compound is probably the acetate of a phenolic substance since a positive (violet) ferric chloride test is obtained only after hydrolysis.

4-Methoxybenzene-1,2,3-tricarboxylic acid (VII). VI (1.92 g.; 0.01 mole) was dissolved in 100 ml. of warm 5% potassium hydroxide solution in a tall-form 400-ml. beaker. The solution was vigorously stirred while 90 ml. of 0.35*M* potassium permanganate was added in 5-ml. increments (each addition upon decolorization of the preceding). The reaction mixture was then worked up as described by Buehler *et al.*[14] yielding 2.04 g. (85%) of practically pure VII, m.p. 221–223°.

For analysis, the product was recrystallized first from acetone-benzene and then from acetic acid. To ensure no anhydride contamination, the purified material was boiled with a small amount of water and the excess water removed in a vacuum oven at room temperature. The product was then dried for 1 hr. in the vacuum oven at 60°; m.p. 223.5–224.5°.

Anal. Calcd. for $C_{10}H_8O_7$: C, 50.01; H, 3.36; neut. equiv., 80.1. Found: C, 50.02; H, 3.36; neut. equiv., 80.5.

Trimethyl ortholevulinate (III).[15] To 125 ml. of anhydrous methanol in a 300-ml. flask was added 1.8 g. (0.05 mole) of dry hydrogen chloride and then 68 g. (0.47 mole) of I. The temperature rose rapidly to reflux before the flask could be cooled by a water bath. When the tendency for the temperature to rise on removal of the bath had ceased (*ca.* 30 min.), the reaction mixture was neutralized to *p*H 8 with sodium methoxide in methanol. After filtration and removal of the excess solvent, the product was distilled under vacuum; b.p. 58–65°/1 mm.; yield, 63.9 g. (77%).

For analysis, the material was redistilled and a center-cut taken, b.p. 88.5–89.5°/10 mm.; d_4^{25}, 1.0274; n_D^{25}, 1.4225; MR_D (calcd.), 44.08; MR_D (obsd.), 43.63, pertinent infrared bands (0.2-cm. cell) at 5.88 μ (carbonyl) and 7.02 μ (CH_3 in CH_3CO).

Anal. Calcd. for $C_8H_{16}O_4$: C, 54.53; H, 9.15; $-OCH_3$, 52.8; sapon. equiv., 176.2. Found: C, 54.40; H, 8.95; $-OCH_3$, 52.3; sapon. equiv., 174.1.

Methyl levulinate 2,4-dinitrophenylhydrazone (IV). (*A*). *From* II. II (0.218 g.; 0.00195 mole), treated with 130 ml. of methanol containing 2 g. of 2,4-dinitrophenylhydrazine and 8 ml. of concd. hydrochloric acid, yielded 0.321 g. (53%)[16] of IV; m.p. 136–139°; mixed melting point with pure IV (m.p. 140–141°), 138–141°.

(*B*). *From* III. III (0.202 g.; 0.00115 mole) treated in the same manner as in (*A*) yielded 0.230 g. (64%)[16] of IV; m.p. 133–138°. One recrystallization from methanol raised the melting point to 140.0–140.5°. A mixed melting point with pure IV showed no depression.

Hydrolysis of V. Preliminary information indicates that at least two compounds are formed by the acid or neutral hydrolysis of V. One compound, only slightly soluble in water, has not yet been studied in detail.

Another substance, very soluble in water, has been recovered from the filtrate (after removal of the insoluble material) by extraction with ether. This substance gives a strong phenol test (violet to purple color) with ferric chloride. On treatment with acetic anhydride, it yields a well crystallized acetate which does not give a phenol test until after hydrolysis.

Acknowledgment. The authors gratefully acknowledge the technical assistance of Miss Mary L. Leslie and express their thanks to Dr. Shelbert Smith who determined the infrared spectra.

BARRINGTON, ILL.

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[14] C. A. Buehler, R. B. Spees, and P. A. Sanguinetti, *J. Am. Chem. Soc.*, **71**, 11 (1949).

[15] See also under the preparation of II.

[16] IV is somewhat soluble in methanol. Since no attempt was made to recover the dissolved product, these are only partial yields.