[Contribution from the Quaker Oats Company, Research Laboratories]

MECHANISM OF HYDROGENATION OF 2-METHYLFURAN

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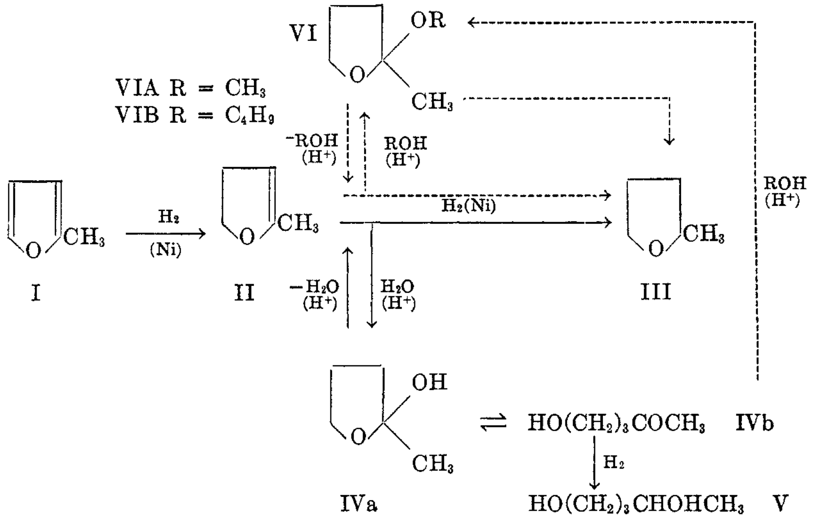
Topchiev (5) and Schniepp, Geller, and von Korff (3) reported the isolation of acetopropanol by partial hydrogenation of 2-methylfuran in aqueous medium containing trace amounts of formic acid. To explain their observations these authors proposed a mechanism involving the dihydrogenation of 2-methylfuran (I) to 2-methyl-4,5-dihydrofuran (II) which is normally hydrogenated rapidly to 2-methyltetrahydrofuran (III) but which in aqueous, acidic, medium, is hydrated competitively to IVa, the cyclic, hemiacetal form of 3-acetopropanol (IVb). Subsequent hydrogenation of IV gives rise to 1,4-pentanediol (V). III, IV, and V are the isolable products of reaction. The occurrence of II was inferred; failure to isolate this dihydrofuran under the experimental conditions employed being readily explicable in terms of the resonance concept.



The formation of IV might be explained by yet another route. Thus, hydrolytic fission of I to levulinaldehyde, and selective hydrogenation of the latter could give rise to IV. On the other hand, it is doubtful that the acidic conditions employed in the work under discussion are strenuous enough to account for the degree of hydrolysis required on the basis of the yield of IV obtained. Accordingly, we favored the concept of partial hydrogenation of the nucleus as the initial step in this reaction, as we did earlier (4) in connection with the hydrogenation of furfuryl alcohol and furylacrolein, but it was considered worthwhile to seek additional supporting evidence.

If the reaction were conducted in alcoholic instead of aqueous medium, the acetal VI, should be obtained rather than the transitory hemiacetal, IVa. Confirmation of this hypothesis was obtained when partial hydrogenation of I over nickel in methanol gave rise to 2-methyl-2-methoxytetrahydrofuran (VIA) as a reaction product. When *n*-butanol was substituted for the methanol, the 2-butoxy compound, VIB, was obtained. In contrast with the earlier work (3) in an aqueous medium, no 1,4-pentanediol (V) was found indicating that further reaction of the acetal, VI, with hydrogen involves hydrogenolysis to III, and/or reversal to II, with subsequent hydrogenation to III.

The occurrence of VI constitutes added proof for the mechanism involving dihydrogenation of the furan ring since this acetal cannot be obtained by alcoholysis of methylfuran. Even more conclusive evidence was obtained from a comparative kinetic study of the hydrogenation of several of the intermediates. The extent of reaction was determined by weighing the 2,4-dinitrophenylhydrazone of IVb formed after acid hydrolysis of the products to convert II or VIA into IVb; unreacted 2-methylfuran was determined by the pyridine sulfate-bromide method (2) and corrected for any potential IV which was present. The results are shown in Table I.

TABLE I

Reaction[a] of I, II, IV, and VIA with Hydrogen, %

COMPOUND	WITHOUT ACID	WITH 0.06 G. FORMIC ACID/MOLE COMPOUND
(I) 2-Methylfuran	88[c]	90[d]
(II) 2-Methyl-4,5-dihydrofuran	130[e]	87
(IV) 3-Acetopropanol	75	55
(VIA) 2-Methyl-2-methoxy tetrahydrofuran	28	42

[a] Experimental conditions: 0.025 mole of compound, 100 ml. of methanol, and 2.0 g. of nickel on kieselguhr catalyst (1) for 40 minutes[b] at 1800 p.s.i. and 160°. [b] Includes the 20 minutes necessary to bring to the desired temperature. [c] Dihydro compounds calculated as IV, 0%. [d] Dihydro compounds calculated as IV, 5%. [e] Estimated percentage based on 98% in 30 minutes.

As expected, no evidence for dihydrogenation was found in the absence of acid, since II hydrogenates much more rapidly than I, and IV almost as rapidly. In the presence of acid, II hydrogenates no faster than I because of competitive conversion to the less reactive acetal, VIA. The relative stability of IV must be due to its partial conversion to the acetal, a process which is accelerated by the presence of acid. By the same token, the decreased stability of the acetal in acid may be due to partial reversal to II. This may explain, in part, why an increase in the amount of acid can reduce the quantity of dihydrogenation products obtained. The determination of the optimum acid concentration for the highest yield of VI led to seemingly contradictory values. The effect of three acid concentrations at three different times is shown in Table II.

The data suggest that time is also a variable. Indeed, it was found that for each acid concentration there was an optimum time. Thus, when all other variables were kept constant the optimum acid concentration was a function of time (Table III).

Since catalyst activity and amount, temperature, concentration, medium, and rate of shaking are also interdependent variables, establishment of an all-inclusive optimum would be a formidable task.

Although this work was carried out with nickel on kieselguhr, Raney nickel can be used, but more acid is required to obtain comparable yields of dihydrogenation products. This difference, which may be due to the greater inherent basicity of Raney nickel, has a bearing on experimental data reported by Adkins (1, 7) on the formation of 1,9-dioxo-5-spirononane (8) (VII) from 3-(2-furyl)-acrolein (VIII) and from 3-(2-furyl)propanol (IX). Adkins obtained only trace amounts of VII from IX using Raney nickel as compared to 33% of VII from VIII over nickel on kieselguhr, and concluded that IX was not an intermediate in the latter reaction. (The dihydrogenation mechanism would predict that either IX or the related furylpropenol should be an intermediate). Adkins' conclusion is not justified since his own data (1, 7) also reveal that VII was obtained in only 3% yield from VIII over Raney nickel under otherwise comparable conditions.

TABLE II

YIELD (AS ACETOPROPANOL) FROM HYDROGENATION OF METHYLFURAN

G. FORMIC ACID PER MOLE METHYLFURAN	TIME OF SHAKING AFTER REACHING 160°		
	2 min., %	3 min., %	5 min., %
0.02	18	12	5
.06	7	20	12
.30	9	9	25

TABLE III

HYDROGENATION[a] OF METHYLFURAN

G. FORMIC ACID PER MOLE METHYLFURAN	TIME (MIN.)[c] TO REACH OPTIMUM	YIELD AS ACETOPROPANOL, %
0.02	2.0	18
.06	3.0	20
.30	5.0	25
.40	5.5	34
.60	8.0	29
.80	10.0	20
1.00	12.0	15

[a] Experimental conditions: 0.025 mole of methylfuran, 1.0 g. of nickel on kieselguhr[b] catalyst, 100 ml. of methanol at 160° and 1800 p.s.i. [b] Harshaw Chemical Co., NI 0101P. [c] Time of shaking after reaching desired temperature without shaking.

EXPERIMENTAL

2-Methoxy-2-methyltetrahydrofuran (VIA). Freshly distilled 2-methylfuran (82 g.) in 100 ml. of methanol containing 0.06 ml. of 98% formic acid was hydrogenated over 6.0 g. of reduced nickel on kieselguhr catalyst (1) in a Parr rocker type hydrogenation apparatus at 160° and 1600 p.s.i. until one mole of hydrogen had been absorbed (150 min.). The contents were cooled, filtered, and neutralized with *N* NaOH. Distillation through a 25-cm. helices-packed column yielded 13.2 g. (11.4%), of VIA boiling at 112–114°; n_D^{20} 1.4120. The material was redistilled and the fraction used for analysis boiled at 113–114°; n_D^{20} 1.4115 [reported (3) 114.5°, n_D^{25} 1.4110].

Anal. Calc'd for $C_6H_{12}O_2$: C, 62.04; H, 10.41; Mol. wt., 116.

Found: C, 62.02; H, 10.47; Mol. wt., 115.

The 2,4-dinitrophenylhydrazone melted at 145–146° and showed no depression with the same derivative from authentic IV.

2-Butoxy-2-methyltetrahydrofuran (VIB). The same hydrogenation procedure was used as for VIA, except that 100 ml. of *n*-butanol was substituted for the methanol. Seventy minutes were required for one mole of hydrogen uptake. Distillation through a 25-cm. helices-packed column yielded 16.1 g. (10.2%) of VIB boiling at 49–50° (6 mm.); n_D^{20} 1.4233. For analysis the material was redistilled at 166–168° at 746 mm. in a nitrogen atmosphere; n_D^{20} 1.4230.

Anal. Calc'd for $C_9H_{18}O_2$: C, 68.31; H, 11.47, Mol. wt., 158.
Found: C, 68.53; H, 11.52; Mol. wt., 152.

The 2,4-dinitrophenylhydrazone melted at 146–147° and showed no depression with the same derivative from authentic IV.

3-Acetopropanol (IV). Freshly distilled 2-methylfuran (82 g.) in 100 ml. of water and 0.3 ml. of 98% formic acid was hydrogenated over 10 g. of reduced Ni on kieselguhr catalyst at 160° and 1600 p.s.i. until one mole of hydrogen had been absorbed (225 min.). The mixture was cooled, filtered, and neutralized with *N* NaOH. Distillation through a 25-cm. helices-packed column yielded 30.2 g. (30%) of IV boiling at 100–106° (6 mm.); n_D^{20} 1.4380. Redistilled at 74–75° (3 mm.) n_D^{20} 1.4360 [reported (3), 75° (3 mm.), n_D^{25} 1.4350].

2,4-Dinitrophenylhydrazone of IV. A solution of 0.5 g. of IV in 10 ml. of methanol and 10 ml. of 2 *N* HCl was warmed on a steam-bath for 5 min. after which 1.0 g. of 2,4-dinitrophenylhydrazine was added and the solution heated for additional 5 min. After cooling, the precipitate was filtered and recrystallized from ethanol. The derivative melted at 145.5–146.0°.

Anal. Calc'd for $C_{11}H_{14}N_4O_5$: N, 19.85. Found: N, 19.83.

2-Methyl-4,5-dihydrofuran (II). The preparation of II by dehydrative distillation (3, 6) of IV went smoothly as long as the IV was impure. However, with highly purified samples of IV, little or no dehydration occurred unless trace amounts of acids (*e.g.* NaH_2PO_4) were added. The compound boiled at 78–79°; n_D^{25} 1.4289 [reported (3) 80°; n_D^{25} 1.4290]. The 2,4-dinitrophenylhydrazone melted at 144–145° and showed no depression when mixed with the 2,4-dinitrophenylhydrazone of IV.

SUMMARY

Additional proof is presented for a previously proposed mechanism which accounts for the occurrence of dihydro derivatives on partial hydrogenation of furans.

The previously reported 2-methoxy- and the new 2-butoxy-2-methyltetrahydrofuran have been prepared by appropriate hydrogenations of methylfuran in methanol and butanol respectively.

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