3. Syn chloride (unlabeled **9**): 30 mg, 9.5% yield; mp and mmp[10] 144–145°.

B. With Labeled 4.[2] The reaction was carried out as described in A, above, to give the following.

1. A mixture of pure syn and anti acetates **5** and **6**: 64.3% yield; ratio of syn:anti 1:3.3.

2. Pure anti chloride **10** (25.9% yield): the pmr spectrum showed no methine at δ 5.18 (anti chloride) which confirmed deuterium at the methine carbon; mass spectral analysis showed 95.2% monodeuterated species and 4.8% unlabeled species.

3. Pure syn chloride (1.5% yield): mass spectral analysis showed 63.2% nondeuterated, 32.7% monodeuterated, and 4.1% dideuterated species; the pmr spectrum (using a computer of average transients) gave an apparent triplet centered at δ 5.97 for anti H (**9**) which integrated for ~0.5H *vs.* aromatic H.

Analysis of the label in acetates **5** and **6** was conducted on the pure alcohols obtained by hydrolysis.[9] The syn alcohol (mp and mmp 158–159°)[9] showed by mass spectral analysis 82.7% unlabeled and 17.3% monodeuterated species; the pmr spectrum ($CDCl_3$) showed, subsequent to treatment of a sample with D_2O to eliminate overlapping signals due to OH, a quartet at δ 5.33 (methine H) which integrated to 0.85 H *vs.* the aromatic H. The anti alcohol (mp and mmp 205–206°)[9] showed by mass spectral analysis[18] 97.4% d_1 and 2.6% d_2 species; pmr showed no observable methine resonance.

Reaction of 4 with *p*-toluenesulfonyl chloride was carried out as previously described[10] to give only syn tosylate (m 122–123° from ether);[20] no anti tosylate[10] was detected. The mass spectrum of this product showed 97.5% d_1 and 2.5% d_2 species; pmr ($CDCl_3$) showed one proton (methine H) at δ 6.35.[9]

Registry No.—**4** (unlabeled), 25907-81-7; **4** (labeled), 51820-05-4; *syn*-**5** acetate, 51933-62-1; *syn*-**5** alcohol, 25866-36-8; *anti*-**6** acetate (unlabeled), 52078-88-3; *anti*-**6** acetate (labeled), 52151-91-4; *anti*-**6** alcohol (labeled), 52079-43-3; *syn*-**7** tosylate, 37781-25-2; *syn*-**9**, 37781-27-4; *anti*-**10** (unlabeled), 52019-95-1; *anti*-**10** (labeled), 52078-89-4; acetic anhydride, 108-24-7; acetyl chloride, 75-36-5; *p*-toluenesulfonyl chloride, 98-59-9.

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(14) Return of an acetate ion pair associated with the activated complex may be analogous to results obtained with acetyl chloride.
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Hydrolysis of 2-Methoxyfuran[1]

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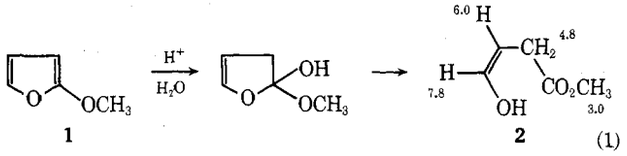
The acid-catalyzed hydrolysis of 2-methoxyfuran in aqueous dimethyl sulfoxide results in the formation of crotonolactone (**4**, 55–65%), methyl succinate semialdehyde (**5**, 16–23%), and methyl *cis*-4-hydroxycrotonate (**6**, 16%), as determined by nmr spectroscopy. These findings are not in agreement with an earlier report[2] and require revision of the proposed mechanism of hydrolysis of 2-methoxyfuran.

The acid-catalyzed hydrolysis of 2-methoxyfuran (**1**) has been reported[2] to yield the enol **2** of the methyl ester of succinic acid semialdehyde, presumably arising *via* a tetrahedral addition intermediate[3] (eq 1). The proposed intermediate is similar in structure to those believed to be formed in many acyl transfer reactions,[4] and in particular to those of ester hydrolysis[5] and formation.[6] It seemed of special interest to determine whether the direction of decomposition of the addition intermediate would be pH dependent, as had been found with the closely related intermediates generated during the lactonization of coumarinic acids,[6] and if so, to measure the partitioning ratio of the different ionic species of the intermediate. While attempting to obtain this information, we have found that the hy-



1 2 (1)

Table I
Hydrolysis of 2-Methoxyfuran

[HCl], M[a]	$k_{obsd} \times 10^3$, sec^{-1}	[DCl], M[b]	$k_{obsd} \times 10^3$, sec^{-1}	
0.001	1.64, 1.68	0.01	0.28[c]	0.24[d]
0.003	4.70, 5.46	0.08	2.8[c]	2.4[d]
0.005	8.05, 8.20, 8.38	0.25	11.2, 12.5[c]	7.8, 9.6[d]
	$k_H = 1.66\ M^{-1}\ sec^{-1}$		$k_D = 0.033\ M^{-1}\ sec^{-1}$	

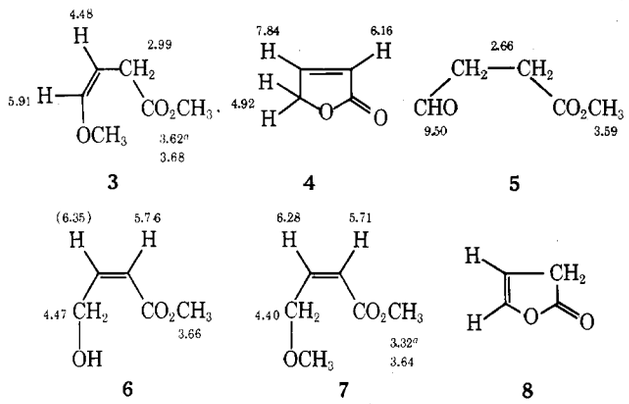
[a] At 25°, 0.8% CH_3CN–H_2O, μ = 0.1. [b] At 32.5°, 41 mol % dimethyl sulfoxide-d_6–deuterium oxide. [c] Disappearance of 2-methoxyfuran. [d] Appearance of 4.

drolysis of 2-methoxyfuran is appreciably more complex than hitherto reported.[2]

Results and Discussion

The identification[2] of the enol **2** as the product of hydrolysis of 2-methoxyfuran was based on the interpretation of the nmr spectrum of the reaction product (in 50 mol % dimethyl sulfoxide) as shown in eq 1. That the assigned structure **2** is probably incorrect is revealed by the published[7a] nmr spectrum (in CCl_4) of the corresponding enolic methyl ether **3** (Chart I). On the other hand, the measured chemical shifts and coupling constants assigned[2] to structure **2** correspond closely to those determined in this laboratory for 4-hydroxycrotonic acid lactone (**4**) in 50 mol % dimethyl sulfoxide–water.[8] In the same solvent, the methyl group of methanol had a chemical shift of 3.23 ppm relative to tetramethylsilane.

Chart I



[a] Individual values of the chemical shifts of the two methyl groups in **3** and **7** (ref 7a) were not assigned.

Kinetic Studies. The disappearance of 2-methoxyfuran in 0.8% acetonitrile–water (μ = 0.1, NaCl) at 25°, followed by the decrease in ultraviolet absorbance at 230 nm, was found to obey the rate law $k_{obsd} = k_H[H^+]$, with k_H = 1.66 M^{-1} sec^{-1} (Table I). This constant agrees very well with the reported[2] value of 1.68 M^{-1} sec^{-1} in water (25°), measured by gas chromatography.

The rate of hydrolysis of 2-methoxyfuran was also determined in 41 mol % dimethyl sulfoxide-d_6–deuterium oxide solvent (at 32.5 ± 1.0°), using nmr spectroscopy. Measurements were made at 0.01, 0.08, and 0.25 M DCl concentration, and the ionic strength was equal to the concentration of added acid. The resulting rate constants were considerably less precise than those in dilute solution by uv spectroscopy, especially at the highest acidity, but were approximately linearly dependent on D^+ concentration and gave k_D = 0.033 M^{-1} sec^{-1} (Table I). The protons at C_3 and C_5[9] were found to disappear at the same rate, in agreement with the previous report,[2] thus ruling out rapid, preequilibrium hydrogen exchange at C_5, such as was found in the hydrolysis of 2-methylfuran.[10] In addition, the appearance of the C_4 and the (single) C_5 protons of the crotonolactone **4** also followed first-order kinetics at a rate equal to that of the disappearance of 2-methoxyfuran (Table I), suggesting that no significant concentration of any intermediates accumulated prior to the formation of **4**.

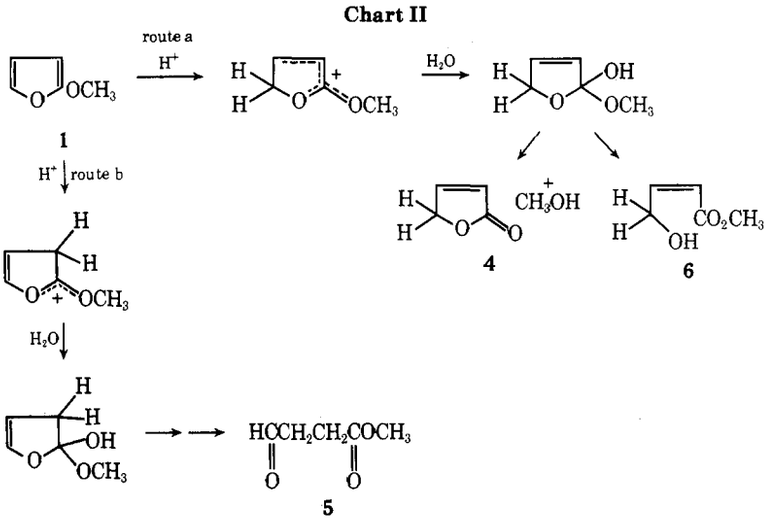
The reaction rate was also measured by the nmr technique in 47 mol % CD_3CN–D_2O at a single acid concentration (0.08 M DCl), yielding k_D = 0.07 M^{-1} sec^{-1}.

Reaction Products. Nmr spectra of reactions carried out in 41 mol % dimethyl sulfoxide-d_6–deuterium oxide were obtained after complete disappearance of 2-methoxyfuran (at least 8 half-lives) over the range of 0.001–0.93 M DCl. These spectra showed that the reaction product was an unexpectedly complex mixture of components. The predominant product (55–65% yield) exhibited chemical shifts, spin–spin multiplicity, and coupling constants identical with those measured in this solvent for the crotonolactone **4** (Chart I) and similar to those reported for $CDCl_3$.[8] The integrated signals showed that the protons at δ 4.92, 6.16, and 7.84 were present in the ratio of 1:1:1 when hydrolysis was performed in solvents containing deuterium oxide (the integration of the signal at δ 6.16 was invariably 10–15% greater than that of the signal at δ 7.84; see below). The splitting pattern for each of the C_3 and C_4 protons changed from a doublet of doublets for the D_2O reaction to a doublet of triplets when hydrolysis was carried out in H_2O. The splitting patterns, integrated areas, and the broadening of the signal at δ 4.92 are consistent with the conclusion that the crotonolactone **4** produced in the presence of deuterium oxide contains a single deuterium atom incorporated at the C_5 positions.

Comparison to authentic material allowed the identification of the second reaction product (16–23% yield) as the methyl ester of succinic acid semialdehyde (**5**) (singlets for the aldehydic proton[11] at δ 9.50 and for the methoxyl group at δ 3.59, Chart I). The weak and broad signal (at least two deuterium atoms are expected to be incorporated in the $-CH_2CH_2-$ group; see below) anticipated at δ 2.66 for the methylene groups of **5** is masked by protonic impurities in dimethyl sulfoxide-d_6.

A third product formed in significant quantities (about 16%) is tentatively identified as *cis*-4-hydroxycrotonic acid methyl ester (**6**) (Chart I). Although this substance does not seem to have been described, the corresponding methyl ether **7** is well known[7a,c] and its nmr spectrum[7a] (Chart I) is consistent with the assignments made here for **6**. The large coupling constant ($J_{2,3}$ = 11.7 Hz)[7a] for the olefinic protons of **7** is reflected in the well-separated doublet of doublets centered at δ 5.76 and assigned to C_2 in **6**. The C_3 proton of **6** (centered approximately at δ 6.35) appears partially masked by the more prominent C_3 proton of the crotono-

Chart II



lactone. This overlap is presumably responsible for the consistent observation mentioned above that the integral of the C_3 proton of **4** was always slightly higher than that of the C_4 proton. For reactions in D_2O, the signal at δ 4.47 (C_4 of **6**) is expected to correspond to one proton only, although precise integration of these weak signals is difficult. The most convincing indication of the existence of **6** is, of course, the presence of the sharp methoxy singlet slightly downfield from the methoxy signal of the aldehyde ester **5**.

The lactone **4** and the two acyclic products **5** and **6** account for about 90–95% of the reaction products. Particular attention was directed at the possibility that the enol lactone **8** might be a reaction product. Although the preparations[12] of **8** and of its tautomer 2-hydroxyfuran[13] have been claimed, the existence of these compounds is in doubt.[14,15] In any event, a signal at *ca.* δ 6.75 would be expected for the C_5 proton of **8** (based on the reported[17] nmr spectrum of the 3-methyl derivative of **8**). The absence of any significant resonance in this area of the reaction product spectrum serves to rule out the possibility that the enol lactone **8** is a stable product of the hydrolysis of 2-methoxyfuran.

No systematic variation in the yield of the crotonolactone **4** was noted in the acidity range of [DCl] = 0.001–0.9 *M*. In 0.04 *M* DCl, the crotonolactone undergoes neither hydrolysis nor hydrogen exchange over a period of 6 days. Similarly, the yield of the aldehyde **5** appears approximately constant over the same range of acidity, as judged from the intensity of the methyl signal at δ 3.59. It is noteworthy that the aldehydic proton signal is not a reliable indication of aldehyde yield in these experiments. The sharp singlet observed at δ 9.50 in 50 mol % dimethyl sulfoxide-d_6–D_2O is appreciably broadened in 0.04 *M* DCl and is essentially undetectable in 0.93 *M* DCl. This behavior is most likely the result of the increasing rate of the (acid-catalyzed) chemical exchange reaction between the aldehyde and its hydrate. In the absence of acid, the nmr spectrum of the aldehyde exhibits a weak triplet at δ 4.84,[18] presumably the signal of the spin-coupled proton of the hydrated aldehyde, whose intensity suggests that about 25% of the total aldehyde exists as the hydrate.[19] That exchange between the aldehyde and its hydrate would become significant on the nmr time scale in this range of acid concentrations is supported by the report[20] of line broadening in the ^{17}O nmr spectrum of acetaldehyde and its hydrate in 0.1–1 *M* HCl and the measured rates of the acid-catalyzed hydration of simple aliphatic aldehydes.[19b,c,21]

The yield of methyl *cis*-4-hydroxycrotonate (**6**) is constant in solutions where [DCl] = 0.001–0.08 *M*, is reduced by half in 0.25 *M* DCl, and falls to nearly zero at higher acidities. It is not certain whether the acyclic alcohol was not formed at high acidity, or underwent rapid subsequent reaction. Under conditions where an appreciable amount of **6** is formed (*e.g.*, 16% in 0.04 *M* DCl after 1.5 hr), the methyl signal associated with **6** had almost completely disappeared after 14 hr, while that of the aldehyde **5** was largely unchanged. Possibly, the 4-hydroxy ester **6** undergoes acid-catalyzed lactonization to the crotonolactone **4**.[22] However, the relative stability of **6** after short reaction times rules out the possibility that lactonization of initially produced **6** constitutes the main pathway for the formation of the crotonolactone **4**.

Reaction Mechanism. For the hydrolysis of 2-methoxyfuran in 41 mol % dimethyl sulfoxide–water, a reaction mechanism consistent with the observations made in this study is outlined in Chart II. According to this proposal, 2-methoxyfuran suffers rate-determining protonation either at the 5 position (route a) or the 3 position (route b). The former pathway, resulting (formally) in 1,4-addition across the dienic system, occurs four times as fast as the competing 1,2-addition of route b. For route a, the allylic oxocarbonium ion is suggested to yield a tetrahedral addition intermediate (of unspecified ionic state) which breaks down mainly by expulsion of methanol but also undergoes significant ring opening to the allylic alcohol **6**. The incorporation of one atom of deuterium at C_5 of the crotonolactone is in accord with the proposed pathway.

In route b, the protonation which occurs at C_3 yields eventually a tetrahedral intermediate which appears to break down solely by ring cleavage, presumably to the enolic form of **5**; rapid tautomerization then gives the observed aldehyde.

The pattern of deuterium incorporation in the crotonolactone **4** (one atom of deuterium at C_5) rules out a mechanism wherein the predominant hydrolytic pathway is that of route b, yielding mainly the (possibly unstable) enol lactone **8**, which undergoes double-bond migration to the crotonolactone **4**. Such a mechanism would necessarily require the presence of a deuterium atom at C_3 of the crotonolactone.

The mechanism of hydrolysis of 2-methoxyfuran thus appears to differ from those proposed for the acid-catalyzed hydrolysis of furan[23] and its alkyl-substituted derivatives,[10,23,24] for which it has been suggested that the major reaction pathway consists of rate-determining β-protonation (*i.e.*, at C_3 of the furan ring).

The identity of the products of hydrolysis of 2-methoxyfuran in dilute aqueous solution is not known. If both hydrolytic pathways also occur in predominantly aqueous medium, the observed[2] solvent deuterium isotope effect and general acid catalysis may contain contributions from both reaction pathways and are thus not amenable to interpretation at this time.

Experimental Section[25]

2-Methoxyfuran (1) (Aldrich Chemical Co.) had bp 103–105° (lit.[26] bp 108–109°) and was kept in the dark in sealed ampoules at −10°. Prior to use, the purity of the compound was routinely checked by nmr spectroscopy and compared to the nmr spectrum of a freshly distilled sample.

1: Uv (CH_3CN) λ_{max} 222 nm (ϵ 6750);[27] nmr ($CDCl_3$)[28] δ 3.73 (s, 3 H, OCH_3), 5.05 (m, 1 H, C_3), 6.14 (m, 1 H, C_4), 6.75 (m, 1 H, C_5); nmr (50 mol % DMSO-d_6–D_2O:) δ 3.79, 5.30, 6.34, 7.00.

4-Hydroxycrotonic acid γ-lactone (4), bp 107–109° (24 mm) [lit.[29] bp 107–109° (24 mm)], was prepared using the procedure of Price and Judge.[29] The nmr spectrum in $CDCl_3$ agreed with the reported values.[8] Nmr (50 mol % DMSO-d_6–D_2O): δ 4.92 (t, 2 H, CH_2), 6.16 (m, 1 H, C_3), 7.84 (m, 1 H, C_4).

Succinic Acid Semialdehyde Methyl Ester (5). Methyl hydrogen succinate[30] was converted to the acid chloride.[31] Rosenmund reduction[32] of the latter gave the aldehyde: bp 68–71° (11 mm) [lit.[32] bp 69–70° (14 mm)]; nmr ($CDCl_3$) δ 2.66 (m, 4 H, CH_2CH_2), 3.62 (s, 3 H, OCH_3), 9.67 (s, 1 H, CHO); nmr (50 mol % DMSO-d_6–D_2O) δ 2.33–2.90 (m, 4 H, CH_2CH_2), 3.59 (s, 3 H, OCH_3), 4.84 [t, 0.25 H, $HC(OD)_2C$], 9.50 (s, 0.75 H, CHO).

Deuterium oxide, concentrated aqueous DCl, CD_3CN, and dimethyl sulfoxide-d_6 were obtained from Merck Sharpe and Dohme of Canada.

Kinetic Measurements. The rate of hydrolysis of 2-methoxyfuran in dilute aqueous HCl solution (25°, μ = 0.1, NaCl) was determined by following the decrease in absorbance at 230 nm, using a Cary 15 spectrophotometer. Reaction was initiated by addition of 25 μl of a stock solution of 2-methoxyfuran in acetonitrile to 3 ml of aqueous HCl solution previously equilibrated in the thermostated cell compartment of the spectrophotometer. The final concentration of substrate was about 3×10^{-4} M, and the absorbance change was 0.8–0.9 units.

The following procedure was used for rate measurements in 41 mol % DMSO-d_6–D_2O. A mixture of 0.5 g of DMSO-d_6 and 0.13 g of D_2O was added to 0.05 g of 2-methoxyfuran in an nmr tube. The sample was allowed to equilibrate to the temperature of the probe (32.5 ± 1.0°), and the nmr spectrum was recorded to check the purity of the reactant. Hydrolysis was initiated by the addition of 50 μl of standard aqueous DCl solution, and the nmr tube was rapidly shaken and immediately reinserted into the probe. The rate of disappearance of 2-methoxyfuran was followed by the decrease in the integrated signal of the protons at C_3 and C_5, while the signals at C_4 and C_5 of the crotonolactone 4 were used to monitor the formation of product. First-order rate constants were calculated by means of the integrated first-order rate equation.

Product Analysis. Nmr spectra of reaction mixtures were recorded after 10–20 half-lives of reaction. The yield of crotonolactone 4 was calculated by comparison of the area of the signal for the C_4 proton to that of an authentic sample of 4. The total concentration of methyl esters 5 and 6 was determined from the combined areas of the methoxy signals at about δ 3.6 and the relative amounts of 5 and 6 were estimated from the relative heights of the signals at δ 3.59 and 3.66.

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Registry No.—2-Methoxyfuran, 25414-22-6.

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