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REVERSIBLE CARBON PROTONATION IN THE HYDROLYSIS OF HETEROCYCLIC ENOL METHYL ETHERS

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Abstract - The kinetics of the hydronium-ion catalysed hydrolysis of the following heterocyclic methyl enol ethers have been measured: 3-methoxybenzofuran, 3-methoxybenzothiophene, 3-methoxyindole, 3-methoxy-1-methylindole, 3-methoxyfuran, 3-methoxythiophene, and 2-methoxythiophene. On the basis of the solvent isotope effect k_H/k_D = 3.08 and the failure to detect deuterium exchange when the solvent was $CD_3CD:D_2O$(9:1 v/v) it was concluded that the rate limiting step in the hydrolysis of 3-methoxybenzofuran is *C*-protonation. The effect of the ring-oxygen atom was measured by comparing the rate of hydrolysis of 3-methoxybenzofuran with that of 3-methoxyindene which occurs 2100 times faster.

In contrast to the behaviour of 3-methyoxybenzofuran the isotope effects, k_H/k_D, for the hydrolyses of 3-methoxyfuran, 3-methoxythiophene, 3-methoxyindole, 3-methoxy-1-methylindole and 2-methoxythiophene are *ca* 0.4 - 0.5 and deuterium exchange is much faster than hydrolysis when the solvent is $CD_3CN:D_2O$ (9:1 v/v). It was therefore concluded that with these compound *C*-protonation is rapid and reversible and that slow step is attack by water on the intermediate cation.

3-Methoxybenzothiophene showed intermediate behaviour with k_H/k_D = 1.36.

It was pointed out by Kresge and Chen that although the normal mechanism for the hydrolysis of enol ethers involves a rate-determining protonation of the double bond there is a possibility of a change in rate-determining step so that the proton-transfer becomes rapid and reversible.[1] It was also pointed out that in the extreme case of a phenol ether this is what happens and that reversible protonation is much faster than hydrolysis. In order to find out at what level of conjugation this change in rate-determining step occured Kresge and his co-workers investigated the hydrolysis of a series of enol ethers but with all the compounds studied it was concluded on the basis of the detection of general-acid catalysis, the solvent isotope effect (k_H/k_D = *ca* 3), and the failure to detect *cis-trans* isomerisation concurrent with hydrolysis, that the rate-determining step was proton transfer.[1,2]

Subsequently, evidence for the sought-after change in rate-determining step was found by Okuyama, Fueno and their co-workers with ketene dithioacetals as substrates[3] and by Hevesi and his co-workers with seleno enol ethers and ketene diseleno acetals.[4] The evidence which includes the observation of deuterium exchange and *cis-trans* isomerization concurrent with hydrolysis, the solvent isotope effects ($k_H/k_D < 1$), and the observation of general-acid catalysis with a non-linear dependence on buffer concentration indicates that with a series of ketene dithioacetals and seleno enol ethers that proton transfer and hydration of the intermediate cation occur at comparable rates but that with the ketene diseleno acetals proton transfer is fast and reversible. Therefore it requires the presence of two sulphurs or one selenium to cause a partial change in rate determining step and only when two seleniums are present is the change in rate-determining step complete. It was suggested that for the ketene dithioacetals the partial change in rate determining step resulted from hydration of the cation being slow rather than from its deprotonation being fast.[3]

We now report that in the hydronium-ion catalysed hydrolysis of the methyl *oxygen* ethers of heterocyclic compounds a regular change in mechanism is found from rate-limiting protonation when the aromaticity of the ring is low as in 3-methoxybenzofuran to rapid and reversible protonation when it is high as with 3-methoxythiophene or 3-methoxy-1-methylindole. In the intermediate case of 3-methoxybenzothiophene deprotonation and nucleophilic attack on the intermediate cation occur at comparable rates.

Thus, when the hydrolysis of 3-methoxythiophene in a mixture of $CD_3CN:D_2O$ (9:1 v/v) which is 0.1 M in DCl is followed by ^{1}H-NMR spectroscopy (Fig.1) the signal of H-2 disappears completely and the signals of H-4 and H-5 become simplified to an A-B system after 3 minutes at 32° but there is no indication of any hydrolysis though formation of a signal due to methanol at $\delta = 3.3$. This only appears after much longer periods (2 days). Similar behaviour was found with 3-methoxy-1-methylindole and 3-methoxyfuran but with 3-methoxybenzothiophene some hydrolysis was detected before exchange was complete.

With 2-methoxythiophene exchange at both positions 3 and 5 occurs. Exchange at position 5 is complete before any hydrolysis could be detected and exchange at position 3 is only 30 times faster than hydrolysis. This is in agreement with what is normally found for electrophilic substitution in thiophene when reaction at the α-position is faster than at the β-position.[5] The 2-methoxy groups provides activation for reaction at both positions but does not have a large effect on the relative rates. No evidence was found for ring opening as reported with 2-methoxyfuran.[6] After hydrolysis in $CD_3CN:D_2O$ (9:1 v/v)

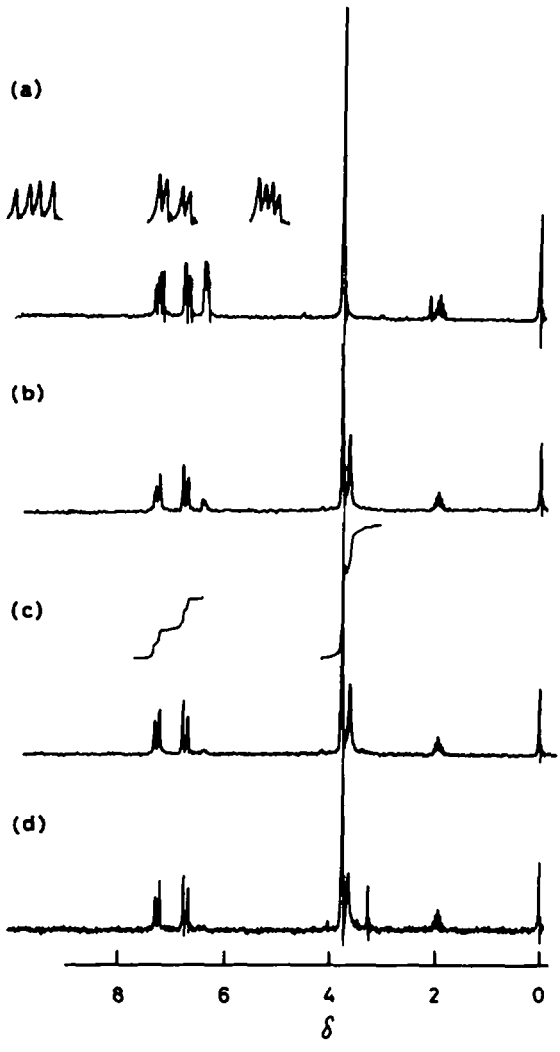
Fig. 1.

(a) ^{1}H-NMR spectrum (60 MHz) of 3-methoxythiophene in CD_3CN at 32°; inset, expansion of ring protons-sweep-width 2 ppm (H-2, δ = 6.35; H-4, δ = 6.70; H-5 δ = 7.20, $J_{2,5}$=3.2 Hz, $J_{2,4}$=1.6 Hz, $J_{4,5}$=5.2 Hz). The multiplet at δ = 1.95 is that of CHD_2CN and the singlet at δ = 2.05 is that of H_2O or HOD.

(b) Spectrum run immediately after addition of 10% 1 M DCl: The signal of H-2 has almost completely disappeared. The multiplet at δ = 1.95 is that of CHD_2CN and the singlet at δ = 3.70 is that of HOD.

(c) After 3 minutes. Signal of H-2 has completely disappeared and signals of H-4 and H-5 have been simplified to an AB system. No signal due to methanol, δ = 3.3, can be observed.

(d) After 2 days a small signal due to methanol at δ = 3.3 can be observed.



there was a strong signal in the ^{1}H-NMR spectrum at δ = 7.80 the correct chemical shift for H-4 of [3,5,5-$^2H_3$]3-thiophene-2-one and the infinity UV spectrum was also that expected for this compound. Presumably the thiol group is not expelled from the tetrahedral intermediate derived from 2-methoxythiophene wherewas the endocyclic oxygen is expelled from that derived from 2-methoxy-furan. With 3-methoxybenzofuran no exchange was detected.

Approximate values of the rates and the ratios of exchange and hydrolysis were calculated from the NMR spectra and are given in Table 1.

These conclusions are consistent with the solvent isotope effects measured in aqueous solution at 25°. Thus for 3-methoxybenzofuran, k_H/k_D is 3.08 the normal value for the hydrolysis of enol ethers[7] and consistent with a mechanism which involves rate-limiting carbon protonation.For 3-methoxyfuran, 3-methoxy-thiophene, 3-methoxyindole and 3-methoxy-1-methylindole, k_H/k_D = 0.41 to 0.52 consistent with a mechanism which involves rapid and reversible proton transfer.[8] With 3-methoxybenzothiophene the isotope effect has an intermediate value

Table 1 Rate constants and wavelength used for the hydrolysis of methyl enol ethers

Compound	Wavelength used/nm	$k_H/M^{-1}s^{-1}$	$k_D/M^{-1}s^{-1}$	k_H/k_D [a]	$k_{ex}/k_{hyd.}$ [b]
3-Methoxyindene	247	103	37.2	2.76	-
3-Methoxybenzofuran	323	4.89×10^{-2}	1.59×10^{-2}	3.08	< 0.05 [c]
3-Methoxybenzothiophene	300	8.42×10^{-3}	6.21×10^{-3}	1.36	31
3-Methoxyfuran	258	0.246	0.480	0.51	83
3-Methoxy-1-methylindole	417	3.51×10^{-3}	7.89×10^{-3}	0.44	1.3×10^{3}
3-Methoxythiophene	323	1.67×10^{-4}	3.21×10^{-4}	0.52	2.6×10^{4}
3-Methoxyindole	380	6.21×10^{-3}	1.49×10^{-2}	0.42	-
2-Methoxythiophene	242	8.35×10^{-4}	1.79×10^{-3}	0.47	30 [d]

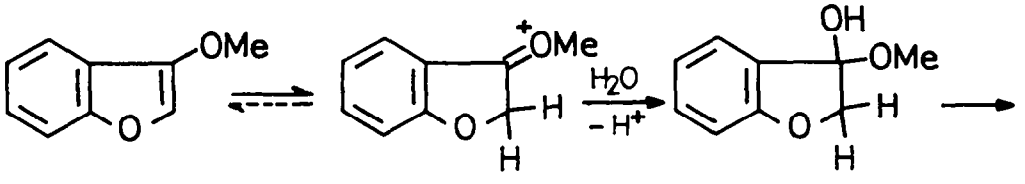
[a] In water at 25°C, I = 1.0 M.

[b] In $CD_3CN:D_2O$ (9:1 v/v) at 32°C.

[c] Exchange not detected.

[d] k_{ex} is for the H-3 which is 60 times slower than that for H-5.

k_H/k_D = 1.36, consistent with the proton transfer and hydration of the intermediate cation occurring at comparable rates. For the oxygen- and sulphur-heterocycles this behaviour closely correlates with the Dewar Resonance Energies (DRE)[9,10] of the parent-ring or for the benzo-series this value minus the DRE for benzene. Thus, Dewar pointed out that the resonance energy of benzofuran and benzene are very similar and concluded that the five-membered ring was non-aromatic.[9] This is in agreement with behaviour of 3-methoxybenzofuran, the hydrolysis of which proceeds with rate-limiting *C*-protonation just like a normal enol ether. Apparently the driving force for deprotonation of ion I is slight.



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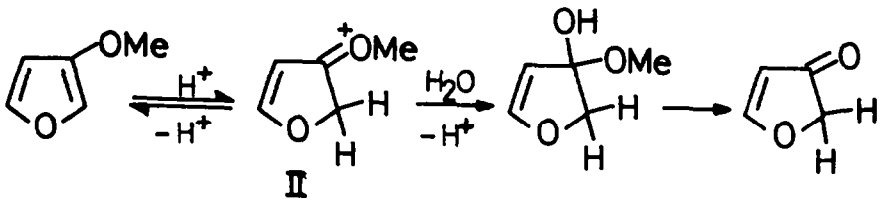
Furan, however, according to Dewar's most recent calculations[11] has a substantial resonance energy of 4.3 kcal $mole^{-1}$ and now the driving force for deprotonation of intermediate ion II is substantial and deprotonation occurs more rapidly than nucleophilic attack with $k_{ex}/k_{hyd.} \approx 83$. The same applies even more strongly with 3-methoxythiophene whose parent ring has a DRE of 6.5 kcal $mole^{-1}$ and for which $k_{ex}/k_{hyd.} = 2.6\times10^{4}$, but with 3-methoxybenzothiophene whose parent ring has a DRE only 2.2 kcal $mole^{-1}$ greater than that of benzene, deprotonation



of the intermediate cation and nucleophilic attack by water occur at comparable rate. With the 3-methoxyindoles however this correlation appears to breakdown as the DRE of indole (23.8 kcal mole^{-1})[9] is less than that of benzothiophene (24.8 kcal mole^{-1})[12] but 3-methoxy-1-methylindole has a value of $k_{ex}/k_{hyd.}$ greater than that of 3-methoxybenzothiophene (Table 1).

The reversibility of the *C*-protonation step in the hydrolysis of the ketene-dithioacetals was demonstrated[3] by the effect of the addition of mercaptoethanol (concentration $\leq$ 1 M) on the rate of disappearance of starting material when curved plots of k_{obs} versus [$HOCH_2CH_2SH$] were obtained. We have investigated the effect of mercaptoethanol on the rates of hydrolysis of two heterocyclic enol ethers: 3-methoxybenzofuran and 3-methoxybenzothiophene. Because these reactions are slower than the hydrolysis of the ketene-dithioacetals studied previously[3] a higher acid concentration of acid (1 M) was used in this work but the organic component was kept constant at 10% (volume) by acetonitrile as before. With the 3-methoxybenzofuran which reacts with rate-limiting *C*-protonation a small (*ca* 9%) non-linear increase in rate was obtained when [$HOCH_2CH_2SH$] was increased from 0 to 1.0 M (Fig. 2).

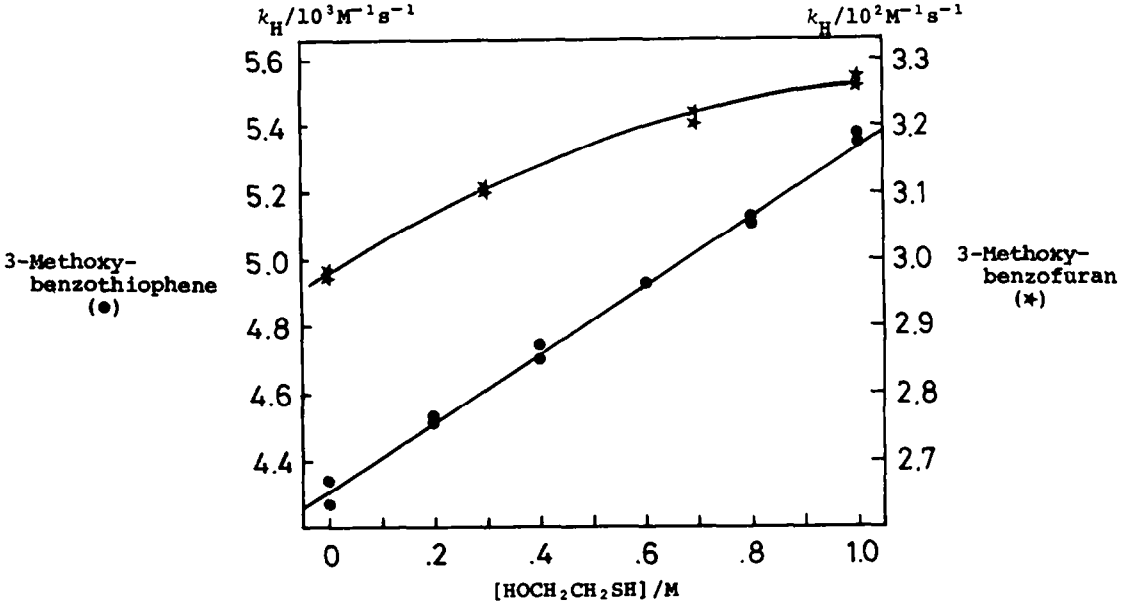


Fig. 2. Effect of 2-mercaptoethanol on the rate of hydrolysis of 3-methoxybenzothiophene (●) and 3-methoxybenzofuran (✱) in 90% aqueous solution (I = 0.9 M) at 25°C.

This is similar to that observed with ketene-dithioacetal in HCl solution[3d] and presumably results from a medium effect. However with 3-methoxybenzothiophene which is thought to react with a partially reversible *C*-protonation there is a linear increase in rate of *ca* 21% when [$HOCH_2CH_2SH$] is increased from 0 to 1.0 M. This presumably results from trapping of the intermediate cation by the thiol but even when the concentration of this is 1 M the absence of non-linearity indicates that a situation where the rate-limiting step is protonation is not being approached.

The homocyclic enol ether analogous to these heterocyclic enol ethers is 3-methoxyindene. The hydrolysis of this compound was investigated by Kresge and his co-workers[13] who concluded that this followed the normal mechanism with *C*-protonation rate limiting. We have determined the isotope effect, k_H/k_D, to be 2.76 (Table 1) which is consistent with this mechanism. Of the heterocyclic enol ethers that we have studied the only one which has the same rate determining step is 3-methoxybenzofuran. The effect of replacing the CH_2 group by an oxygen is to cause a 2100 fold decrease in rate which may partly arise from stabilization of the initial state by conjugation of the double bond with oxygen and partly due to destabilization of the positively charged transition state through the electron-withdrawing inductive effect of the oxygen.

In conclusion this investigation shows how it is possible to obtain the complete spectrum of reaction mechanisms for the hydrolysis of *oxygen* enol ethers.

EXPERIMENTAL

All m.p. and b.p.s. are uncorrected. IR spectral data were obtained on a Perkin-Elmer 157G spectrophotometer. ^{1}H-NMR spectra were obtained on a Varian EM-360A (60 MHz) spectrophotometer. UV spectra were measured with a Shimadzu UV-250 spectrophotometer and mass spectra were taken with a Hitachi RMS-4 mass spectrometer. The pH was measured by Cole-Parmer model 5994 Digisense pH meter fitted with a Orion semi-micro combination pH electrode model 911600.

Kinetics of hydrolysis

The aqueous solutions were made up with deionized and degassed water and the ionic strength was maintained at 1 M by potassium chloride. Solutions of different acid concentrations were prepared by mixing appropriate volumes of 1 M standard hydrochloric acid (E. Merck) and 1 M potassium chloride solution. The pH was adjusted by adding dilute hydrochloric acid or sodium hydroxide solution. The chemicals used were "Analar" grade.

A stock solution was prepared by dissolving 2 to 5 μL of the enol ether in 2 mL spectroscopic grade acetonitrile (Aldrich). This solution (20 μL) was injected into 2.0 mL of aqueous solution in a 10 mm quartz cell which was thermostatted in the cell compartment of a Shimadzu UV-250 spectrophotometer. The decay of the enol ether or the growth of the keto-form was monitored at the wavelength given in Table 1 by an Apple II microcomputer operating on-line via an IEEE interface. Normally, the hydrolyses were followed to more than 90% completion and 80 absorbance values were collected at convenient time intervals and the observed first order rate constants were calculated by a general-least-squares method[14] from the following equation

$$\ln (A_0-A_t) = k_{obs}t + (\ln (A_0-A_\infty) \text{ or}$$

$$k_{obs} = \frac{1}{t} \ln \left(\frac{A_0-A_\infty}{A_0-A_t}\right)$$

The second-order rate constants for hydrolysis, k_H, were obtained from plots of k_{obs} against C_H using a linear least squares method.

For the benzothiophene and the two indoles, oxygen must be driven off by purging the solutions with nitrogen and sealed with rubber septum. Otherwise, the oxygen combines with the products of hydrolysis (i.e. the carbonyl compounds) to form thio-indigo or indigo.

Acidic solutions of the 2-mercaptoethanol were prepared by mixing one volume of a stock solution of the 2-mercaptoethanol in spectroscopic grade acetonitrile with nine volumes of 1 M hydrochloric acid. The 2-mercaptoethanol (E. Merck) was distilled before use. The disappearance of the 3-methoxybenzofuran and 3-methoxybenzothiophene was followed at 275 and 300 nm respectively.

Kinetics of exchange

The enol ether (15-30 μL) was dissolved in CD_3CN (405 μL) and the ^{1}H-NMR spectrum was measured. DCl (1 M or 0.01 M, 45 μL) was added and the ^{1}H-NMR spectrum run at convenient time intervals with solution being kept at temperature and sealed under nitrogen atmosphere. The relative rates of exchange to hydrolysis were estimated from times required for equivalent amounts of decay of a ring proton and appearance of methanol.

3-Methoxybenzofuran[15]

This was prepared by the method used by Kresge and co-workers for the preparation of 3-methoxyindene.[13] The yield was 90% b.p. 63-64°C/0.3 mm Hg, ^{1}H-NMR (DMSO-d_6): δ 3.90 (s, 3H, OCH_3), 7.30 (s, 1H, H-2), 7.10-7.80 (m, 4H, phenyl-H). IR (film) ν 3060, 2950, 1605, 1585 cm^{-1}. MS m/e 133, 148 (M^+). From the ^{1}H-NMR, the product was an enol ether rather than a ketal which is probably an intermediate in this reaction.

3-Methoxybenzothiophene[16]

The procedure was the same as 3-methoxybenzofuran. The yield was 90%. b.p. 88-89°C/0.5 mm Hg (Lit b.p. 95-100°C/0.2 mm Hg)[16b]. ^{1}H-NMR (CCl_4): δ 3.93 (s, 3H, OCH_3), 6.25 (s, 1H, H-2), 7.20-7.90 (m, 4H, phenyl-H). IR (film) ν 3120, 3060, 2950, 1575, 1530 cm^{-1}. MS m/e 149, 164 (M^+). The product was confirmed to be a methyl enol ether by ^{1}H-NMR.

3-Methoxyindole[17]

The procedure was the same as above. The yield was 40%. b.p. 107-108°C/ 0.01 mm Hg. (Lit b.p. 170°/18-19 mm Hg. m.p. 69-70°C)[17] ^{1}H-NMR ($CDCl_3$): δ 3.82 (s, 3H, OCH_3), 6.51 (d, 1H, J=2.6 Hz, H-2), 7.35 (s, 1H, NH), 7.00-7.80 (m, 4H, phenyl-H). IR (film) ν 3420, 3060, 3000, 2940, 2830, 1620, 1585, 1560 cm^{-1}. MS m/e 147 (M^+).

3-methoxy-1-methylindole[17]

The procedure was the same as before. The yield was 90%. b.p. 85-86°C/ 0.03 mm Hg. ^{1}H-NMR ($CDCl_3$): δ 3.58 (s, 3H, NCH_3), 3.78 (s, 3H, OCH_3), 6.42 (s, 1H, H-2), 6.80-7.60 (m, 4H, phenyl-H). IR (film) ν 3100, 3050, 1610, 1580, 1560 cm^{-1}. MS m/e 146, 161 (M^+). CMR (TMS): 32.3, 58.1, 108.9, 109.1, 117.9, 118.1, 119.6, 122.3, 134.8, 141.0.

3-Methoxyindene

Attempt to prepare the compound by a method similar to the above compounds failed.[13] A solid precipitated out during the reaction. It was insoluble in $CDCl_3$. The compound was prepared by dehydrochlorination of 2-bromo-1-methoxy-indene.[18] The yield was 65%. b.p. 47-48°C/0.01 mm Hg. ^{1}H-NMR (CCl_4): δ 3.26 (d, 2H, J=2.4 Hz, H-1), 3.94 (s, 3H, OCH_3 5.18 (t, 1H, J=2.4 Hz, H-2), 7.00-7.50 (m, 4H, phenyl-H). IR (Film) ν 3040, 2940, 2890, 1615, 1605, 1575 cm^{-1}.

3-Methoxyfuran

This was made by standard method.[19] b.p. 112-113°C/760 mm Hg. ^{1}H-NMR (CD_3CN): δ 3.70 (s, 3H, OCH_3), 6.24 (dd, 1H, J=1.0, 2.0 Hz, H-5), 7.17 (dd, 1H, J=1.0, 2.0 Hz, H-2), 7.28 (t, 1H, J=2.0 Hz, H-4).

3-Methoxythiophene

This was prepared by methoxydebromination of 3-bromothiophene with sodium methoxide.[20] b.p. 52-56°C/ 30 mm Hg. ^{1}H-NMR ($CDCl_3$):δ 3.67 (s, 3H, OCH_3), 6.30 (dd, 1H, J=1.6, 3.2 Hz, H-2), 6.65 (dd, 1H, J=1.6, 5.2 Hz, H-5), 7.05 (dd, 1H, J=3.2, 5.2 Hz, H-4).

2-Methoxythiophene

This was made by methoxydeiodination of 2-iodothiophene with sodium methoxide.[21] b.p. 52-53°C/ 30 mm Hg. ^{1}H-NMR (CCl_4): δ 3.74 (s, 3H, OCH_3),6.00 (dd, 1H , J=1.6, 3.6 Hz, H-3), 6.34 (dd, 1H, J=1.6, 5.6 Hz, H-5), 6.54 (dd, 1H, J=3.6, 5.6 Hz, H-4).

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