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THE REARRANGEMENT AND SOLVOLYSIS OF FURFURYL ARENESULFINATES[a,1]

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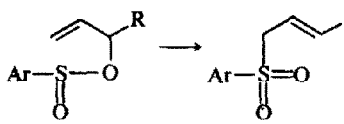
Abstract—Furfuryl benzenesulfinate, furfuryl *p*-toluenesulfinate and 5-nitrofurfuryl benzenesulfinate were synthesized, and their behaviour under various conditions was investigated. The first two esters were found to undergo readily rearrangement to sulfone. In nonhydroxylic solvents, a mixture of furfuryl aryl sulfone and 2-methyl-3-furyl aryl sulfone is obtained. The ratio between the two sulfones changes with the polarity of the solvent. In hydroxylic solvents, only rearrangement to the furfuryl aryl sulfone takes place, and this is accompanied by solvolysis of the ester. A kinetic study of the reaction in ethanol and aqueous ethanol solvents indicated an ionization mechanism. It is suggested that under these conditions the sulfone is formed by recombination of ion pairs. A kinetic study of the rearrangement under nonsolvolytic conditions was also performed in order to obtain the effect of the solvent and the effect of added salts on the rate of rearrangement. This study has shown that the rate of rearrangement is sensitive to the ionizing power of the solvent. The addition of perchlorate was found to have a stronger effect on the formation of the furfuryl sulfone than on the 2-methyl-3-furyl sulfone. In this case an ionic mechanism is also suggested, and the two sulfones may arise by recombination from two different species of ion pairs.

INTRODUCTION

The rearrangement and solvolysis of esters of arenesulfinic acids[2] have received considerable attention in the past. Kenyon *et al*[3] reported that the rearrangement of α-phenylethyl *p*-toluenesulfinate to the corresponding sulfone was favoured by an increase in solvent polarity and that in formic acid the optically active ester was converted to completely racemic sulfone. These results were considered as consistent with an ionic mechanism. However, since in the presence of sodium formate a small amount of optically active sulfone of retained configuration was detected, it was interpreted as evidence for an intramolecular mechanism for rearrangement. Wragg, McFadyen and Stevens[4] investigated the rearrangement of a number of sulfinate esters to sulfones and suggested an intermolecular ionic mechanism for their results. Neither one of these two reports provides any information with regard to the type of ionization. The more recent, and mechanistically detailed investigations by Darwish *et al*[5] prove quite useful in this respect. These authors have examined the rearrangement of t-butyl, benzhydryl, α-phenylethyl and trityl arenesulfinates under various conditions and have shown that the important route to sulfone formation is ion pair recombination, and not recombination of free ions. A similar interpretation has been advanced for the rearrangement of benzyl benzenesulfinates.[6]

The rearrangement of allylic and propargylic arenesulfinates proceeds by a different mechanism. The rearrangement of the first type of esters was first studied by Cope *et al*,[7] but these authors have reached no final decision with regard to mechanism. A subsequent study by Darwish and Braverman[8] on the behavior of a number of allylic 2,6-dimethylbenzenesulfinates has revealed some unique features. It has been found that even under solvolytic conditions, these esters undergo rearrangement in high yield to sulfone, and that the rearrangement of unsymmetrically substituted allylic esters involves simultaneous isomerization of the allylic group (Eq 1).



(1)

A kinetic study of the rearrangement indicated relatively low sensitivity of the rate to the nature of the substituent and solvent. On the basis of these observations and other pertinent data, it has been suggested[8] that the rearrangement to sulfone proceeds by a cyclic intramolecular mechanism (i.e., a concerted[2,3] sigmatropic shift[9]). As a natural extension of this work, the thermal behavior of several propargylic benzenesulfinates has been investigated.[10] The rearrangement of these

*Dedicated to the memory of the late Professor D. Darwish, of the University of Alberta, Edmonton, Alberta.

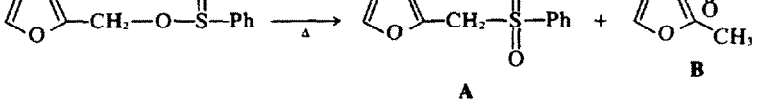
esters to sulfones involves a simultaneous acetylene-allene isomerization and has also been suggested to take place by a concerted[2,3] sigmatropic shift. This reaction has also been studied, independently, by Stirling *et al*,[11] and they have reached the same conclusion with regard to mechanism. Finally, this type of rearrangement has recently been used by us in the preparation of conjugated diallenic sulfones, which were found to undergo a novel cyclization to thiophene-1,1-dioxides.[12]

The solvolysis of arenesulfinates can involve either sulfur-oxygen or carbon-oxygen bond fission. An unequivocal indication for S–O bond cleavage in the alcoholysis of sulfinate esters is the production of the parent alcohol and a new sulfinate ester, the latter corresponding to the alcohol used as solvent. On the other hand, if C–O bond fission occurred under the same conditions the product would be sulfinic acid, ether and/or sulfone. For example, Kenyon *et al*[13] have found that ethyl *p*-toluenesulfinate yields only *d*-2-octyl *p*-toluenesulfinate when heated with *d*-2-octanol, and that on refluxing a solution of (-)-α-phenylethyl *dl*-*p*-toluenesulfinate in ethanol with added potassium acetate or carbonate, α-phenylethanol of retained configuration is formed. These results are clear evidence for S–O bond fission. Herbrandson and Cusano[14] have also observed S–O bond fission in the ethoxide-ion catalyzed ethanolysis of epimeric (-)-methyl *p*-iodobenzenesulfinates. Bunton and Hendy[15] determined the position of bond fission in the hydrolysis of methyl and benzhydryl *p*-toluenesulfinates in aqueous dioxan by the use of H_2O^{18} enriched solvent. The base-catalyzed reaction of both esters, as well as the acid-catalyzed hydrolysis of the first ester, have thus been shown to involve S–O bond fission. The same type of cleavage has also been reported by Darwish and Noreyko[16] for the solvolysis of various *p*-methoxyneophyl arenesulfinates in aqueous and absolute ethanol in the presence of such bases as ethoxide ion, potassium acetate and 2,6-lutidine. On the other hand exclusive carbon-oxygen bond fission by an ionization mechanism has been reported for the solvolysis of esters likely to develop stable carbonium ions such as t-butyl, α-phenylethyl, benzhydryl[5] and *p*-anisyl[6] arenesulfinates under conditions appropriate for the (competing) rearrangement to sulfone.

In view of recent interest in the chemical behaviour of furfuryl systems,[17] with regard to "allylic" or "benzylic" reactivity, we have investigated the rearrangement and solvolysis of furfuryl arenesulfinates.

RESULTS AND DISCUSSION

Rearrangement of furfuryl arenesulfinates. This study was initiated by an examination of the rearrangement of furfuryl benzenesulfinate, which was prepared by treatment of furfuryl alcohol with benzenesulfinyl chloride in pyridine at −70°. The two methylenic protons of this ester are diastereotopic[18] and show two doublets in the nmr at τ 5·14 and 5·58 (J = 12 Hz). Besides other spectral data this information is useful in characterization of this type of compounds. We have found that under buffered non-solvolytic conditions, this ester undergoes thermal rearrangement to a mixture of furfuryl phenyl sulfone (**A**) and 2 - methyl - 3 - furyl phenyl sulfone (**B**, Eq 2, see Table 1). Each of the two sulfones is stable under the reaction conditions.



(2)

Formation of sulfone **B** appears to be the first observation of an allylic-type rearrangement in the furfuryl system, in an unimolecular reaction. An attempt to observe such a rearrangement in the case of furfuryl thiocyanate[17b] was without success. On the other hand, in nucleophilic bimolecular substitution, such as displacement of chloride by cyanide, rearrangement to the 5-position is known to occur.[19]

Examination of the data in Table 1 shows that the ratio of the two sulfones **A**:**B** is sensitive to the polarity of the solvent and changes from 16:1 in formamide to 1:4 in benzene with dimethylformamide as an exception. This result tends to indicate a greater change in charge separation between the ground state and transition state for the formation of sulfone **A** relative to that for sulfone **B**. In order to establish whether sulfone **B** is formed by a concerted mechanism similar to the allylic sulfones,[8] the effect of temperature, substitution and ionizing power of the medium on the rearrangement, have been examined.

Variation of the temperature from 102° to 153° had no influence on the **A**:**B** ratio for the reaction in dimethylformamide. Assuming that formation of sulfone **B** by a concerted mechanism requires a greater energy of activation, one would expect a decrease in the **A**:**B** ratio with increase in temperature. It has been shown[17a] that substituents

Table 1. Reaction conditions for the rearrangement of furfuryl benzenesulfinate to furfuryl phenyl sulfone (A) and 2-methyl-3-furyl phenyl sulfone (B)

Solvent[a]	[Ester], M	Temp, °C	Time, hr	Sulfone yield, %	Sulfone ratio B/A
DMF	0·0507	153	1·5	89	4
DMF	0·0610	128	11	87	4
DMF	0·0464	102	76	80	4
Formamide	0·0512	50	11	85	0·06
Acetonitrile	0·0450	78	96	40[b]	1·5
Chlorobenzene	0·0260	132	45	80[b]	4·5
Benzene	0·0436	117	19	25[b]	4
THF	0·0524	100	360	70[b]	1

[a] [2,6-lutidine] = 0·1 M.
[b] uncompleted reaction.

in the furan ring have a dramatic effect upon the reactivity of α-methylfurfuryl *p*-nitrobenzoates in unimolecular solvolysis. Thus introduction of a 5-nitro group causes a reduction in rate by a factor of nearly one million. Therefore, we expected the rate of rearrangement to type **A** sulfone for 5-nitrofurfuryl benzenesulfinate to be markedly slower than the unsubstituted furfuryl ester, while the rate of rearrangement to type **B** sulfone to be enhanced, if this product were formed by a concerted mechanism. However, it has been found that this ester is quite unreactive, and when heated above 100° in either chlorobenzene, formamide or dimethylformamide, it undergoes extensive decomposition. Similarly, we were prevented from making a comparison with the reactivity of α-methylfurfuryl benzenesulfinate, since this ester underwent spontaneous rearrangement to the corresponding sulfone, during its preparation by the normal procedure, reaction between benzenesulfinyl chloride and α-methylfurfuryl alcohol in pyridine solution at dry ice-acetone temperature. In contrast, introduction of a methyl substituent into the phenyl group does not show any significant effect. Thus, furfuryl *p*-toluenesulfinate behaves very similarly to the unsubstituted ester, with a ratio of furfuryl *p*-tolyl sulfone to 2-methyl-3-furyl *p*-tolyl sulfone of 15:1 and 1:5, on heating in formamide and DMF, respectively, under conditions similar to those used for the unsubstituted ester.

In order to obtain information with regard to the effect of the ionizing power of the medium, a kinetic study of the reaction under various conditions was performed. The first-order rate constants for the rearrangement of furfuryl benzenesulfinate were conveniently measured by the decrease in intensity of the methylene nmr signal of this ester, and are shown in Table 2.

Examination of the data of Table 2 shows a strong sensitivity of rate of rearrangement of the furfuryl ester to the ionizing power of the solvent. Thus the rate increases by a factor of three powers

Table 2. Rate constants for the rearrangement of furfuryl benzenesulfinate

Solvent[a]	Temp, °C	[Ester], M	$k \times 10^5$, sec^{-1}
DMF[b]	128	0·0461	12·31 ± 0·24
DMF	120	0·0990	5·41 ± 0·25
DMF	117	0·0658	4·55 ± 0·21
DMF	102	0·0464	1·21 ± 0·02
DMF	50	—	0·0045[c]
Formamide[d]	50	0·0506	12·7 ± 0·5
Formamide	40	0·0529	5·14 ± 0·18

[a] In the presence of 0·1 M 2,6-lutidine.
[b] In this solvent $\Delta H^* = 25{\cdot}9 \pm 0{\cdot}5$ kcal/mole, and $\Delta S^* = -12{\cdot}3 \pm 1{\cdot}3$ eu.
[c] Extrapolated from the values at higher temperatures.
[d] In this solvent, $\Delta H^* = 17{\cdot}6 \pm 1{\cdot}6$ kcal/mole, and $\Delta S^* = -22{\cdot}2 \pm 5{\cdot}2$ eu.

of ten in going from DMF to formamide, at 50°. The effect of added salts on the rate of rearrangement in DMF has also been investigated, and the results are presented in Table 3.

The data of Table 3 indicate that the rate of rearrangement to sulfone as well as the ratio of the two sulfones formed are sensitive to the addition of salts to the reaction solution. An especially high and interesting effect is shown by the addition of sodium benzenesulfinate. In the presence of an equimolar concentration of this common ion, the rate increases by more than three times, and the ratio of the two sulfones **B**:**A** changes from 4:1 to 1:2. In contrast, in 80% ethanol water (Table 5), addition of a similar quantity of sodium benzenesulfinate has practically no effect on either the rate of reaction or the fraction of sulfone formed. This result may be interpreted by competition between ionization of the ester and, apparently, a faster direct bimolecular nucleophilic displacement of sulfinate ion by the added common ion. As a result a larger fraction of sulfone **A** is formed. This explanation may be supported by the observation that in the presence of an equimolar concentration

Table 3. Rate constants for the rearrangement of furfuryl benzenesulfinate in DMF[a], with added salts

Added Salt	[Salt], M	[Ester], M	Temp, °C	$k \times 10^5$, sec^{-1}	Sulfone ratio B/A
$KClO_4$	0·0326	0·0556	100	1·22 ± 0·06	2·7
$KClO_4$	0·0611	0·0542	100	1·30 ± 0·07	2·5
$KClO_4$	0·1077	0·0612	100	1·48 ± 0·05	2·3
$KClO_4$	0·0995	0·0544	128	16·52 ± 0·44	2·3
$PhSO_2Na$	0·0433	0·0458	100·5	3·67 ± 0·20[c]	0·5
—			100	1·1[b]	4

[a] In the presence of 0·1 M 2,6-lutidine.
[b] Extrapolated from higher temperatures.
[c] Kinetics are presumably pseudo-first order, since sulfinate ion concentration is unchanged during this reaction. See text for details.

of sodium azide in DMF, almost all the ester was transformed to furfuryl azide.

Turning now to the effect of the added potassium perchlorate, we find that a plot of the rate constants for ester disappearance at 100° vs the concentration of the added salt gives a straight line, which intercepts the y axis at a point corresponding to the rate constant in the absence of perchlorate ion (Fig 1). This result indicates a normal salt effect, and the *b* value calculated from the Winstein[20] equation $k = k^\circ (1 + b[KClO_4])$, is 3·2. This *b* value is similar to those obtained for the ionization of *p*-methoxyneophyl tosylate in DMF at 75° in the presence of lithium perchlorate ($b = 1·4$)[21], and for the isomerization of 4,4'-dimethylbenzhydryl thiocyanate in acetonitrile at 25°, in the presence of sodium perchlorate ($b = 2$).[22] Seeking further information with regard to the mechanism of formation of each one of the two sulfones, we tentatively analyze the results on the salt effect in the light of the following two assumptions: (a) Sulfone A is formed by an ionization mechanism, while sulfone B by a concerted one; (b) Both sulfones are formed by an ionization mechanism, but from different ionic species. If the first assumption is correct, one can calculate the rate of sulfone formation for each sulfone by the use of the following two relations: $k = k_1 + k_2$ and $k_1/k_2 = x_1/x_2$, where, k is the rate constant of ester disappearance, k_1 and k_2, the rate constants for the formation of sulfone A and B, respectively, and x_1/x_2 is the ratio of the two sulfones A and B. The values of k_1 and k_2 thus obtained are summarized in Table 4.

If assumption *a* is correct, one would expect that the added salt will affect the rate of formation of sulfone A, which is formed by an ionization mechanism, but it should not affect the rate of formation of sulfone B, which is assumed to proceed by a concerted mechanism. However, inspection of the data of Table 4 shows that the values of k_2 are not constant. Furthermore, a plot of log k_1 against the concentration of perchlorate ion does not correspond to a normal salt effect, as observed for ester disappearance, since the intercept with the y axis is not equal to the rate constant in the absence of added salt (0·22) but higher than that (Fig 2). These results lead to the conclusion that the rate of formation of sulfone B is also influenced by the addition of salt, and the assumption that it may be formed by a concerted mechanism is not correct. Consequently, it appears that the second assumption is correct. The added perchlorate affects the rate of formation of both sulfones, but the effect is larger for sulfone A. This is also evident from the ratio of the two sulfones B/A, which decreases with increase in perchlorate concentration (Table 3).

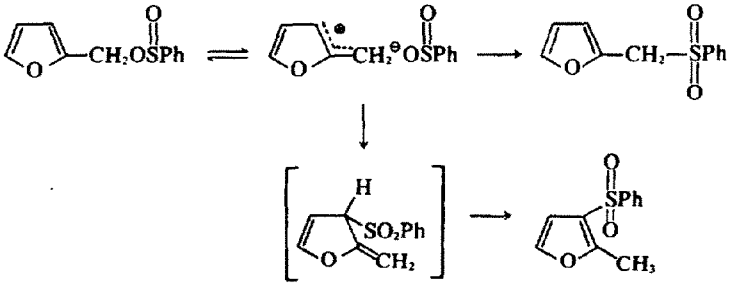
Finally, from the study of the allylic arenesulfinates it could be calculated[8] that the rate of rearrangement of allyl 2,6-dimethylbenzenesulfinate to the corresponding sulfone is three powers of ten faster than estimated for an ionization process. Accordingly, if sulfone B

Table 4. Rate constants[a] for the formation of sulfones A and B in DMF

Added Salt	[Salt], M	Temp, °C	$k_1 \times 10^5$, sec^{-1}	$k_2 \times 10^5$, sec^{-1}
$KClO_4$	0·0326	100	0·33 ± 0·02	0·89 ± 0·04
$KClO_4$	0·0611	100	0·37 ± 0·02	0·93 ± 0·05
$KClO_4$	0·1077	100	0·45 ± 0·02	1·03 ± 0·04
$KClO_4$	0·0995	128	5·01 ± 0·13	11·51 ± 0·3
$PhSO_2Na$	0·0433	100·5	2·45 ± 0·13	1·22 ± 0·04
—	—	100	0·22	0·88
—	—	128	2·41 ± 0·06	9·90 ± 0·24

[a] Calculated according to assumption *a* (see text).

were formed by a concerted mechanism, one would expect a much higher value for the ratio B/A than that actually observed even in the non-polar solvents. In the light of the above results, we believe that both sulfones are formed by an ionization mechanism, possibly through the intermediacy of two different ionic species, such as dissociated ions and ion pairs or two different types of ion pairs. We prefer the last possibility since under solvolytic conditions (see below) sulfone formation proceeds primarily by combination of ion pairs. In this case sulfone A may arise from solvent-separated ion pairs, while sulfone B from recombination of intimate ion pairs. Recombination of the sulfinate anion with the resonance stabilized carbonium ion at the furfuryl carbon yields sulfone A directly, while attack on the furan ring at the 3-position carbon, followed by a rapid prototropic shift gives sulfone B (Scheme 1). It is worthwhile noting that this step requires the presence of a base,[23] otherwise decomposition of the intermediate takes place. During the last process the aromatic character of the furan ring is temporarily lost. However, the relatively low resonance energy (16 kcal/mole) of this heterocyclic system[24] may explain the differences observed between the furfuryl and benzyl esters.[5a,6]



SCHEME 1

Solvolysis of furfuryl benzenesulfinate. In view of the results observed with furfuryl arenesulfinates in nonhydroxylic solvents, indicating the partial occurance of allylic rearrangement during the O→S shift, and in the light of the observation of practically exclusive rearrangement to sulfone even under solvolytic conditions for the allylic arenesulfinates,[8] it became interesting to study the behaviour of furfuryl benzenesulfinate under such conditions. This ester was found to react readily on heating in anhydrous or aqueous ethanol at moderate temperatures, in the presence of 2,6-lutidine acting as buffer. The products obtained by the reaction in anhydrous ethanol were mostly furfuryl ethyl ether, together with furfuryl phenyl sulfone (Eq. 3). The isomeric sulfone may also be formed in trace amounts under these conditions, but not in aqueous ethanol.

These products indicate the operation of C–O bond fission process. In order to establish mechanistic details about the formation of the observed products a kinetic study was performed, using the titrimetric method. A summary of first-order rate constants for the solvolysis of furfuryl benzenesulfinate, and the fraction of furfuryl phenyl sulfone produced under various conditions, is presented in Table 5.

From the examination of the data in this Table, information on the reaction mechanism can be gleaned. Considering first the effect of the solvent, one finds that the rates of solvolysis and sulfone formation are greatly enhanced by increasing the ionizing power of the solvent. A graph of log k for solvolysis of furfuryl benzenesulfinate in 100%, 80% and 60% ethanol at 40°, plotted against log k for ionization of p-methoxyneophyl toxylate[25] in the same solvents at 25° gives a straight line with a slope of 1·5. The same value was also obtained for the solvolysis of p-anisyl benzenesulfinate,[6] believed to proceed by an ionization mechanism. These data may be used as supporting evidence for an ionization mechanism also for the solvolysis and rearrangement of furfuryl benzenesulfinate. The addition of sodium benzenesulfinate has practically no effect on the fraction of sulfone formed. This observation tends to exclude the formation of sulfone by recombination of dissociated ions, as the sole or predominant route of reaction. On the basis of the evidence presented, we feel that under these conditions the formation of furfuryl phenyl sulfone proceeds primarily by an ionization and ion pair recombination mechanism, similar to that suggested for the rearrangement of benzyl[6] and benzhydryl[5a] arenesulfinates.

The rate of solvolysis (and rearrangement) of furfuryl benzenesulfinate in anhydrous ethanol at

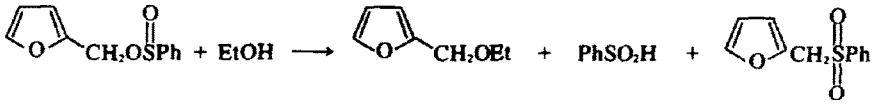

(3)

Table 5. Rate constants and sulfone yields[a] on solvolysis of furfuryl benzenesulfinate

Solvent[b]	[Ester], M	Temp, °C	$10^4 k$, sec^{-1}	Sulfone %
EtOH	0·0575	60·2	0·458 ± 0·007	41·4
EtOH[c]	0·0452	80·5	2·62 ± 0·04	39·8
80% EtOH-H_2O	0·0586	40	1·06 ± 0·03	35·8
80% EtOH-H_2O[d]	0·0517	40	1·08 ± 0·03	36·7
60% EtOH-H_2O	0·0510	40	5·65 ± 0·10	31·8

[a] Calculated by difference, using percent of acid formed at "infinity" time.
[b] In the presence of ~0·1 M of 2,6-lutidine.
[c] In this solvent $\Delta H^* \simeq 19{\cdot}5 \pm 0{\cdot}3$ kcal/mole, and $\Delta S^* - 20{\cdot}3 \pm 1{\cdot}1$ eu.
[d] In the presence of 0·0502 M of sodium benzenesulfinate.

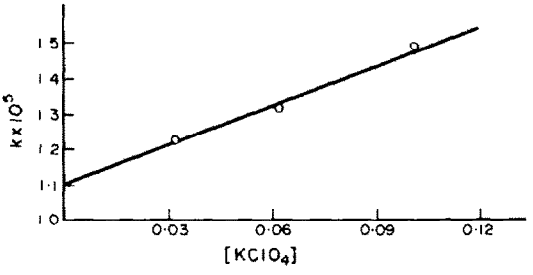


Fig 1. Plot of rate constants for the rearrangement of furfuryl benzenesulfinate in DMF at 100° vs concentration of added perchlorate.

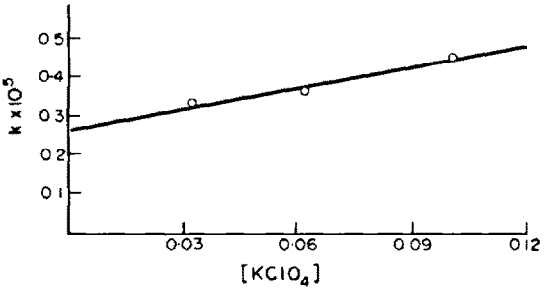


Fig 2. Plot of rate constants for formation of sulfone A according to assumption *a* (see text) vs concentration of potassium perchlorate.

75° ($k = 18{\cdot}2 \times 10^{-5}\ sec^{-1}$) is greater than that of *p*-anisyl benzenesulfinate ($k = 3{\cdot}53 \times 10^{-5}\ sec^{-1}$)[6] by a factor of 5·2, under the same conditions. This value is in full agreement with those obtained for the reactivity of analogous systems such as furfuryl *p*-nitrobenzoates,[17a] thiocyanates,[17b] dimethylthioncarbamates,[17c] and chlorides.[26] Consequently, the stabilization of the carbonium ion by the furan ring is much greater than that brought about by a phenyl group, exceeding even that of a *p*-methoxyphenyl group.

Finally, it may be tempting to use tentatively the results presented above for the behaviour of furfuryl benzenesulfinate under solvolytic conditions as supporting evidence against the operation of a concerted[2, 3] sigmatropic shift for the formation of sulfone **B**, under nonsolvolytic conditions, since comparison with the allyl esters[8] would imply very little, if any, solvolysis. However, not only is solvolysis the main reaction path, but also the fraction of sulfone **B**, under these conditions, is quite negligible. Obviously, this argument can have some validity only if the activation energies of the concerted[2, 3] sigmatropic shifts are similar for the two systems. However, since the activation energy for the furfuryl case is necessarily higher, because of the loss in aromaticity in the transition state it may turn out to be high enough to allow effective competition of the ionization process, and thus leading to the products actually observed.

EXPERIMENTAL

M.ps and b.ps are uncorrected. IR spectra were recorded on Perkin Elmer Grating Infrared Spectrophotometer Model 237, and NMR spectra were recorded on Varian HA 100 NMR Spectrometer, using TMS as internal standard. Mycroanalyses were performed by the Mycroanalytical Laboratory, at the Weizmann Institute of Science, Rehovot.

Solvents. Formamide and dimethylformamide were purified by the methods described by Vogel[27] and Fieser[28a] Acetonitrile was purified by the method described by Smith, *et al.*[25] Tetrahydrofuran was dried according to the method described by Fieser and Fieser.[29] Chlorobenzene was dried over $CaCl_2$, the fraction boiling at 132–133° was collected. EtOH was dried by treatment with magnesium ethoxide as described by Fieser.[28b] X% ethanol-water means a soln prepared by mixing X volumes of ethanol with (100–X) volumes of boiled and distilled water at 25°. The same pipette was used for measuring all volumes.

Reagents and materials. 2,6-lutidine was purified by refluxing with, and distillation from, barium oxide (b.p. 140–142°). Commercially available furfuryl alcohol (Fluka, puriss grade) was used after distillation. α-Methylfurfuryl alcohol was prepared by reduction of 2-acetylfuran (Aldrich) with sodium borohydride, as described by Noyce and Kaiser.[17a] The same method was used for the reduction of 5-nitrofurfural to 5-nitrofurfuryl alcohol. 5-Nitrofurfural was prepared from 5-nitrofurfuryl nitrate[30] by the method described by Kochergin and Karpov.[31] Benzene- and *p*-toluenesulfinic acids were prepared before use from the corresponding sodium salts (Fluka), by acidification with cold conc HCl.

Benzene- and *p*-toluenesulfinyl chlorides were prepared by reaction of the corresponding sulfinic acid with thionyl chloride. In a typical preparation a soln of 35·7 g (0·30 mole) $SOCl_2$ in 50 ml dried pentane was added gradually with stirring over a period of 2 h to a 24·2 g quantity (0·175 mole) of benzenesulfinic acid in 300 ml of dried pentane. After evaporation of the solvent and excess $SOCl_2$ under reduced pressure, first at the water aspirator and then at the oil pump for a few h, 27·26 g (98·6% yield) of benzenesulfinyl chloride were obtained as a yellowish oil.

Arenesulfinates

Furfuryl benzenesulfinate. This ester was prepared by a procedure similar to that used by Darwish and Noreyko,[16] for the preparation of *p*-methoxyneophyl arenesulfinates. Thus, to a soln of 16·05 g (0·10 mole) benzenesulfinyl chloride in 30 ml pyridine, cooled in a dry ice-acetone bath was gradually added a soln of 9·8 g (0·10 mole) furfuryl alcohol in 10 ml pyridine. After 1 h, the cooling bath was removed, and the mixture was allowed to warm up to room temp. A volume of 300 ml ether was then added and the ether soln was washed with 3 portions of 100 ml, of 5% HCl aq, several times with 5% $NaHCO_3$ aq and several times with water. After the extract was dried over $MgSO_4$, filtered through activated carbon, and the ether was removed under reduced pressure by means of a water pump, 15·8 g (yield 71·4%) of furfuryl benzenesulfinate was obtained. The ester was crystallized from ether by cooling in the freezer, m.p. 28°, IR absorption ($CHCl_3$) showed bands at 910, 1120 and 1147 cm^{-1}, characteristic of sulfinates,[32] and bands at 817, 884 and 935 cm^{-1}, characteristic of the furan ring.[33a] The NMR spectrum (CCl_4) showed signals at τ 2·29–2·58 (5H, m), 2·70 (1H, d, J = 1 Hz), 3·79 (2H, s), 5·14 (1H, d, J = 12 Hz), 5·58 (1H, d, J = 12 Hz). The last two signals are assigned to the two methylenic protons which are known as diastereotopic.[18] (Found: C, 59·46; H, 4·49; S, 14·56. Calcd. for $C_{11}H_{10}O_3S$: C, 59·46; H, 4·54; S, 14·43%).

Furfuryl p-toluenesulfinate, was prepared from furfuryl alcohol and *p*-toluenesulfinyl chloride as described for the corresponding benzenesulfinate ester (yield 63%). The IR spectrum ($CHCl_3$) showed absorption bands at 907, 1120 and 1145 cm^{-1}, due to the sulfinate group,[32] and bands at 813, 880 and 930 cm^{-1}, due to the furan ring.[33a] The NMR spectrum ($CDCl_3$) exhibited signals at τ 2·44 (2H, d, J = 8 Hz), 2·76 (2H, d, J = 8Hz), 2·68 (1H, s), 3·74 (2H, s), 5·04 (1H, d, J = 12 Hz), 5·48 (1H, d, J = 12 Hz) and 7·65 (3H, s).

5-Nitrofurfuryl benzensulfinate, was prepared from 5-nitrofurfuryl alcohol and benzenesulfinyl chloride as described for the unsubstituted ester (yield 72·8%). Crystallization from ether gave a yellow solid, m.p. 90°, IR absorption ($CHCl_3$) showed characteristic bands at 815, 935, 1130, 1350 and 1500 cm^{-1}. The NMR spectrum ($CDCl_3$) displayed peaks at τ 2·21–2·47 (5H, m), 2·83 (1H, d, J = 4 Hz), 3·52 (1 H, d, J = 4 Hz), 5·03 (1H, d, J = 14 Hz) and 5·40 (1H, d, J = 14 Hz).

Attempted synthesis of α-methylfurfuryl benzenesulfinate

The synthesis of this ester was attempted by using the procedure described above for the other esters. However, in every case, even on using cold (0°) HCl aq for washing the product in the work up process, only the corresponding sulfone could be isolated. α-Methylfurfuryl phenyl sulfone, m.p. 103–4° showed IR absorption (CCl_4) at 940 and 884 cm^{-1}, characteristic of the furan ring,[33a] and at 1320, 1300, 1150 and 1135 cm^{-1}, characteristic of the sulfone group.[33b] Its NMR spectrum ($CDCl_3$) showed signals at τ 2·36–2·57 (5H, m), 2·77 (1H, s), 3·68–3·79 (2H, m), 5·63 (1H, *q*, J = 6 Hz), 8·31 (3H, d, J = 6Hz).

Rearrangement of sulfinates to sulfones

Solns of furfuryl benzenesulfinate and 2,6-lutidine in the appropriate solvents were prepared and heated in sealed ampoules in a constant temp bath, or refluxed, for the time periods and at the temps specified in Table 1. After cooling to room temp, the products were extracted with ether, and washed consecutively several times with water, 5% HCl, 5% $NaHCO_3$ and water again. After drying over K_2CO_3, the ether was removed and the IR and NMR spectra were recorded. The ratio of the two sulfones was determined with the aid of the NMR spectrum. The two sulfones were crystallized from light petroleum. Furfuryl phenyl sulfone (A) was isolated from the reaction in formamide, m.p. 65°. The compound showed IR absorption ($CHCl_3$) at 1320, 1310, 1140 and 1150 cm^{-1} characteristic of the sulfonyl group,[33b] and at 935, 884 and 815 due to the furan ring.[33a] Its NMR spectrum (CCl_4), exhibited signals at τ 2·32–2·62 (5H, m), 2·84 (1H, d, J = 1 Hz), 3·75 (2H, s), 5·74 (2H, s). (Found: C, 59·62; H, 4·40; S, 14·31. Calcd. for $C_{11}H_{10}O_3S$: C, 59·46; H, 4·54; S, 14·43%).

The isomeric sulfone, 2-methyl-3-furyl phenyl sulfone, was isolated from the reaction in DMF, m.p. 98–9°, IR absorption peaks (CCl_4) at 1325, 1305, 1130, 1150, 940 and 982 cm^{-1}, and NMR signals (CCl_4) at τ 2·13–2·59 (5H, m), 2·86 (1H, d, J = 2 Hz), 3·52 (1H, d, J = 2 Hz) and 7·45 (3H, s). Found: C, 59·30; H, 4·38; S, 14·24 Calcd. for $C_{11}H_{10}O_3S$: C, 59·46; H, 4·54; S, 14·43%).

The rearrangement of furfuryl *p*-toluenesulfinate was followed by the procedure described above for the unsubstituted ester. Furfuryl *p*-tolyl sulfone, m.p. 95–6°, showed IR absorption ($CHCl_3$) at 1323, 1305, 1143, 1153, 940, 884 and 813 cm^{-1}, and NMR absorption ($CDCl_3$) at τ 2·42 (2H, d, J = 8 Hz), 2·74 (2H, d, J = 8 Hz), 2·77 (1H, d, J = 2 Hz), 3·66–3·78 (2H, m), 5·62 (2H, s) and 7·58 (3H, s). The isomeric sulfone, 2-methyl-3-furyl *p*-tolyl sulfone, m.p. 92° showed IR absorption ($CHCl_3$) at 1323, 1303, 1143, 1155, 940, 884 and 813 cm^{-1}, and NMR absorption ($CDCl_3$) at τ 2·22 (2H, d, J = 8 Hz), 2·72 (2H, d, J, 8Hz), 2·80 (1H, d, J = 2 Hz), 3·46 (1H, d, J = 2 Hz), 7·45 (furyl methyl, s) and 7·61 (phenyl methyl, s).

Sodium azide test. An equimolar soln of furfuryl benzenesulfinate (0·143 g) and of sodium azide (0·263 g) in DMF was refluxed for 1½ h. After extraction of the products as described in the previous paragraph, the IR and NMR spectra of the residue were recorded. In the IR spectrum a strong peak at 2095 cm^{-1} was assigned to the azido group, while the NMR spectrum showed signals at τ 2·63 (1H, d, J = 2 Hz), 3·71 (2H, s) and 5·77 (2H, s) due to the furfuryl azide, as well as signals due to 2-methyl-3-furyl phenyl sulfone, in a ratio of 10:1. The two compounds were separated by TLC, using CCl_4 as eluent.

Solvolysis of furfuryl benzenesulfinate. Solns of the ester (0·05 M) and 2,6-lutidine (0·1 M) in anhyd or aqueous EtOH were prepared, sealed in ampoules, and heated in a constant temp bath at 40°, 60° or 80°. After isolation of the products by the normal procedure, the IR and NMR spectra of the residues indicated the presence of furfuryl ethyl ether and furfuryl phenyl sulfone. In the reaction using anhyd EtOH, 2-methyl-3-furyl phenyl sulfone was also formed in appx. 4%. Separation between the ether and sulfone was achieved by means of chromatography

on alumina, using benzene and chloroform as eluents. Furfuryl ethyl ether showed characteristic IR absorption (CCl_4) at 1215 cm^{-1}, and NMR signals (CCl_4) at τ 2·83 (1H, d, J = 2 Hz), 3·76 (2H, s), 5·68 (2H, s) 6·59 (2H, q, J = 7 Hz), 8·86 (3H, t, J = 7 Hz). The spectral data for the two sulfones are given above.

Kinetic Measurements

(a) *Rearrangement of furfuryl benzenesulfinate.* Appropriate quantities of the ester and 2,6-lutidine were weighed into a volumetric flask, and the appropriate solvent was added to the mark. Portions of this soln were transferred to ampoules containing a volume of slightly over 5 ml. After the ampoules were sealed and immersed in a constant temp bath, they were removed at different time intervals and quenched in ice-water. After equilibration to room temp, a 5 ml aliquot was removed from the ampoule and delivered into a 50 ml separatory funnel containing 25 ml of ether and 10 ml of water. After shaking the stoppered funnel, the water layer was discarded. The ether layer was washed 3 times with 10 ml of 1% HCl aq, once with 10 ml of 5% $NaHCO_3$, and again 3 times with 10 ml of water. After drying over K_2CO_3 and evaporation of the ether at the water aspirator, 0·5 ml of CCl_4 was added to the residue and its NMR spectrum recorded, using TMS as internal standard. The rate constants were calculated from the first order kinetic expression, $k = (2{\cdot}303/t)\log(a/a-x)$, where a represents the sum of signal areas of one of the methylene protons of the ester (τ 5·14, 1H) of one methylene proton of sulfone A (τ 5·74, half peak area used), and of the H_4 signal of sulfone B at τ 3·52 (or, alternatively, a 1/3 area of the signal at τ 7·45), while (a-x) is the area of the first signal only. Plots of log (a-x) vs time gave good straight lines for each run. Errors were calculated by means of the least square method. All calculations and plots were obtained by means of an IBM 360/50 computer, using the APL language.

(b) *Solvolysis reaction.* The preparation of the solns and the use of the sealed ampoule technique were as described in the previous section. After heating in a constant temp bath, quenching, and equilibrating to room temp, the ampoule was opened and a 5 ml aliquot was removed by means of a pipette and titrated with a 0·0084 N soln of NaOMe in MeOH using phenolphthalein as indicator. For the runs in 60% and 80% aqueous EtOH it was necessary to add 20 ml of abs EtOH before titration, to prevent spontaneous hydrolysis of the sulfinate, catalyzed by NaOMe. The rate constants were calculated from the first order kinetic expression, $k = (2{\cdot}303/t)\log(T_\infty - T_0/T_\infty - T_t)$. Errors were calculated by means of the least square method. All calculations were obtained as described in the previous section.

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