

THE REARRANGEMENT AND SOLVOLYSIS OF FURFURYL ARENESULFINATES<sup>1</sup>

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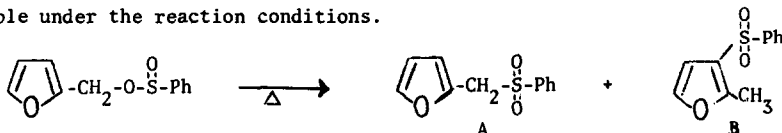
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Previously, we have shown that while the rearrangement of allylic arenesulfonates to sulfones involves simultaneous isomerization of the allylic group and proceeds by a cyclic intramolecular mechanism<sup>2</sup> (i.e., a [2,3] sigmatropic shift<sup>3</sup>), the rearrangement of benzylic arenesulfonates to the corresponding sulfones takes place by an ionic mechanism, and under solvolytic conditions is accompanied by solvolysis<sup>4</sup>. In view of recent interest in the chemical behaviour of furfuryl systems<sup>5</sup>, with regard to "allylic" or "benzylic" reactivity, we have investigated the rearrangement of furfuryl arenesulfonates.

We have found that under buffered non-solvolytic conditions, furfuryl benzenesulfinate<sup>6</sup> undergoes thermal rearrangement to a mixture of furfuryl phenyl sulfone(A) and 2-methyl-3-furyl phenyl sulfone(B). Each of the two sulfones is stable under the reaction conditions.



Formation of sulfone B appears to be the first observation of an allylic-type rearrangement in the furfuryl system in a unimolecular reaction.<sup>5,7</sup> 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. In order to establish whether sulfone B is formed by a concerted mechanism, we have performed the following experiments. Firstly, variation of the temperature from 100° to 150° had no influence on the A:B ratio for this reaction in dimethylformamide. Secondly, the rate of rearrangement of the furfuryl ester exhibits a strong sensitivity to the ionizing power of the solvent, as exemplified by an increase in rate by a factor of one thousand in going from dimethyl-formamide to formamide at 50°. While 5-nitrofurfuryl benzenesulfinate was quite unreactive and decomposed extensively above 100°, the  $\alpha$ -methylfurfuryl ester rearranged spontaneously to the corresponding sulfone even at -70°. In contrast, the reactivity of furfuryl *p*-toluenesulfinate was very similar to that of the unsubstituted ester. Finally, from the study of the allylic sulfonates<sup>8</sup>, one would expect much lower values for the ratio A:B, if sulfone B were formed by a concerted mechanism.

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. 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. 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<sup>9</sup> may explain the differences observed between the furfuryl and benzyl<sup>4</sup> esters.

Under solvolytic conditions, only benzylic-type<sup>4,11</sup> reactivity was observed. Thus, only rearrangement to sulfone A could be detected, accompanied by solvolysis products. A graph of  $\log k$  for solvolysis of furfuryl benzenesulfinate in 100% 80% and 60% ethanol-water at 40° plotted against  $\log k$  for ionization of *p*-methoxyneophyl tosylate<sup>10</sup> in the same solvents at 25° gives a straight line with a slope of 1.5. These data may be used as supporting evidence for an ionization mechanism. 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.

A comparison between the rates of solvolysis of furfuryl and *p*-anisyl benzenesulfonates, indicates that the former ester is five times more reactive. This value is in full agreement with those obtained for the reactivity of other furfuryl systems.<sup>5,12</sup> 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.

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