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SULFUR-OXYGEN BOND CLEAVAGE OF SECONDARY AND TERTIARY *p*-TOLUENESULFONATES UNDER NUCLEOPHILIC SOLVOLYTIC CONDITIONS

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The overwhelming retention of stereochemistry observed in the solvolysis of **1** in acetic acid[1] has raised various mechanistic quandaries. Various mechanistic schemes have been proposed and experts in the field have privately suggested that our observations might be readily explained by sulfur-oxygen bond cleavage rather than by carbon-oxygen bond cleavage. Although sulfur-oxygen bond cleavage of *p*-toluenesulfonates under nucleophilic solvolytic conditions has been reported for various phenyl *p*-toluenesulfonates[2-5] and in the case of the highly hindered neopentyl *p*-toluenesulfonate,[6] it has been generally assumed that the possibility of sulfur-oxygen bond cleavage was of little or no concern in connection with the solvolytic behavior of secondary and tertiary *p*-toluenesulfonates. In order to solidify our published position on the solvolysis of **1**,[1] we felt that the experimental conditions necessary for sulfur-oxygen bond cleavage of secondary and tertiary tosylates merited investigation. We now wish to report that sulfur-oxygen bond cleavage can be the major mode of reaction for certain secondary and tertiary *p*-toluenesulfonates under strongly nucleophilic solvolytic conditions.

When **1** was heated to 180° for 4 days in a 1*N* sodium methoxide in methanol solution we obtained only **2** (89% yield). Within the limits of analysis by infrared spectrophotometry (± 3%), **2** was stereochemically pure. No trace of either **3** or **4** could be detected. Since 7-methoxybicyclo[2.2.1]heptane was not converted to 7-hydroxybicyclo[2.2.1]heptane under

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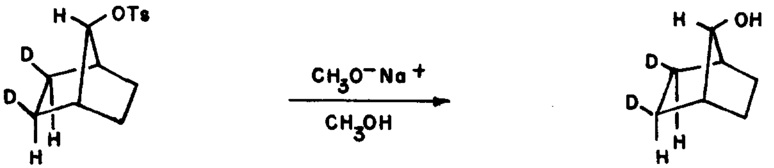

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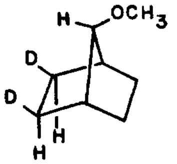
the reaction conditions and could be recovered from the reaction conditions, it followed that neither 3 nor 4 was formed from 1 in the presence of methoxide. This indicated that



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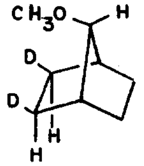

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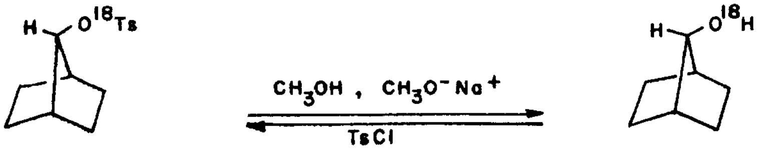
under the conditions used, nucleophilic attack on sulfur took precedence over nucleophilic attack on carbon, which would have produced 4, and over solvolytic ionization of 1 with carbon-oxygen bond cleavage, which would have given a mixture of 3 and 4.

In addition to 2 we obtained sodium tosylate and dimethyl ether from the reaction. These products are consistent with a displacement of the 7-norbornyl alkoxide and formation of methyl tosylate. Control experiments have shown that methyl tosylate is rapidly converted to dimethyl ether and sodium tosylate under the reaction conditions.

Conclusive evidence for sulfur-oxygen bond cleavage was obtained via the use of oxygen-18 labelled material. When 5 was subjected to the reaction conditions, we obtained 6 which



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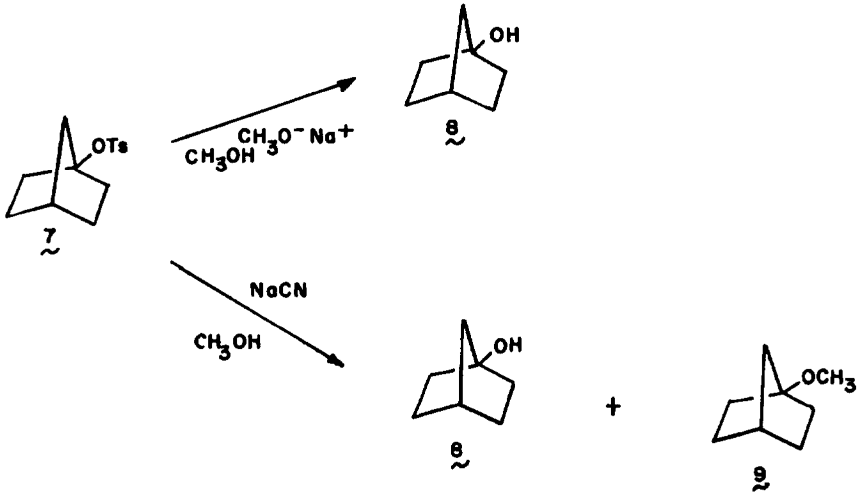
showed no detectable loss of oxygen-18 on analysis by mass spectrometry. However, when 5 was solvolyzed in acetic acid buffered with sodium acetate only acetates were formed. These acetates had lost the oxygen-18 label, indicating that carbon-oxygen bond cleavage must have resulted on acetolysis. This indicated that the presence of a strong nucleophile was probably a prerequisite for sulfur-oxygen bond cleavage.

Attack at sulfur was not limited to methoxide. When 1 was heated to 200° for 5 days in a solution of 1N sodium cyanide in methanol, we obtained 43% of 2 and 28% of a 92:8 mixture of 3 to 4. This indicated that in the presence of cyanide ion, both sulfur-oxygen and carbon-oxygen bond cleavage were occurring. The formation of 2 would result from attack of cyanide ion on sulfur, while 3 and 4 would be expected from carbon-oxygen bond cleavage, followed by reaction of the developing carbonium ion with solvent.[1]

Similarly, the tertiary tosylate, 7,[7] gave an 89% yield of 8 after 5 days at 200° in a solution of 1N sodium methoxide in methanol. After 5 days at 200° in a solution of 1N sodium cyanide in methanol, 7 was converted to 8 (83%) and 9 (6%). The reactions of 7 under the two sets of conditions corresponded closely to those observed for 1. In both cases attack on sulfur by methoxide occurred to the exclusion of carbon-oxygen bond cleavage, while attack on sulfur by cyanide was only competitive with solvolytic carbon-oxygen bond cleavage.



An indication of when nucleophilic attack on sulfur might be expected under solvolytic conditions is easily obtained. Reduction of 1 with lithium aluminum hydride in ether gave only 2 while reduction of 7 under similar conditions gave only 8. We feel that sulfur-oxygen bond cleavage on hydride reduction offers ample warning that sulfur-oxygen bond cleavage might also be expected under certain nucleophilic solvolytic conditions.

In summary, our results indicate that sulfur-oxygen bond cleavage can occur as a major pathway in the reactions of secondary and tertiary tosylates, when the tosylates are relatively unreactive and strong nucleophiles are present. These findings indicate that extreme caution should be used in interpreting the results of solvolytic reactions on relatively unreactive sulfonate esters, especially if the solvent is buffered with a reasonably nucleophilic base. However, it should be stressed that the nucleophilic character of acetic acid buffered with sodium acetate (common solvolytic condition) is not stringent enough to promote sulfur-oxygen bond cleavage, even in the case of very unreactive secondary tosylates such as **1**.

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