# Nucleofugality of the Sulfinate Group in Carbocation-Forming Processes

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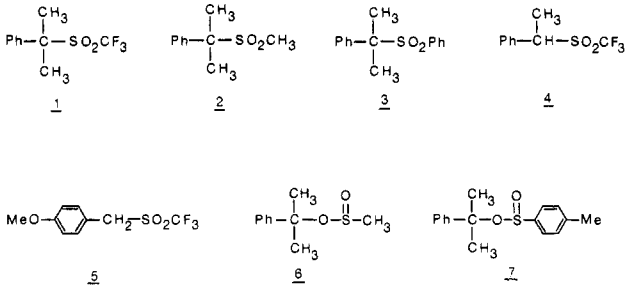
The solvolytic reactivity of a variety of sulfones and sulfinate esters has been determined which allows one to place the sulfinate leaving group in a relative nucleofugality scale. Cumyl trifluoromethyl sulfone (**1**) reacts in a variety of solvents to give substitution products. The $m_{OTs}$ value of 0.82 is indicative of the involvement of the cumyl cation (**9**) formed in a $k_c$ process. In terms of rate, **1** is 170 times less reactive than cumyl chloride but 286 times more reactive than cumyl *p*-nitrobenzoate. The analogous cumyl methyl sulfone (**2**) and cumyl phenyl sulfone (**3**) solvolyze approximately $10^7$ times more slowly than **1**. The sulfinate esters cumyl methanesulfinate (**6**) and cumyl *p*-toluenesulfinate (**7**) are considerably more reactive than the analogous sulfones. Methanolysis of **6** was also subject to acid catalysis, where a mechanism analogous to the $A_{AL}1$ mechanism of hydrolysis of esters of carboxylic acids was suggested. The less hindered $\alpha$-phenethyl trifluoromethyl sulfone (**4**) and *p*-methoxybenzyl trifluoromethyl sulfone (**5**) solvolyzed at rates that approached those of the analogous *p*-nitrobenzoates. This was indicative of the importance of relief of steric congestion in solvolyses of the more hindered tertiary sulfone **1**.

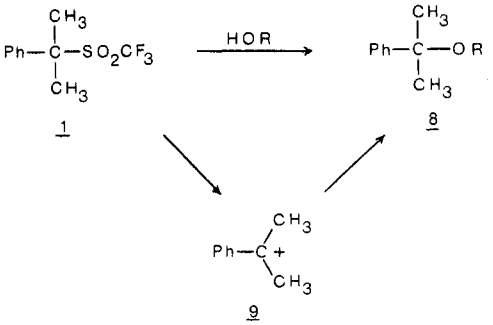
Under appropriate conditions, one of the many reactions that sulfones can undergo is loss of the sulfinate moiety ($RSO_2^-$) as a leaving group. Some recent examples illustrating the increasing importance of this leaving group in organic chemistry include loss of sulfinate in carbocationic,[1] $S_N2$,[2] electron transfer,[3] 1,2-elimination,[4] 1,3-elimination,[5] and 1,4-elimination[6] processes. This leaving group has also been exploited in the total synthesis of anthracycline antibiotics.[7] Additionally, Hendrickson's earlier studies[8] have firmly established the trifluoromethanesulfinate group ($CF_3SO_2^-$) as having relatively high reactivity as a leaving group. We have also observed reactions involving formal loss of $CF_3SO_2^-$ in reaction of $\alpha$-keto triflates with certain bases,[9] in the reaction of aryl triflates with diethylphosphite anion[10] and in the reaction of Grignard reagents with triflic anhydride.[11] We have also seen solvolytic loss of benzenesulfinate anion as a secondary process in solvolyses of $\alpha$-mesyloxy sulfones and $\alpha$-bromo sulfones.[12]

Despite these qualitative studies showing the importance of sulfinate as a leaving group, there is little quantitative data in the literature concerning the leaving group ability of the sulfinate moiety. In view of the developing importance of this leaving group, we have now carried out quantitative studies on the reactivity of sulfones **1–5** as well as the sulfinate esters **6** and **7** under solvolytic conditions. These studies allow one to evaluate the leaving group ability (nucleofugality) of the sulfinate group with respect to other common leaving groups in carbocation-generating processes.



## Results and Discussion

**Solvolytic Reactions of Sulfones and Sulfinate Esters 1–7.** Initial solvolytic studies were carried out on the tertiary 2-phenyl-2-propyl (cumyl) systems **1–3**. Cumyl trifluoromethyl sulfone (**1**) reacted smoothly in various solvents at room temperature to give the straightforward substitution products **8**. Rates were very solvent dependent, showing large increases with solvent ionizing power. The *m* value, when rate data is plotted vs. $Y_{OTs}$ values[13] (Figure 1) is 0.82 ($r = 0.995$). Using *Y* values based on *tert*-butyl chloride, the *m* value is 0.91, but the corre-



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(11) Reaction of aryl- or alkylmagnesium bromides and iodides with trifluoromethanesulfonic anhydride gave the starting aryl or alkyl halide along with $CF_3SO_3^-$ and $CF_3SO_2^-$. See: Creary, X. *J. Org. Chem.* **1980**, *45*, 2727–2729.
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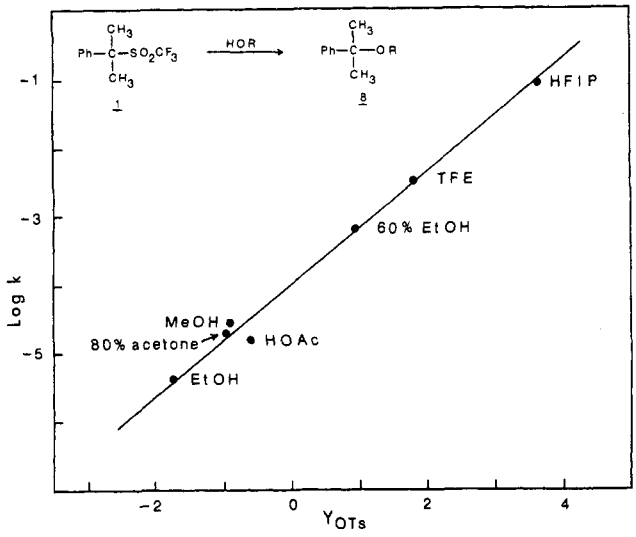



**Figure 1.** A plot of log $k$ for solvolysis of 1 vs. $Y_{OTs}$.

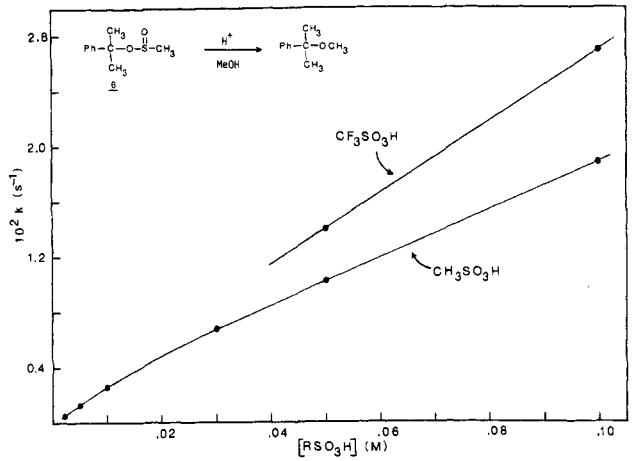
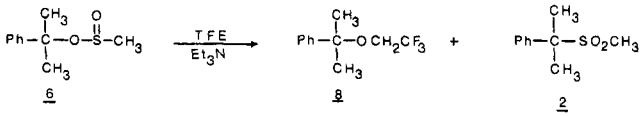



**Figure 2.** A plot of $k$ for solvolysis of 6 in methanol vs. $[RSO_3H]$.

lation is not as high ($r$ = 0.97). These data all support the $k_c$ nature of solvolyses of sulfone 1, leading to the intermediate cumyl cation **9**, with $CF_3SO_2^-$ as a leaving group. Sulfones **2** and **3** require high temperatures in trifluoroethanol to achieve solvolyses. Under these conditions, mixtures of substitution product **8** (R = $CH_2CF_3$) and the elimination product, $\alpha$-methylstyrene (**10**), are produced, presumably via the same intermediate **9**.

Solvolysis of the sulfinate ester **6** in trifluoroethanol buffered with triethylamine produced a product of internal return, the sulfone **2**, in addition to the substitution product **8** (R = $CH_2CF_3$). This observation is completely in accord with previous studies[14] that have established the involvement of ion pairs in solvolyses of sulfinate esters.




The solvolysis of **6** in methanol is quite slow at room temperature. However, the addition of methanesulfonic acid or triflic acid drastically increases the reaction rate, as shown in Table II and Figure 2. The acid-catalyzed methanolysis of **6** gives only the substitution product **8** (R = $CH_3$) and no sulfone **2** resulting from internal return. It is suggested that this acid-catalyzed methanolysis proceeds by the mechanism shown in Scheme I. This mechanism is completely analogous to the $A_{AL}1$ mechanism[15] of hydrolysis of certain esters of carboxylic acids. A control experiment showed that cumyl alcohol in

(14) Darwish, D.; McLaren, R. *Tetrahedron Lett.* **1962**, 1231–1237. (b) Darwish, D.; Preston, E. A. *Ibid.* **1964**, 113–118.

**Table I. Solvolysis Rates of Substrates in Various Solvents**

| compd | solvent[a] | temp, °C | $k$, $s^{-1}$ | rel rate[h] |
|---|---|---|---|---|
| $Ph(CH_3)_2CCl$ | MeOH[b] | 25.0 | $4.89 \times 10^{-3}$ | 170 |
| 1 | MeOH[c] | 25.0 | $2.87 \times 10^{-5}$ | 1 |
| | EtOH[c] | 25.0 | $4.37 \times 10^{-6}$ | |
| | 60% EtOH[b] | 25.0 | $6.65 \times 10^{-4}$ | |
| | HOAc[c] | 25.0 | $1.62 \times 10^{-5}$ | |
| | 80% acetone[c] | 25.0 | $2.09 \times 10^{-5}$ | |
| | TFE[b] | 25.0 | $3.51 \times 10^{-3}$ | |
| | HFIP[b] | 25.0 | $9.14 \times 10^{-2}$ | |
| 7 | TFE[b] | 25.0 | $2.35 \times 10^{-3}$ | 0.67 |
| 6 | TFE[b] | 25.0 | $4.33 \times 10^{-4}$ | 0.12 |
| $Ph(CH_3)_2$-COPNB | 80% acetone | 25.0[d,e] | $7.2 \times 10^{-8}$ | $3.5 \times 10^{-3}$ |
| 3 | TFE[b] | 140.0 | $3.17 \times 10^{-5}$ | $\sim 10^{-7}$ |
| 2 | TFE[g] | 160.0 | $4.13 \times 10^{-5}$ | |
| | | 140.0 | $1.04 \times 10^{-5}$ | |
| | | 25.0[d] | $1.09 \times 10^{-10}$ | $<10^{-7}$ |
| 4 | TFE[c] | 100.0 | $1.70 \times 10^{-4}$ | |
| | | 80.0 | $2.70 \times 10^{-5}$ | |
| | | 25.0[d] | $4.97 \times 10^{-8}$ | |
| 12 | TFE[c] | 25.0 | $6.55 \times 10^{-4}$ | |
| 5 | TFE[c] | 70.0 | $9.38 \times 10^{-5}$ | |
| | | 25.0 | $5.27 \times 10^{-7}$ | |
| 13 | TFE[b] | 25.0 | $1.81 \times 10^{-1}$ | |
| 14 | TFE[c] | 70.0 | $3.2 \times 10^{-5}$ | |

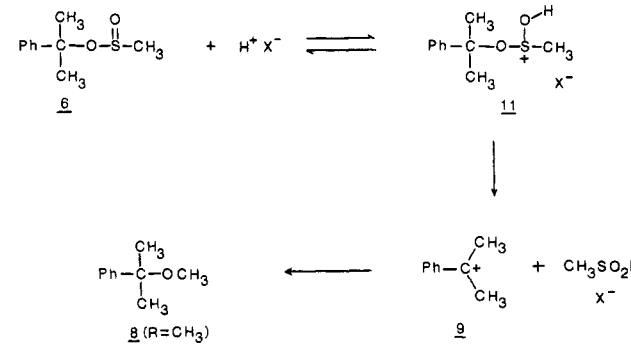
[a] HOAc = 0.05 M NaOAc in acetic acid containing 1% acetic anhydride. TFE = trifluoroethanol. 80% acetone contains 20% water (by volume). 60% EtOH contains 40% water (by volume). HFIP = 97% hexafluoroisopropyl alcohol containing 3% water (by weight). [b] Rate determined spectrophotometrically; see Experimental Section. [c] Rate determined titrimetrically; see Experimental Section. [d] Extrapolated rate. [e] Reference 17. [f] Rate determined by NMR spectroscopy; see Experimental Section. [g] Rate determined by gas chromatography; see Experimental Section. [h] At 25 °C.

**Table II. Acid-Catalyzed Methanolysis Rates of 6 at 25 °C**

| [acid] in MeOH[a] | k, $s^{-1}$ |
|---|---|
| 0.100 M MsOH | $1.88 \times 10^{-2}$ |
| 0.050 M MsOH | $1.02 \times 10^{-2}$ |
| 0.030 M MsOH | $6.76 \times 10^{-3}$ |
| 0.010 M MsOH | $2.62 \times 10^{-3}$ |
| 0.005 M MsOH | $1.32 \times 10^{-3}$ |
| 0.002 M MsOH | $5.28 \times 10^{-4}$ |
| 0.100 M TfOH | $2.69 \times 10^{-2}$ |
| 0.050 M TfOH | $1.41 \times 10^{-2}$ |

[a] MsOH = $CH_3SO_3H$; TfOH = $CF_3SO_3H$.

**Scheme I**



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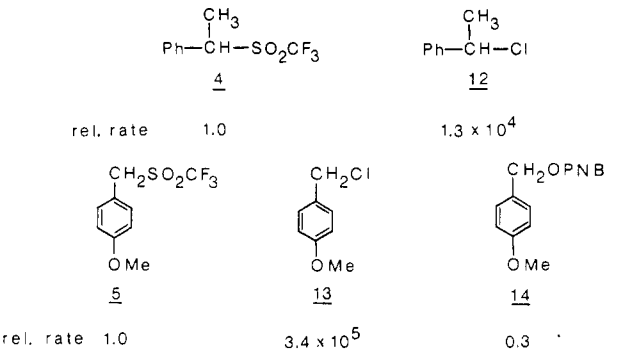
methanol was converted to 8 (R = $CH_3$), at comparable acid concentrations, at a much slower rate than the acid-catalyzed methanolysis of **6**. This rules out cumyl alcohol (the product of sulfinyl–oxygen cleavage) as an intermediate in the acid-catalyzed methanolysis of **6** and argues in favor of alkyl–oxygen cleavage in the acid-catalyzed methanolysis. The sulfinate ester **6** appears to be much more susceptible to this $A_{AL}1$ pathway than analogous carboxylic esters. The somewhat lower rates in methanesulfonic acid vs. triflic acid rates (Figure 2) reflect incomplete ionization of methanesulfonic acid in methanol at higher concentrations. The acid-catalyzed process differs from the uncatalyzed process in that the leaving group ($CH_3SO_2H$) is neutral rather than anionic. Hence the product of internal return, the sulfone **2**, is less likely under acidic conditions.

**Relative Reactivity Studies.** The rate data in Table I allow the establishment of a relative reactivity scale. The sulfone **1** is 170 times less reactive than cumyl chloride in methanol.[16] The sulfone **1** is, however, 286 times more reactive than cumyl *p*-nitrobenzoate.[17] This places the leaving group ability of $CF_3SO_2^-$ between that of chloride and *p*-nitrobenzoate in the cumyl system. A further comparison of sulfone **1** with **2** reveals that the nucleofugality of $CF_3SO_2^-$ greatly exceeds that of $CH_3SO_2^-$. While sulfone **1** solvolyzes with a half-life of 400 min at 25 °C in methanol, sulfone **2** is recovered unchanged after 6 h at 150 °C in this solvent. The half-life for solvolysis of **1** at 25 °C is 196 s in trifluoroethanol, while the half-life of the analogue **2** at 140 °C in the same solvent is 19 h. A reactivity difference between **1** and **2** of greater than $10^7$ can be calculated from the data in Table I. (We hesitate to give a more precise figure because of the 10% uncertainty in the rate constants for **2** as determined by gas chromatography and the large temperature extrapolation involved). The cumyl phenyl sulfone (**3**) is only slightly more reactive (3 times) than **2**. Finally, sulfinate esters **6** and **7**, which give sulfinate by fragmentation of a carbon–oxygen bond, are substantially more reactive than the analogous sulfones **2** and **3**, which fragment a carbon–sulfur bond in forming sulfinate.

The trifluoromethanesulfinate/methanesulfinate rate ratio of greater than $10^7$ is even larger than the triflate/mesylate rate ratio of $10^4$–$10^5$.[18] The rate-increasing effect of the $CF_3$ substituent (relative to $CH_3$) is therefore greater in sulfone solvolyses than in sulfonate solvolyses. A rationale is provided by the fact that the electronegative $CF_3$ group is attached directly to the sulfur atom which develops substantial negative charge in sulfone solvolyses. In sulfonate solvolyses, the inductive effect of $CF_3$ is smaller since the developing negative charge is borne more completely by oxygen.

In view of the fact that cumyl sulfones **1**–**3** have a tertiary carbon attached to a tetracoordinate sulfur atom, relief of strain as the carbon–sulfur bond fragments could play an important role in determining solvolysis rates of these systems. To evaluate the role of steric factors, the less hindered secondary trifluoromethyl sulfone **4** and the primary trifluoromethylsulfone **5** were examined. Solvolytic rates were compared to rates for the corresponding chlorides. The secondary system **4** was $1.3 \times 10^4$ times less reactive than the chloro analogue, α-phenethyl chloride (**12**) in TFE. The primary trifluoromethylsulfone **5** was




$3.4 \times 10^5$ times less reactive than *p*-methoxybenzyl chloride (**13**) and comparable in reactivity to the corresponding *p*-nitrobenzoate **14**. These data suggest that relief of strain plays some role in increasing the solvolysis rates of the more hindered cumyl sulfone **1**, which is only 170 times less reactive than the corresponding chloride. Solvolysis rates of unhindered trifluoromethyl sulfones therefore appear to approach those of the analogous *p*-nitrobenzoates.

**Conclusions.** The trifluoromethanesulfinate leaving group lies between that of chloride and *p*-nitrobenzoate in terms of reactivity in solvolyses of cumyl systems. The methanesulfinate and benzenesulfinate leaving groups are approximately $10^7$ less reactive than trifluoromethanesulfinate. In less hindered secondary and primary systems, the leaving group ability of $CF_3SO_2^-$ approaches that of *p*-nitrobenzoate. Sulfinate esters are substantially more reactive ($10^7$) in solvolytic processes than the isomeric sulfones. Further increases in reactivity of sulfinate esters can be observed under acid catalysis. Under such acid catalysis, sulfinate esters solvolyze by a suggested $A_{AL}1$ type of mechanism.

## Experimental Section

**Benzyl Trifluoromethyl Sulfone.** This sulfone was prepared by the reaction of triflic anhydride with benzylmagnesium chloride using the general procedure previously described.[11] Addition of 36 mL of a solution of $PhCH_2MgCl$ prepared from 5.06 g of benzyl chloride and 1.15 g of magnesium in 35 mL of ether to a −78 °C solution of 9.0 g of triflic anhydride in 60 mL of ether gave 5.60 g of crude sulfone contaminated with a small amount of benzyl chloride. To remove the benzyl chloride, the crude sulfone was heated under reflux with 25 mL of Skelly F and 3 mL of ether for 15 min. After the mixture was cooled to −10 °C, 5.13 g (72%) of benzyl trifluoromethyl sulfone, mp 99–101 °C (lit.[8a] mp 103 °C) was collected on a Büchner funnel.

**Preparation of Sulfone 4.** This sulfone was prepared by using the general method of Hendrickson.[8a] A mixture of 12.0 g of powdered anhydrous potassium carbonate, 22 mL of dry acetonitrile, 3.515 g of benzyl trifluoromethyl sulfone, and 3.45 g of methyl iodide was heated with stirring at reflux for 5 h and 15 min. The mixture was taken up into ether and water, and the ether extract was washed with dilute $Na_2S_2O_3$ solution. After being dried over $MgSO_4$, the ether solvent was removed by rotary evaporator. Distillation, using a short-path distillation head, gave, after a small forerun containing α-methylstyrene, 2.918 g (78%) of **4**: bp 60 °C (0.03 mm); NMR ($CDCl_3$) δ 7.45 (5 H, s), 4.54 (1 H, q, $J$ = 7.3 Hz), 1.83 (3 H, d, $J$ = 7.3 Hz). Anal. Calcd for $C_9H_9F_3O_2S$: C, 45.38; H, 3.81. Found: C, 45.61; H, 3.80.

**Preparation of Sulfone 1.** This sulfone was prepared by using the general method of Hendrickson.[8a] Sodium hydride (0.416 g of 60% NaH–40% mineral oil) was washed with two portions of Skelly F, and the Skelly F was decanted. Dry tetrahydrofuran (30 mL) was added followed by 2.00 g of sulfone **4**. After 15 min, when hydrogen evolution ceased, 2.33 g of methyl iodide was added to the clear solution at about 10 °C. The mixture was then kept at room temperature for 5 h and 40 min. The mixture was taken up into ether and water, washed with $Na_2S_2O_3$ solution and saturated NaCl solution, and dried over $MgSO_4$. The solvent was

(16) Okamoto, Y.; Inukai, T.; Brown, H. C. *J. Am. Chem. Soc.* **1958**, *80*, 4972–4976.
(17) Brown, H. C.; Rao, C. G.; Ravindranathan, M. *J. Am. Chem. Soc.* **1978**, *100*, 7946–7953.
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removed with a rotary evaporator, and the solid residue was slurried with cold pentane, leaving 1.996 g (94%) of sulfone **1**: mp 73 °C dec (immediate); NMR ($CDCl_3$) $\delta$ 7.8–7.4 (5 H, m), 1.95 (6 H, s). Anal. Calcd for $C_{10}H_{11}F_3O_2S$: C, 47.61; H, 4.40. Found: C, 47.74; H, 4.57.

**Preparation of Sulfone 2.** Phenylmagnesium bromide was prepared from 1.67 g of bromobenzene and 0.27 g of magnesium in 20 mL of ether. The mixture was cooled in a water bath, and 0.9 g of $CH_3SH$ in 6 mL of ether was added dropwise. After the mixture was refluxed for 15 min, a solution of 1.90 g of cumyl bromide in 4 mL of ether was added, and the resulting mixture was refluxed for 5 h. Aqueous $NH_4Cl$ solution was added, and a standard workup followed. After being dried over $MgSO_4$, the solvent was removed with a rotary evaporator, and the residue was distilled through a 5-in. Vigreux column, giving 1.45 g of cumyl methyl sulfide: bp 40–41 °C (0.05 mm); NMR ($CDCl_3$) $\delta$ 7.7–7.1 (5 H, m), 1.78 (3 H, s), 1.67 (6 H, s).

A solution of 0.75 g of cumyl methyl sulfide in 15 mL of methylene chloride was cooled in an ice bath as 2.00 g of *m*-chloroperbenzoic acid was added in small portions. The mixture was then stirred at room temperature for 30 min, taken up into ether, and then washed with KOH solution. After a washing with a NaI–$Na_2S_2O_3$–KOH mixture, the organic phase was washed with saturated NaCl solution and dried over $MgSO_4$. Solvent removal using a rotary evaporator gave 0.88 g (98%) of sulfone **2**. Recrystallization from 80% hexanes–20% ether gave a sample of mp 81–82 °C (lit.[19] mp 83–85 °C): NMR ($CDCl_3$) $\delta$ 7.7–7.6 (2 H, m), 7.5–7.3 (3 H, m), 2.51 (3 H, s), 1.86 (6 H, s).

**Preparation of Sulfone 3.** This sulfone was prepared by using a modification of the previously described procedure.[20] A solution of 1.22 g of thiophenol in 3 mL of ether was added to phenylmagnesium bromide prepared from 1.66 g of bromobenzene and 0.27 g of magnesium in 20 mL of ether. After the mixture was refluxed for 15 min, 1.811 g of cumyl bromide was added, and the resulting mixture was refluxed for 3.5 h. A standard aqueous workup gave 2.10 g of cumyl phenyl sulfide. Oxidation of 1.48 g of cumyl phenyl sulfide in 15 mL of methylene chloride with 3.10 g of 85% *m*-chloroperbenzoic acid gave, after a standard aqueous workup and washing with a NaI–$Na_2S_2O_3$–NaOH solution, 1.44 g (85%) of **3**. Recrystallization from hexane gave a sample of mp 89–90 °C (lit.[20] mp 90–91 °C): NMR ($CDCl_3$) $\delta$ 7.7–7.2 (10 H, m), 1.79 (6 H, s).

**Preparation of Sulfone 5.** This sulfone was prepared by using the general method of Hendrickson.[8a] Potassium trifluoromethanesulfinate was prepared from trifluoromethanesulfonyl chloride (6.0 g) and potassium iodide (11.82 g) in cold acetone (25 mL) as previously described.[8a] The mixture of KCl and $K^+CF_3SO_2^-$ formed in this procedure was not further separated. A suspension of 2.75 g of the potassium trifluoromethanesulfinate–potassium chloride mixture and 1.01 g of *p*-methoxybenzyl chloride in 10 mL of acetonitrile was heated at 65 °C for 17 h and then refluxed for 3 h. The mixture was taken up into ether and water, washed with two additional portions of water and saturated NaCl solution, and dried over $MgSO_4$. The solvent was removed with a rotary evaporator, and the product (1.602 g) was slurried with Skelly F. The sulfone **5** (1.562 g, 95%), mp 100–101 °C, was collected: NMR ($CDCl_3$) $\delta$ 7.5–6.9 (4 H, AA'BB' q), 4.52 (2 H, s), 3.81 (3 H, s). Anal. Calcd for $C_9H_9F_3O_2S$: C, 42.52; H, 3.57. Found: C, 42.48; H, 3.50.

**Preparation of Sulfinate Ester 6.** A solution of 2.00 g of cumyl alcohol and 1.75 g of methanesulfinyl chloride[21] in 15 mL of methylene chloride was cooled to about −35 °C as a solution of 2.40 g of triethylamine in 7 mL of methylene chloride was added dropwise over a 15-min period. The mixture was warmed to −10 °C and then recooled to −60 °C and ether was added. Water was then added, and a rapid aqueous workup followed. After the organic extract was dried over $MgSO_4$, the solvents were removed with a rotary evaporator, leaving 2.92 g (100%) of crude **6**: NMR ($CDCl_3$) $\delta$ 7.8–7.2 (5 H, m), 2.62 (3 H, s), 1.87 (3 H, s), 1.75 (3 H, s). The NMR spectrum showed about 5% of cumyl chloride as an impurity. When the preparation was carried out at high temperatures, the amount of cumyl chloride in the product increased. Ester **6** was stored at −20 °C.

**Preparation of Sulfinate Ester 7.** A solution of 1.01 g of cumyl alcohol and 1.43 g of *p*-toluenesulfinyl chloride[22] in 15 mL of methylene chloride was cooled to −30 °C as 1.02 g of triethylamine in 3 mL of methylene chloride was added dropwise. The mixture was warmed to 0 °C, and ether was added. A standard aqueous workup followed using cold water, dilute HCl, and saturated sodium chloride washes. After drying over $MgSO_4$, the solvents were removed with a rotary evaporator, leaving 2.11 g (100%) of crude ester **7** as a clear oil: NMR ($CDCl_3$) $\delta$ 7.8–7.2 (9 H, m), 2.37 (3 H, s), 1.93 (3 H, s), 1.79 (3 H, s). On prolonged standing in $CDCl_3$, **7** decomposed giving $\alpha$-methylstyrene. Ester **7** was therefore stored at −20 °C.

**Solvolyses of 1 in Methanol and Trifluoroethanol.** A solution of 227 mg of **1** in 11 mL of methanol containing 117 mg of $Et_3N$ was kept at 45 °C for 6.5 h. The methanol was removed by rotary evaporator, and the residue was taken up into ether, washed with a KOH solution, dilute HCl solution, and saturated NaCl solution, and dried over $MgSO_4$. Solvent removal by rotary evaporator left 102 mg (75%) of **8** (R = $CH_3$). Using an analogous procedure, reaction of 220 mg of **1** in 10 mL of TFE containing 113 mg of $Et_3N$ for 2 h at room temperature gave 149 mg (78%) of **8** (R = $CH_2CF_3$): NMR ($CDCl_3$) $\delta$ 7.6–7.2 (5 H, m), 3.39 (2 H, q, $J$ = 8.6 Hz), 1.55 (6 H, s).

**Solvolysis of 6 in Trifluoroethanol.** A solution of 104 mg of **6** and 66 mg of $Et_3N$ in 7 mL of TFE was kept at 25 °C for 20 h. The TFE was removed by rotary evaporator, and after a standard aqueous workup as described above, the ether solvent was removed. The residue (77 mg) was analyzed by gas chromatography, which showed **8** (R = $CH_2CF_3$) and sulfone **2**. The ratio of **8** (R = $CH_2CF_3$) to **2**, as determined by NMR, was 1.67 to 1.

**Trifluoromethanesulfonic Acid Catalyzed Methanolysis of 6.** A solution of 263 mg of **6** in 15 mL of 0.05 M $CF_3SO_3H$ was kept at 25 °C for 10 min. $Et_3N$ (250 mg) was then added, and the solvent was removed by rotary evaporator. The residue was taken up into ether, and the ether phase was washed with a KOH solution, dilute HCl solution, and saturated NaCl solution. After being dried over $MgSO_4$, the solvent was removed with a rotary evaporator, leaving 158 mg (79%) of **8** (R = $CH_3$). Gas chromatographic analysis showed no trace of sulfone **2**.

**Kinetics Procedures.** Rates of solvolysis of sulfone **1** were monitored either titrimetrically by using procedures analogous to those previously described[23] or spectrophotometrically. In EtOH, the liberated $CF_3SO_2H$ was monitored by titration with 0.01 M $Et_3N$ in ethanol. In methanol and 80% aqueous acetone (which contained 0.025 M $Et_3N$), at various times, aliquots were quenched in cold ethanol and unreacted $Et_3N$ was titrated 0.01 M $HClO_4$ in methanol. In acetic acid (which contained 0.05 M NaOAc), unreacted NaOAc was titrated with 0.01 M $HClO_4$ in HOAc. In trifluoroethanol (TFE), 97% hexafluoroisopropyl alcohol, and 60% aqueous ethanol (all containing $10^{-3}$ M $Et_3N$) rates were monitored spectrophotometrically by following the decrease in absorbance at 223 nm as a function of time. The run was initiated by injection of approximately 10 $\mu$L of a solution of 10 mg of **1** in 1 mL of ether into a thermostated cuvette containing 2.5 mL of the appropriate solvent. This general method was used to initiate all spectrophotometric runs.

Solvolysis rates of **2** and **3** in TFE could not be determined with the titrimetric method. At the temperatures necessary to achieve solvolysis, oxidation and/or disproportionation of the sulfinic acid released prevented rate measurements by titrimetric methods. The solvolysis rate of **2** in TFE was therefore determined by gas chromatography, using biphenyl as an internal standard, using a 6-ft 5% SE-30 on Chromosorb G column at 148 °C. Small portions of a solution containing 55 mg of **2**, 12 mg of biphenyl, and 31 mg of $Et_3N$ in 11 mL of TFE were sealed in Pyrex tubes, and the tubes were placed in a constant temperature

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bath at the appropriate temperature. At various times, individual tubes were cooled and then analyzed for unreacted **2** by gas chromatography.

The solvolysis rate of **3** in TFE was determined by NMR spectroscopy. A sealed NMR tube containing **3** in TFE (also containing 0.025 M $Et_3N$) was heated in a constant temperature bath for given times and then quenched in cold water. The disappearance of the methyl singlet at $\delta$ 1.79 was monitored directly by 300-MHz NMR.

The rates of solvolyses of **4**, **5**, and $\alpha$-phenethyl chloride (**12**) in TFE (0.025 M in $Et_3N$) were determined titrimetrically with the previously described TFE rate procedure.[23] Aliquots were quenched in cold HOAc, and unreacted base was back-titrated with 0.01 M $HClO_4$ in HOAc.

Solvolysis rates of sulfinate esters **6** and **7** in TFE ($10^{-3}$ M in $Et_3N$) were spectrophotometrically determined by monitoring the absorbance change at 244 nm. Rates of **6** in methanol containing methanesulfonic acid or trifluoromethanesulfonic acid were determined spectrophotometrically at 226 nm.

The methanolysis rate of cumyl chloride was determined spectrophotometrically at 25 °C at 225 nm. Our directly determined rate at this temperature is 4.6% smaller than the previously reported rate[16] at 25 °C determined by extrapolation of titrimetric data from lower temperatures.

The solvolysis rate of *p*-methoxybenzyl chloride (**13**) in TFE was determined spectrophotometrically by monitoring the absorbance decrease at 240 nm.

The solvolysis rate of *p*-methoxybenzyl *p*-nitrobenzoate (**14**) in TFE (0.025 M $Et_3N$) was determined by titration of the unreacted $Et_3N$ with 0.01 M *p*-nitrobenzoic acid in methanol. End points were not sharp and the rate constant reported is ±10%.

**Acknowledgment** is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

**Registry No.** 1, 98821-05-7; 2, 25195-63-5; 3, 53439-66-0; 4, 98821-06-8; 5, 98821-07-9; 6, 98821-08-0; 7, 98821-09-1; 8 (R = $CH_3$), 935-67-1; 8 (R = $CH_2CF_3$), 98821-11-5; 12, 672-65-1; 13, 824-94-2; 14, 53218-10-3; $Ph(CH_3)_2CCl$, 934-53-2; $Ph(CH_3)_2COPNB$, 7429-06-3; $CH_3SH$, 74-93-1; benzyl trifluoromethyl sulfone, 4855-02-1; triflic anhydride, 358-23-6; cumyl bromide, 3575-19-7; cumyl methyl sulfide, 98821-10-4; thiophenol, 108-98-5; cumyl phenyl sulfide, 4148-93-0; potassium trifluoromethanesulfinate, 41804-89-1; *p*-methoxybenzyl chloride, 824-94-2; cumyl alcohol, 617-94-7; methanesulfinyl chloride, 676-85-7; *p*-toluenesulfinyl chloride, 10439-23-3.

# Solvolytic Hydroperoxide Rearrangements. 2. Oxa Bicyclic Hemiketal Peroxides from Homoallylic and Cyclopropylcarbinyl Precursors

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Studies in this laboratory have resulted in the discovery of a novel hydrogen peroxide mediated ring expansion that is suitable for the synthesis of medium to large ring oxa bicyclic compounds. This rearrangement involves the solvolysis of homoallylic brosylates or spiro cyclopropyl carbinols in THF–$H_2O_2$ and results in a two-carbon ring expansion producing hydroxy ketone derivatives in excellent yields. The reaction involves initial solvolytic entry into the cyclopropylcarbinyl–cyclobutyl carbocation manifold followed by an electron-deficient oxygen rearrangement of the cyclobutyl isomer.

Ring expansions have played an important part in synthetic organic methodology. Many methods are available for expanding rings by one, two, or more carbons. Recently, we communicated the development of a new and efficient two-carbon ring expansion reaction of carbocycles that yields medium-sized rings by hydrogen peroxide mediated solvolysis of homoallylic brosylates.[1] In this paper we describe the details of that study and its further development as a stereoselective ring expansion reaction.

The Criegee perester–hydroxy ketone rearrangement of decalin hydroperoxide has long been known to produce an oxa-bridged bicyclic product; however, this reaction has received little attention other than investigation of its rather unusual mechanism.[2] Our interest in the Criegee-type rearrangement and ring expansions in general grew out of consideration of possible synthetic approaches to a relatively new class of sesquiterpenes that have an

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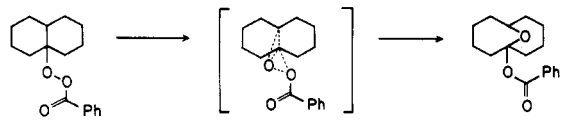
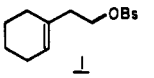
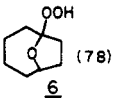
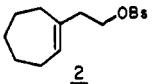
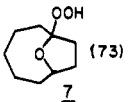
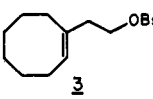
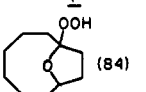
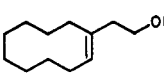
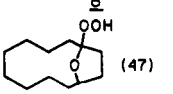
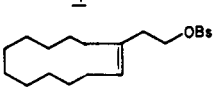
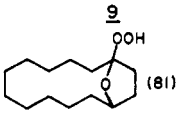



**Table I. Solvolyses of Brosylates in $H_2O_2$–THF**

| substrate | time, h (temp, °C) | product (yield, %) |
|---|---|---|
|  1 | 0.5 (25) |  6 (78) |
|  2 | 1 (25) |  7 (73) |
|  3 | 3 (25) |  8 (84) |
|  4 | 26 (40) |  9 (47) |
|  5 | 72 (37) |  10 (81) |

11-oxabicyclo[6.2.1]undecane ring structure.[3] This ring structure along with other oxygen-bridged systems can be

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