Cyclopropanesulfonyl Chloride: Its Mechanisms of Hydrolysis and Reactions with Tertiary Amines in Organic Media[1]

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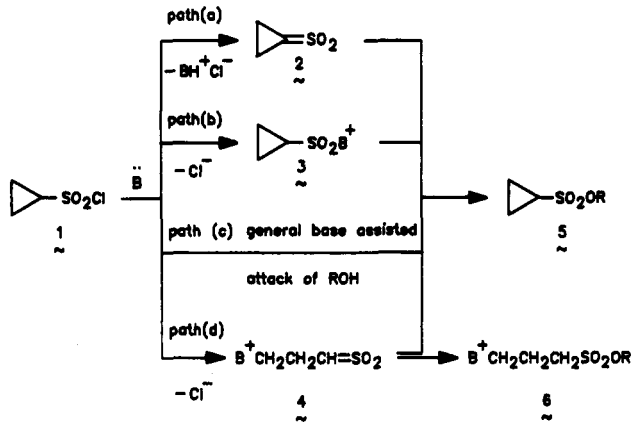
Cyclopropanesulfonyl chloride (1) has been synthesized and its reactions examined to see if the three-membered ring leads to unusual reactions in either 1 or the corresponding sulfene, cyclopropanethione *S,S*-dioxide (2). pH–rate profiles, primary kinetic isotope effects (KIE's), and pH–product ratio experiments are in full agreement with mechanisms of hydrolysis of 1 like those of a simple alkanesulfonyl chlorides (*J. Am. Chem. Soc.* **1992**, *114*, 1743–1749), specifically, (a) below pH 7.2 by S_N2-S reaction with water and (b) above pH 7.3, elimination by hydroxide to form the sulfene (2) which is trapped by (i) water below pH 12.0 and (ii) hydroxide above pH 12.0. The products of the reaction of cyclopropanesulfonyl-*1-d* chloride (9) with triethylamine and 2-propanol in dichloromethane indicate that most of the reaction goes via 2; the analogous reaction with trimethylamine apparently proceeds by a direct formation of the sulfonylammonium chloride (14) which then yields the α-deuterated *N,N*-dimethyl sulfonamide (12, R = Me). The evident sulfene formation processes in the reaction of triethylamine with ethanesulfonyl, 2-propanesulfonyl, and cyclopropanesulfonyl chlorides show very low primary KIE's (<1.5), pointing to highly product-like transition states. Reaction of 1 with an enamine (1-pyrrolidino-2-methylpropene, 20) in the presence of a base in either water or dichloromethane gave cyclopropanesulfonpyrrolidide (23) and an aldehyde adduct (24), but no four-membered cycloadduct (21).

Cyclopropanesulfonyl chloride (1) is one of the simplest possible sulfonyl chlorides that have remained undescribed in the chemical literature.[3] In our extended study[2,5] of the chemical behavior of alkanesulfonyl chlorides and related compounds, it became apparent on consideration of the possible reactions of cyclopropanesulfonyl chloride that there were interesting questions not easily answered in the light of current knowledge.[6] Its reaction with base in the presence of water or an alcohol, for example, could be imagined to go by any of the four routes in Scheme I. Path a, yielding the sulfene 2, corresponds to that most commonly observed in the reaction of hydroxide or tertiary amines with compounds of the general structure RR'CH-SO_2Cl. Cyclopropanethione *S,S*-dioxide (2), a heterocyclic analogue of methylenecyclopropane, is a strained species with potential for interesting rearrangements,[7] e.g. to methylenethiirane *S,S*-dioxide ("allene episulfone"). But by the same token, to the extent that the transition state for the formation of 2 approaches it in structure, the rate of formation of 2 can be expected to be slowed relative to that of unstrained analogues, with the result that another reaction might appear instead. The second pathway (b) involves nucleophilic catalysis by the tertiary amine, a

Scheme I



route well-precedented in the conversion of arenesulfonyl chlorides to esters by alcohols in the presence of pyridine.[8] Path c is, of course, the direct displacement process which appears in the reaction of arenesulfonyl chlorides with hydroxide, amines, and a number of other nucleophiles,[6,8,9] with ethenesulfonyl chloride and hydroxide ion[10] and with most sulfonyl chlorides with water or alcohols.[2,5,6,8] The reaction may be a simple direct displacement or may involve the assistance of an additional component of the reaction mixture acting as a general base; the reaction of benzenesulfonyl chloride with aryl oxides in water, for example, shows, in addition to nucleophilic displacement by the aryl oxide, a minor reaction in which an aryl oxide anion aids the hydrolysis of the acid chloride.[11] Should

(1) Organic Sulfur Mechanisms. 36. Part 35, see ref 2.
(2) King, J. F.; Lam, J. Y. L.; Skonieczny, S. *J. Am. Chem. Soc.* **1992**, *114*, 1743–1749.
(3) A preliminary report on the early part of this study has been presented: King, J. F.; Lam, J. Y. L. *Abstracts of the 72nd Canadian Chemical Conference*, Victoria, B. C., June 1989; abstract 485, pp 137–138. After most of the work in this manuscript had been completed we became aware of an independent synthesis of 1 by Block and Schwan (SUNY, Albany).[4] We thank Professors Block and Schwan for keeping us informed of the progress of their work before publication.
(4) Block, E.; Schwan, A.; Dixon, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 3492–3499.
(5) (a) King, J. F. *Acc. Chem. Res.* **1975**, *8*, 10. (b) King, J. F.; Rathore, R. In *The Chemistry of Sulphonic Acids and their Derivatives*; Patai, S., Rappoport, Z., Eds.; J. Wiley and Sons Ltd.: Chichester, England, 1991; Chapter 19, pp 697–766.
(6) Reviews: Gordon, I. M.; Maskill, H.; Ruasse, M. F. *Chem. Soc. Rev.* **1989**, *18*, 123–151. Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, *17*, 65–181.
(7) L'abbé, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 276–289.
(8) Rogne, O. *J. Chem. Soc. B* **1968**, 1294–1296; **1970**, 727–730, 1056–1058; **1971**, 1334–1337, 1855–1858; *J. Chem. Soc., Perkin Trans. 2* **1972**, 472–474.
(9) Vizgert, R. V. *Uspekhi Khim.* **1963**, *32*, 1–20.
(10) King, J. F.; Hillhouse, J. H.; Skonieczny, S. *Can. J. Chem.* **1984**, *62*, 1977–95. King, J. F.; Loosmore, S. M.; Hillhouse, J. H.; Khemani, K. C. *Can. J. Chem.* **1989**, *67*, 330–334.

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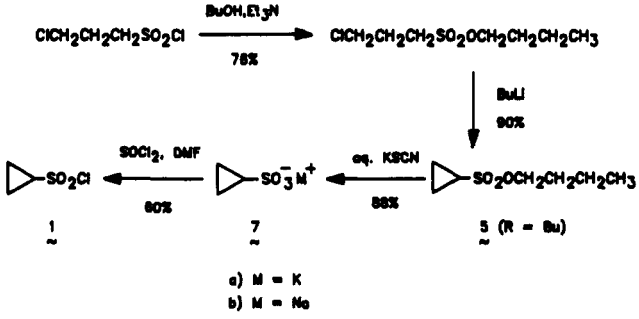
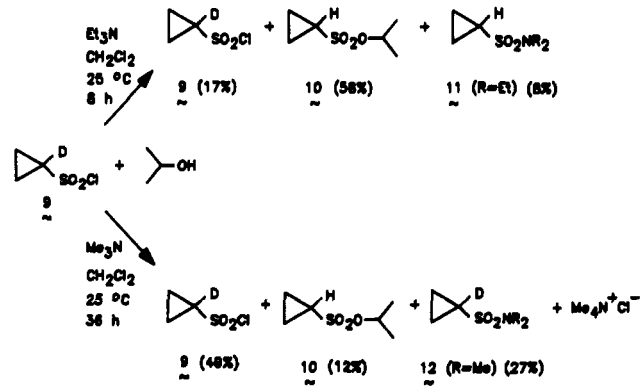
Scheme II



Scheme III



the other paths be sufficiently slow, one or other form of path c would become the observed route.

Path d has no precise precedent and may be regarded as a "homovinylogous" nucleophilic attack, the cyclopropane counterpart of the vinylogous nucleophilic attack observed in the reaction of ethenesulfonyl chloride with tertiary amines,[10] (eq 1). Such ring opening of cyclopropanes has been observed with 1,1-bis(phenylsulfonyl)cyclopropane[12] and in 1-(phenylsulfonyl)bicyclo[1.1.0]butanes;[13] it was looked for but not found with *p*-tolyl cyclopropyl sulfone.[14]

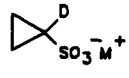
$$R_3N + CH_2{=}CHSO_2Cl \rightarrow [R_3N^+CH_2CH{=}SO_2\ Cl^-] \rightarrow \text{products} \quad (1)$$

To distinguish among these possibilities we have prepared and characterized cyclopropanesulfonyl chloride (1) and looked at some of its reactions in the presence of base in both aqueous and organic media.

Results and Discussion

The straightforward procedure shown in Scheme II gave cyclopropanesulfonyl chloride (1) as a colorless oil with appropriate spectra (see the Experimental Section); it was characterized by conversion to the crystalline cyclopropanesulfon-*p*-toluidide, which showed infrared and ^1H and ^{13}C NMR spectra and an exact mass in full agreement with the assigned structure. In addition a single-crystal X-ray structure determination of *p*-cyanophenyl cyclopropanesulfonate (5, R = *p*-cyanophenyl), prepared by the reaction of 1 with *p*-cyanophenol and triethylamine, confirmed the structure of 1, in addition to providing information on the conformation of the cyclopropanesulfonyl group.[15] After completion of this work we learned of Block and co-workers'[4] independent preparation of 1 by chlorination of cyclopropyl disulfide; the NMR spectra of their sample and ours agree.

Reaction of 1 with either (a) triethylamine in D_2O–1,2-dimethoxyethane (followed by potassium hydroxide in the workup) or (b) sodium deuteroxide (1 M) in D_2O gave the corresponding α-deuterated cyclopropanesulfonate salt (8),



8 a) M = K b) M = Na

as would be expected from the intermediate sulfene (2). These salts were readily converted into the deuterated sulfonyl chloride (9) which in turn on reaction with trialkylamines and 2-propanol led to the results shown in Scheme III; control experiments showed that neither the ester (10) nor the amides (11) exchanged α-hydrogens under the reaction conditions. We note the following features of these experiments: (a) triethylamine reacts 5 times (or more) faster than trimethylamine; (b) the exchanged ester (10) without any detectable isopropyl cyclopropanesulfonate-*1-d* is formed as the major product in the reaction with triethylamine; (c) the *exchanged* amide (11, R = Et) is the only *N,N*-diethyl sulfonamide isotopomer in evidence and the *unexchanged* amide (12, R = Me) the only detected *N,N*-dimethyl sulfonamide. The lack of any sign of isopropyl cyclopropanesulfonate-*1-d* or of the [3]betylate[16] (6, B = Me_3N, R = Pr^i) clearly excludes significant involvement of either path c or path d. The formation of the exchanged ester (10) suggests path a but does not, in itself, prove it, since 10 could conceivably arise by way of path b, specifically via 9 → 14 → 15 → 13 → 10. Some credence for the latter route is lent by the formation of the sulfonamides (11 and 12) since these may be presumed to have been formed from the sulfonylammonium salts (13 and 14); there is ample evidence for such species (a) being formed either by direct displacement reactions from sulfonyl chlorides or by trapping of sulfenes and (b) undergoing facile H–D exchange at the α-carbon.[17] Closer analysis of the trimethylamine reaction shows that the non-sulfene route through the sulfonylammonium salt does not account for the D-substitution results. Production of 12 (R = Me) as the major product requires that the H–D exchange (14 → 13) be slow relative to the conversion 14 → 12, whereas the formation of 10 by direct displacement on 13 would require that the exchange be fast; these are clearly incompatible requirements. Both 10 and 12 could arise from the sulfonylammonium salt 14, however, if the ester were formed, not by direct displacement at the sulfur but by elimination to form the sulfene, i.e. via 9 → 14 → 2 → 10. It would appear then that the sulfene is, in fact, formed in the reaction of 9 (and presumably 1) with trimethylamine, but that it is a minor process (<15%

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(13) Gaoni, Y. *Tetrahedron Lett.* **1988**, 1591–1594.
(14) Truce, W. E.; Lindy, L. B. *J. Org. Chem.* **1961**, *26*, 1463–1467.
(15) King, J. F.; Lam, J. Y. L.; Payne, N. C. Unpublished results.
(16) King, J. F.; Loosmore, S. M.; Aslam, M.; Lock, J. D.; McGarrity, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 7108–7122.
(17) King, J. F.; du Manoir, J. R. *J. Am. Chem. Soc.* **1975**, *97*, 2566–2567. King, J. F.; Skonieczny, S.; Khemani, K. C.; Lock, J. D. In *Nucleophilicity*; Harris, J. M., Manus, S. P., Eds.; *Advances in Chemistry Series*, No. 215; American Chemical Society: Washington, 1987; pp 385–398.

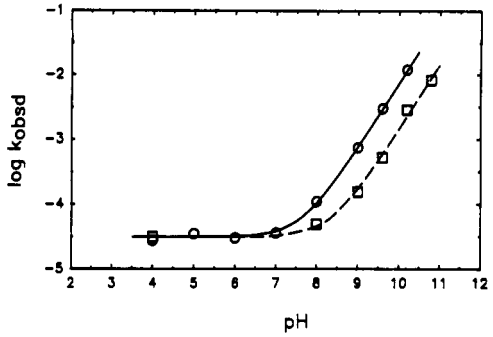


Figure 1. pH–rate profiles for the hydrolysis of cyclopropanesulfonyl chloride (1) (circles and solid line) and cyclopropanesulfonyl-*1-d* chloride (9) (squares and broken line) in 0.1 M KCl at 25.0 °C. The lines are calculated from $k_{obsd} = k_{OH}[OH^-]$, with k_w 3.1 × 10^{-5} s^{-1}, k_{OH} for 1, 180 M^{-1} s^{-1}, and k_{OH} for 9, 35 M^{-1} s^{-1}; the points are experimental.

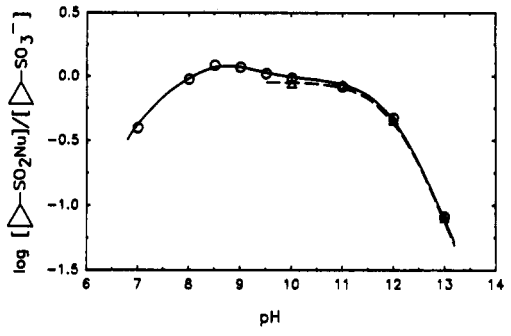
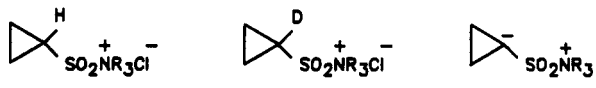


Figure 2. pH–product ratio profiles for the reaction of cyclopropanesulfonyl chloride (1) with nucleophiles (Nu^-): (a) solid line and circles, Nu^- = 2-chlorophenoxide anion with NuH_T = [2-chlorophenol] + [2-chlorophenoxide] = 0.05 M; (b) broken line and triangles, Nu^- = $CH_3SO_2N^-Ph$, with [methanesulfonanilide anion] = 0.05 M. Calculation of the lines is detailed in ref 21; the points are experimental.

of the total reaction) and **2** may be formed by either (or both) of two routes (i) **9** → **14** → **2** or (ii) direct elimination, **9** → **2**.



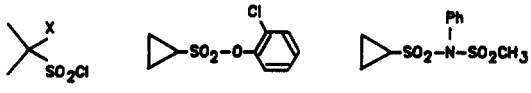
13 **14** **15**

With triethylamine, on the other hand, it is most likely that the direct formation of the sulfene **2** is the major path. Triethylamine is both a stronger base and a poorer nucleophile[18] than trimethylamine; the faster rate of reaction of triethylamine and the formation of the exchanged ester **10** are most compatible with the direct sulfene process. The amide (**11**, R = Et) may arise either via **9** → **2** → **15** → **13** → **11** or by way of **9** → **14** → **15** → **13** → **11**.

It was clear at this point that the reactions of cyclopropanesulfonyl chloride (**1**) were potentially complex and that kinetic studies with related trapping experiments might help to clarify the picture. Those carried out in aqueous media have given the more straightforward set of results and will be described first. As has been noted above, reaction of **1** with 1 M NaOD in D_2O gave **8b**. Unreacted **1** recovered after partial reaction was completely undeuterated, and cyclopropanesulfonate anion does not exchange its α-hydrogen under these conditions. There appears to be no credible intermediate species derived by addition of OD^- to **1** which would lead to (a) H–D exchange and (b) formation of **8b**, and we conclude that this reaction very probably proceeds by direct formation of the sulfene **2**.

In complete accord with this picture were the results obtained by measuring the rates of the hydrolysis of **1** and cyclopropanesulfonyl-*1-d* chloride (**9**), as a function of pH. The observed pseudo-first-order rate constants, k_{obsd}, obtained by the pH-stat technique, gave the plot, shown in Figure 1, with the two characteristic features already observed with alkanesulfonyl chlorides,[2] namely, (a) a curve deriving from an equation of the form $k_{obsd} = k_w + k_{OH}[OH]$, with (b) identical k_w values for both the undeuterated and α-deuterated substrates (**1** and **9**), and (c) a sizeable kinetic isotope effect (KIE) in the hydroxide-promoted reactions. The rate constants so obtained (at 25.0 °C in 0.1 M KCl) for **1** and **9** were k_w, 3.1 × 10^{-5} s^{-1}; k_{OH} for **1**, 180 M^{-1} s^{-1}; k_{OH} for **9**, 35 M^{-1} s^{-1}; k_H/k_D for the hydroxide-promoted reactions, 5.1; pH_i (the pH at which $k_w = k_{OH}[OH^-]$): for **1**, 7.24; for **9**, 7.95. For comparison the corresponding rate constants for 2-propanesulfonyl and 2-propanesulfonyl-*2-d* chlorides (**16a** and **16b**) are[2] k_w, 3.8 × 10^{-5} s^{-1}, k_{OH} for **16a**, 120 M^{-1} s^{-1}; k_{OH} for **16b**, 30 M^{-1} s^{-1}; k_H/k_D for **16**, 4.0.

The k_w terms, which are important in these examples below pH 7.0, clearly refer to the usual hydrolysis process observed by previous workers at uncontrolled pH (cf. ref 4). The mechanism assigned to this is a simple direct displacement at sulfur (S_N2-S) by water. In accord with this the deuterated sulfonyl chloride **9** at pH 4–6 gave (after neutralization with sodium hydroxide) only the deuterated salt **8**. A solvent kinetic isotope effect has been observed in the hydrolysis of methanesulfonyl and benzenesulfonyl chlorides,[19] pointing to general base catalysis by a second water molecule[20] with these substrates and presumably with **1** as well.



18 a) X = H, b) X = D **17** **18**

The sizeable primary KIE of the k_{OH} term agrees well, of course, with the intermediacy of the sulfene **2**, formed by the E2, or perhaps the irreversible E1cB, reaction (cf. ref 2). To confirm this picture we examined the product ratio, as a function of pH, of the reaction of **1** with 2-chlorophenol to form a mixture of 2-chlorophenyl cyclopropanesulfonate (**17**) and the cyclopropanesulfonate anion **7**. The pH–product ratio profiles for this reaction and for the corresponding reaction of **1** with methanesulfonanilide to form **18** are shown in Figure 2.

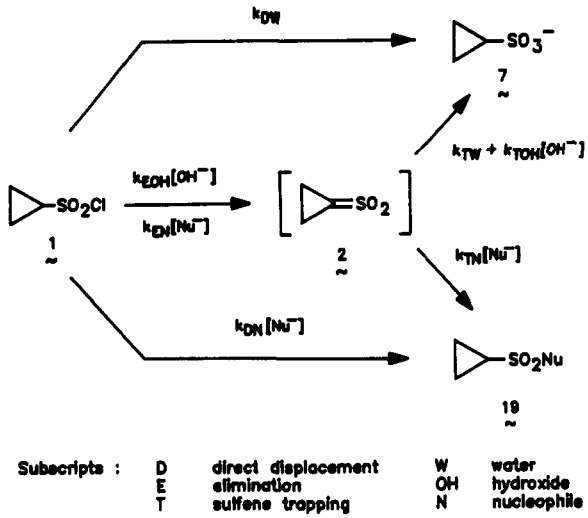
Again the results agree with sulfene mechanism. The curves are qualitatively similar to those already reported[2]

(18) Closely analogous to the reaction **9** → **14** (or **1** → **13**) is that between *p*-toluenesulfonyl chloride and trialkylamines. With trimethylamine reaction occurs immediately upon mixing (to form $ArSO_2NMe_3^+Cl^-$ which then goes to $ArSO_2NMe_2$), whereas with triethylamine little or no reaction is in evidence even after 1 h (as judged in both cases by their ^1H NMR spectra in $CDCl_3$). Cf.: Horner, L.; Nickel, H. *Liebigs Ann. Chem.* **1955**, *597*, 20–47, and also Jones, L. W.; Whalen, H. F. *J. Am. Chem. Soc.* **1925**, *64*, 1343–1352.

(19) Robertson, R. E.; Laughton, P. M. *Can. J. Chem.* **1957**, *35*, 1319–1324.

(20) King, J. F.; Khemani, K. C. *Can. J. Chem.* **1989**, *67*, 2162–2172.

Scheme IV



for the same nucleophiles with methanesulfonyl chloride and are quantitatively accounted for by the same mechanism (cf. ref 2), which is shown in Scheme IV for the specific case of the reactions of 1.[21] In the pH range 7–9.5 the increase in the proportion of the ester 17 arises chiefly from the increase in the concentration of the 2-chlorophenoxide anion in the pH range close to its pK_a (8.48); above pH_i (7.24) this is accompanied by sulfene formation leading to formation of a mixture of the ester 17 and the salt 7. Between pH 9.5 and 12 sulfene formation dominates and the product ratio reflects the competition between water and the aryl oxide anion in the trapping of the sulfene 2. Above pH 12 trapping of 2 by hydroxide to form 7 becomes increasingly important, leading to a sharp drop in the product ratio, [17]/[7]. The curve for the methanesulfonanilide reaction (which was measured only for the pH range 10–13) is similar and yields the same value (110 M^{-1}) for k_{TOH}/k_{TW}, the ratio of the rate constants for trapping of 2 by hydroxide and water.

Returning to the reactions in an organic medium we measured the rates of reaction of 1 and 9, plus some analogues for comparison, with triethylamine and 2-propanol in dichloromethane at 20.0 °C (see Table I). Two features of these results stand out. First, the KIE's for these species are very small: 1.4 for cyclopropanesulfonyl chloride, 1.2 for 16, and 1.0 for ethanesulfonyl chloride.[24] Although there is ample evidence to indicate that the sulfene is formed under these conditions with the simple alkanesulfonyl chlorides,[5] this result prompted a specific test. We found that $CH_3CD_2SO_2Cl$ with triethylamine and 2-propanol in dichloromethane under these conditions gave a good yield of the ester estimated from ^1H and ^{13}C NMR to consist of >99% of the monodeuterated isotopomer, $CH_3CHDSO_2OPr^i$. This clearly points to the intermediacy of the sulfene, which in turn requires a mechanism of formation yielding a very low KIE. Within this framework the KIE of 1.4 for the cyclopropanesulfonyl chloride reaction is entirely consistent with direct formation of 2.

The second notable result in Table I is the change in the relative rates of 1 vs 2-propanesulfonyl chloride (16a) with change in conditions. Whereas the specific rates of sulfene formation were only slightly different with hydroxide ion in water (180 M^{-1} s^{-1} for 1, 120 M^{-1} s^{-1} for 16a), with triethylamine in dichloromethane 16a reacts about 100 times faster than 1. It is our view that both the sharp change in rate constant ratios and the drop in KIE's with the change from hydroxide–water to triethylamine–dichloromethane, are probably best accommodated by the variable transition-state picture. Previous work has provided a basis for regarding sulfene formation from sulfonyl chlorides as an E1cB-like E2 reaction.[2,5] In the triethylamine–dichloromethane reaction the low KIE is consistent with a transition state in which the C–H bond is almost completely broken. If this were accompanied by a substantial formation of the sulfene double bond, one would expect to see signs of considerable ring strain deriving from conversion of an sp^3 carbon in a three-membered ring into sp^2; this would result in a slower reaction of 1 vs 16a. With hydroxide in water, on the other hand, the formation of sulfenes is less exothermic and the reaction may be expected to have a less "product-like" transition state. The KIE points to a roughly half-broken C–H bond, and the approximately equal values of k_{OH} for 1 and 16a suggest a rather delicate balance between the extra energy in the transition state for formation of 2 arising from angle strain and the greater intrinsic acidity of cyclopropyl hydrogens relative to the C-2 hydrogens in propane.[25]

With regard to the question of the formation of 2 from 1 we may conclude from the above discussion that there is a very strong basis for believing that the reaction of 1 with hydroxide in water yields 2 which then reacts as a conventional sulfene. For the reaction of 1 with triethylamine in dichloromethane there is good but not overwhelming evidence for the intermediacy of 2. Trying another approach to confirm the formation of 2, we explored the reaction of 1 with base in the presence of an enamine (20), which, if the reaction were to proceed in the most usual way for sulfenes, would lead to 21, probably in a stepwise pathway via 22 (cf. ref 5b, especially pp 736–737 and sources cited) (Scheme V).

(21) The solid line in Figure 2 is calculated from the following: $[RSO_2Nu]/[7] = (k_{DN}[Nu^-] + a[Nu^-]k_{TN}/k_{TW})/\{k_{DW} + a(1 + [OH^-]k_{TOH}/k_{TW})\}$ where $a = (k_{EOH}[OH^-] + k_{EN}[Nu^-])/(1 + [OH^-]k_{TOH}/k_{TW} + [Nu^-]k_{TN}/k_{TW})$. Parameters and their origins: (a) k_{DW} 3.1×10^{-5} s^{-1}, k_{EOH} 180 M^{-1} s^{-1}, i.e. the measured values of k_W and k_{OH}, respectively; (b) the sum $k_{DN} + k_{EN} = k_N = 2.2 \times 10^{-2}$ M^{-1} s^{-1}, determined by kinetic measurements at pH 7.5 and 7.8 with Nu_T = [2-chlorophenol] + [2-chlorophenoxide] = 0.05 M; the ratio k_{DN}/k_{EN}, and hence k_{DN} 0.015 M^{-1} s^{-1} and k_{EN} 7×10^{-3} M^{-1} s^{-1}, was obtained by manual fitting of the curve in the pH range 6–9; (c) k_{TOH}/k_{TW} 110 M^{-1}, derived from the pH–yield profile for the reaction of 1 with 2-chlorophenoxide and methanesulfonanilide anions (see Figure 2); (d) $k_{TN}/k_{TW} = 19$ for 2-chlorophenoxide and 18 for methanesulfonanilide, both from manual curve fitting of the product ratios (Figure 2) in the range pH 10–11. (e) $[Nu^-]$ from $[Nu^-] = K_aNu_T/([H^+] + K_a)$ where the total concentration of the nucleophile ($Nu_T = [Nu^-] + [NuH]$) and K_a is the acid dissociation constant, 3.31×10^{-9} M for 2-chlorophenol[22] and 1.05×10^{-9} M for methanesulfonanilide.[23]

(22) Albert, A.; Serjeant, E. P. *Ionization Constants of Acids and Bases*; Methuen & Co.: London, 1962.

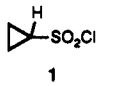
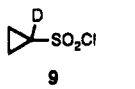
(23) King, J. F. In *The Chemistry of Sulphonic Acids and their Derivatives*; Patai, S., Rappoport, Z., Eds.; J. Wiley and Sons Ltd: Chichester, England, 1991; Chapter 6, pp 249–259.

(24) We have not measured the specific rate for CH_3CHDSO_2Cl; the observed value for $CH_3CD_2SO_2Cl$ may well reflect a cancellation of (small positive) primary and (small negative) secondary KIE's.

(25) The *kinetic* acidity of the α-hydrogen of a cyclopropylsulfonyl group is such as to lead to H–D exchange rates roughly 30–50 times greater than those of the 2-propylsulfonyl analogues.[26] The *equilibrium* acidities, however, appear to be either approximately equal[27] or, in the case of the trifluoromethyl sulfones, greater for the 2-propyl sulfone than for the cyclopropyl (pK_a's in DMSO:[28] $(CH_2)_2CHSO_2CF_3$, 26.6; $(CH_3)_2CHSO_2CF_3$, 21.8). These features may be rationalized in terms of the extent of carbon–sulfur double bond character in the transition states or anions and may serve to provide further examples of the considerable variation in energy with what must be small changes in structure that characterize anionic species in the cyclopropylsulfonyl and related systems.

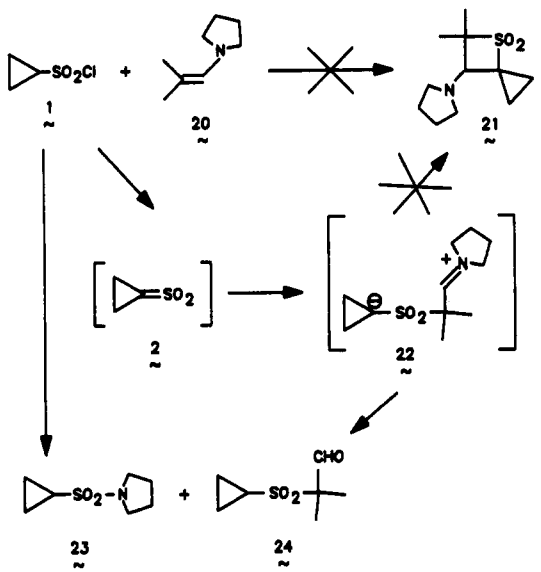
(26) Van Wijnen, W. T.; Steinberg, H.; De Boer, T. J. *Tetrahedron* 1972, *28*, 5423–5432. Kirmse, W.; Mrotzeck, U. *J. Chem. Soc., Chem. Commun.* 1987, 709–710.

Table I. Rate Constants for the Reaction of Alkanesulfonyl Chlorides with Triethylamine and 2-Propanol in Dichloromethane[a]

RSO_2Cl	Et_3N/M	2-propanol/M	k_{obsd}/s^{-1} [a]	$k_2/M^{-1}\,s^{-1}$ [b]	k_H/k_D
$CH_3CH_2SO_2Cl$	0.005	0.2	1.05×10^{-3}	2.1×10^{-2}	
					1.0
$CH_3CD_2SO_2Cl$	0.005	0.2	1.05×10^{-3}	2.1×10^{-2}	
$(CH_3)_2CHSO_2Cl$ **16a**	0.04	1.0	6.96×10^{-3}	1.7×10^{-2}	
					1.2
$(CH_3)_2CDSO_2Cl$ **16b**	0.04	1.0	5.78×10^{-4}	1.4×10^{-2}	
 **1**	1.0	1.0	2.60×10^{-4}	2.6×10^{-4}	
					1.4
 **9**	1.0	1.0	1.86×10^{-4}	1.9×10^{-4}	

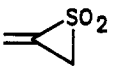
[a] At 20.0 °C; initial concentration of RSO_2Cl, 0.001 M. [b] $k_2 = k_{obsd}/[Et_3N]$.

Scheme V



In our hands **1** with **20** and with either (a) triethylamine in dichloromethane (followed by aqueous workup) or (b) dilute aqueous NaOH (initial pH 10) gave cyclopropanesulfonpyrrolidide (**23**) and the aldehyde **24**, the latter most likely arising as a result of protonation of **22** (with Et_3NH^+ or H_2O) precluding cyclization to **21**. Block et al.[4] found evidence that formation of a strained sulfene–enamine adduct is possible in the absence of a proton source. They observed that the reaction of 1-(trimethylsilyl)cyclopropanesulfonyl chloride with CsF and 1-(*N*,*N*-diethylamino)-1-propyne gave the spiro adduct expected from reaction of the ynamine with **2**; their attempts to prepare the same adduct from **1**, triethylamine, and an excess of the ynamine were unsuccessful.

The present study may be taken with that of Block and co-workers to provide a good case for the following picture: (a) cyclopropanethione *S*,*S*-dioxide (**2**) is formed as a short-lived intermediate by precedented pathways from either **1** or 1-(trimethylsilyl)cyclopropanesulfonyl chloride and (b) **2** reacts at room temperature to give products appropriate to a sulfene with no sign of any isomerization to methylenethiirane *S*,*S*-dioxide (**25**). According to the ab initio MO calculations of Block, Schwan, and Dixon,[4] **25** is more stable than **2** by 0.2 kcal mol^{-1}; formation of **25** from **2** has not been excluded, however, and may well appear in other circumstances, e.g. under the conditions of flash thermolysis.



25

Experimental Section

General. ^1H NMR spectra were obtained with a Varian XL200 or Germini-200 spectrometer and ^{13}C NMR spectra with either a Varian XL300 or the Gemini instrument; spectra of $CDCl_3$ solutions were calibrated with Me_4Si and those of D_2O solutions with sodium (trimethylsilyl)propanesulfonate. Mass spectra were run on a Finnigan MAT 8230 instrument using electron impact except where otherwise noted and infrared spectra on a Bruker IFS 32 FTIR spectrometer using NaCl plates for neat liquids or KBr pellets for solid samples. Melting points were determined on a Reichert hot stage and are uncorrected.

1,2-Dimethoxyethane (DME) and tetrahydrofuran (THF) were dried by distillation from CaH_2; CH_2Cl_2 was dried by distillation from P_2O_5. $AgNO_3$ was dried in an oven before weighing. The simple alkanesulfonyl chlorides, their α-deuterated isotopomers, and methanesulfonanilide were obtained and purified as described previously.[2] 2-Chlorophenol was reagent-grade distilled before use. Standard sodium hydroxide solution (0.1 M, Fisher) was used as supplied or diluted appropriately. Butyllithium was the 1.6 M solution in hexanes supplied by Aldrich Chemical Co. Unless otherwise stated, other solvents and reagents were reagent-grade commercial materials used as supplied. Solvent evaporation after extraction was carried out under reduced pressure using a Büchi Rotovap apparatus.

Butyl 3-Chloro-1-propanesulfonate. Triethylamine (21.0 g, 0.2 mol) in CH_2Cl_2 (10 mL) was added to a stirred, ice-cooled solution of 3-chloro-1-propanesulfonyl chloride[16] (18.3 g, 0.1 mol) and 1-butanol (9.2 g, 0.12 mol) in CH_2Cl_2 (150 mL), and stirring was continued for 20 min. The mixture was washed (aqueous HCl) and dried ($MgSO_4$), and the solvent was evaporated. The residue was distilled under reduced pressure to give $Cl(CH_2)_3SO_2O(CH_2)_3CH_3$ (16.8 g, 76% yield) as a pale yellow oil: bp 150 °C (2.0 Torr); IR ν_{max} 1171, 1360, 2876, 2965 cm^{-1}; ^1H NMR δ 1.0 (t, 3 H), 1.5 (sextet, 2 H), 1.8 (quintet, 2 H), 2.4 (quintet, 2 H), 3.3 (t, 2 H), 3.7 (t, 2 H), 4.2 (t, 2 H); ^{13}C NMR δ 13.5, 18.7, 26.8, 31.1, 42.5, 47.3, 70.0. Similarly prepared were the following: (a) **2-propyl 3-chloro-1-propanesulfonate**, from 3-chloro-1-propanesulfonyl chloride (0.5 g, 2.8 mmol), 2-propanol (0.2 g, 3.3 mmol), Et_3N (0.6 g, 6.0 mmol), in 85% yield: bp 150 °C (0.01 Torr); IR ν_{max} 1171, 1345, 2988 cm^{-1}; ^1H NMR δ 1.4 (d, 6 H), 2.3 (quintet, 2 H), 3.2 (t, 2 H), 3.7 (t, 2 H), 4.9 (septet, 1 H); ^{13}C NMR δ 23.3, 27.0, 42.8, 48.8, 77.3. (b) **3-Chloro-1-propanesulfonpyrrolidide**, from pyrrolidine (0.25 g, 3.5 mmol), Et_3N (0.8 g, 7.9

mmol), 3-chloropropanesulfonyl chloride (0.5 g, 2.8 mmol), in 65% yield: mp 80–81 °C (ethanol); IR ν_{max} 1138, 1329 cm^{-1}; ^{1}H NMR δ 1.9 (t, 4 H), 2.3 (quintet, 2 H), 3.1 (t, 2 H), 3.3 (t, 4 H), 3.7 (t, 2 H); ^{13}C NMR δ 25.9, 26.5, 43.1, 46.4, 47.7. (c) **N,N-Dimethyl-3-chloropropanesulfonamide**, from dimethylamine (0.15 g, 3.3 mmol), Et_3N (0.8 g, 7.8 mmol), 3-chloropropanesulfonyl chloride (0.5 g, 2.8 mmol), in 95% yield: bp 170 °C (0.05 Torr); IR ν_{max} 1146, 1333, 2961 cm^{-1}; ^{1}H NMR δ 2.3 (quintet, 2 H), 2.9 (s, 6 H), 3.1 (t, 2 H), 3.7 (t, 2 H); ^{13}C NMR δ 26.5, 37.7, 43.3, 45.4. (d) **N,N-Diethyl-3-chloropropanesulfonamide**, from diethylamine (0.25 g, 3.4 mmol), Et_3N (0.8 g, 7.8 mmol), 3-chloropropanesulfonyl chloride (0.5 g, 2.8 mmol), in 91% yield: bp 180 °C (0.05 Torr); IR ν_{max} 1142, 1327, 2977 cm^{-1}; ^{1}H NMR δ 1.2 (t, 6 H), 2.2 (quintet, 2 H), 3.0 (t, 2 H), 3.2 (q, 4 H), 3.6 (t, 2 H); ^{13}C NMR δ 14.3, 26.7, 41.5, 43.0, 49.2. (e) **2-Propyl ethanesulfonate**, from ethanesulfonyl chloride (0.5 g, 3.9 mmol), 2-propanol (0.25 g, 4.2 mmol), Et_3N (1.0 g, 10.0 mmol), in 60% yield: bp 90 °C (0.01 Torr); IR ν_{max} 1169, 1347, 2988 cm^{-1}; ^{1}H NMR δ 1.4 (t, 3 H), 1.4 (d, 6 H), 3.0 (q, 2 H), 4.9 (septet, H); ^{13}C NMR δ 8.2, 23.1, 45.7, 76.3.

3-Chloropropyl Isopropyl Sulfone. 3-Chloropropyl isopropyl sulfide was prepared (as described for the phenyl analogue[27a]) from 2-propanethiol (5.0 g, 65.8 mmol), 1-bromo-3-chloropropane (10.4 g, 66.2 mmol), and NaOH (2.9 g in 100 mL H_2O), in 64% yield: ^{1}H NMR δ 1.27 (d, 6 H), 2.03 (quintet, 2 H), 2.69 (t, 2 H), 2.93 (septet, 1 H), 3.66 (t, 2 H); ^{13}C NMR δ 23.3, 27.3, 32.4, 34.8, 43.6. 3-Chloropropyl isopropyl sulfone was prepared (cf. reference) from 3-chloropropyl isopropyl sulfide (5.0 g, 32.8 mmol), glacial acetic acid (80 mL), and H_2O_2 (10 g, 50%) in 48% yield: IR ν_{max} 1121, 1302 cm^{-1}; ^{1}H NMR δ 1.42 (d, 6 H), 2.35 (quintet, 2 H), 3.12 (m, 3 H), 3.72 (t, 2 H); ^{13}C NMR δ 15.2, 24.4, 43.1, 46.1, 53.4.

1-Butyl Cyclopropanesulfonate (5, R = Bu). Solutions of 1-butyl 3-chloro-1-propanesulfonate (12.5 g, 58.3 mmol) and of butyllithium (2.5 M, 24.0 mL) (both in THF) were added simultaneously to dry ice–acetone cooled THF (600 mL) with stirring under nitrogen. After addition was complete, the solution was allowed to warm up to 0 °C and then quenched with water (2 mL). The THF was removed under reduced pressure and the residue extracted with CH_2Cl_2. The extract was washed with water and dried ($MgSO_4$) and the solvent removed to give 1-butyl cyclopropanesulfonate (9.3 g, 90% yield) which was used for next-step synthesis without further purification. A sample was distilled in the cold-finger apparatus to give a pale yellow oil: bp 60 °C (2.0 Torr); IR ν_{max} 1169, 1354, 2965, 2876 cm^{-1}; ^{1}H NMR δ 1.0 (t, 3 H), 1.1 (m, 2 H), 1.3 (m, 2 H), 1.5 (sextet, 2 H), 1.8 (quintet, 2 H), 2.5 (m, 1 H), 4.2 (t, 2 H); ^{13}C NMR δ 5.5, 13.5, 18.7, 27.4, 31.2, 70.2. Similarly prepared were the following: (a) **2-propyl cyclopropanesulfonate (10)** from 2-propyl 3-chloro-1-propanesulfonate (0.5 g, 2.8 mmol), butyllithium (1.6 M, 10 mL), in 80% yield: bp 80 °C (0.01 Torr); IR ν_{max} 1173, 1352, 2988 cm^{-1}; ^{1}H NMR δ 1.0–1.4 (m, 4 H), 1.4 (d, 6 H), 2.4 (tt, 1 H), 4.9 (septet, 1 H); ^{13}C NMR δ 5.8, 23.4, 28.7, 77.1. (b) **Cyclopropanesulfonpyrrolidide (23)**, from butyllithium (1.6 M, 5 mL), 3-chloropropanesulfonpyrrolidide (0.3 g, 1.4 mmol), in 73% yield: bp 170 °C (0.05 Torr); IR ν_{max} 1148, 1333 cm^{-1}; ^{1}H NMR δ 1.0 (m, 2 H), 1.2 (m, 2 H), 2.0 (t, 4 H), 2.4 (tt, 1 H), 3.4 (t, 4 H); ^{13}C NMR δ 4.2, 25.5, 25.9, 47.7; exact mass calculated for $C_7H_{13}NO_2S$ 175.0667, found 175.0671. (c) **N,N-Diethylcyclopropanesulfonamide (11)**, from butyllithium (1.6 M, 5 mL), N,N-diethyl-3-chloropropanesulfonamide (0.4 g, 1.9 mmol), in 75% yield: bp 160 °C (0.05 Torr); IR ν_{max} 1142, 1329, 2936 cm^{-1}; ^{1}H NMR δ 0.9 (m, 2 H), 1.1 (m, 2 H), 1.2 (t, 6 H), 2.2 (tt, 1 H), 3.3 (q, 4 H); ^{13}C NMR δ 5.2, 14.4, 29.7, 41.8; exact mass calculated for $C_7H_{15}NO_2S$ 177.0824, found 177.0823. (d) **N,N-Dimethylcyclopropanesulfonamide (12)**, from butyllithium (1.6 M, 5 mL), N,N-dimethyl-3-chloropropanesulfonamide (0.4 g, 2.2 mmol), in 78% yield: bp 150 °C (0.05 Torr), IR ν_{max} 1335, 1146, 2959 cm^{-1}; ^{1}H NMR δ 1.0 (m, 2 H), 1.1 (m, 2 H), 2.2 (tt, 1 H), 2.8 (s, 6 H); ^{13}C NMR δ 4.2, 24.9, 38.2; exact mass calculated for $C_5H_{11}NO_2S$ 149.0511, found 149.0508. (e) **Cyclopropyl isopropyl sulfone**, from butyllithium (1.6 M, 17 mL), 3-chloropropyl isopropyl sulfone (2.5 g, 13.6 mmol), in 95% yield: IR ν_{max} 1130, 1293 cm^{-1}; ^{1}H NMR δ 1.00–1.10 (m, 2 H), 1.20–1.25 (m, 2 H), 1.43 (d, 6 H), 2.36 (tt, 1 H), 3.17 (septet, 1 H); ^{13}C NMR δ 4.2, 15.5, 26.1, 53.9.

Potassium Cyclopropanesulfonate (7a). A solution of 1-butyl cyclopropanesulfonate (5, R = Bu) (9.3 g, 52.2 mmol), potassium thiocyanate (5.25 g, 54.1 mmol) in DME (200 mL), and water (200 mL) was refluxed for 24 h. The solution was washed with Et_2O (2 × 100 mL) and concentrated to 15 mL under reduced pressure at 100 °C. Cold absolute ethanol (45 mL) was then added to precipitate the crystalline cyclopropanesulfonate (7a) (6.2 g, 74% yield) which was collected in a Buchner funnel and washed with cold absolute ethanol. The filtrate was concentrated and absolute ethanol added to obtain more 7a (2.3 g); total yield of 7a, 88.0%: mp 332–334 °C; IR ν_{max} 1186, 1240, 3100, 3021 cm^{-1}; ^{1}H NMR δ 0.9 (m, 4 H), 2.4 (m, 1 H); ^{13}C NMR δ 7.8, 32.0.

Cyclopropanesulfonyl Chloride (1). A solution of potassium cyclopropanesulfonate (7a) (5.9 g, 37 mmol), thionyl chloride (30 mL), and DMF (5 drops) was refluxed at 60 °C for 10 h and worked up as previously described[2] to give cyclopropanesulfonyl chloride (1) (3.0 g, 60% yield) as a pale yellow liquid: bp 60 °C (2.0 Torr); IR ν_{max} 1046, 1159, 1196, 1250, 3065 cm^{-1}; ^{1}H NMR δ 1.4 (m, 2 H), 1.6 (m, 2 H), 3.3 (m, 1 H); ^{13}C NMR δ 9.2, 43.2.

Cyclopropanesulfon-p-toluidide. Triethylamine (0.32 g, 3.2 mmol) in CH_2Cl_2 (5 mL) was added to a stirred, ice-cooled solution of 1 (150 mg, 1.1 mmol) and p-toluidine (0.16 g, 1.5 mmol) in CH_2Cl_2 (30 mL), and the mixture was refluxed for 24 h. The mixture was then washed (aqueous H_2SO_4) and dried ($MgSO_4$), the solvent evaporated, and the residue recrystallized (ethyl acetate–pentane) to give colorless crystals of cyclopropanesulfon-p-toluidide (150 mg, 64% yield): mp 80 °C; IR ν_{max} 1148, 1325, 3058, 3254 cm^{-1}; ^{1}H NMR δ 1.0 (m, 2 H), 1.2 (m, 2 H), 2.3 (s, 3 H), 2.5 (tt, 1 H), 6.5 (s, 1 H, NH), 7.2 (s, 4 H); ^{13}C NMR δ 5.6, 20.9, 29.6, 122.5, 130.0, 134.0, 135.6; exact mass calculated for $C_{10}H_{13}O_2SN$ 211.0667, found 211.0671. Similarly prepared were the following: (a) **p-cyanophenyl cyclopropanesulfonate (5, R = p-cyanophenyl)**, from p-hydroxybenzonitrile (0.3 g, 2.5 mmol), Et_3N (0.6 g, 5.9 mmol), 1 (0.3 g, 2.1 mmol), in 80% yield: mp 62 °C (Et_2O); IR ν_{max} 1171, 1393, 2238 cm^{-1}; ^{1}H NMR δ 1.2–1.4 (m, 4 H), 2.7 (tt, 1 H), 7.3 (d, 2 H), 7.6 (d, 2 H); ^{13}C NMR δ 6.4, 28.2, 111.1, 117.7, 123.2, 134.0, 152.4. (b) **2-Chlorophenyl cyclopropanesulfonate (17)**, from 2-chlorophenol (0.22 g, 1.7 mmol), Et_3N (0.3 g, 3.0 mmol), 1 (0.2 g, 1.4 mmol), in 91% yield: bp 140 °C (0.05 Torr); IR ν_{max} 1171, 1374, 3167 cm^{-1}; ^{1}H NMR δ 1.1–1.3 (m, 4 H), 2.7 (tt, 1 H), 7.2–7.5 (m, 4 H); ^{13}C NMR δ 6.4, 28.7, 124.4, 127.2, 127.9, 128.0, 145.8; exact mass calculated for $C_9H_9ClO_3S$ 231.9961, found 231.9963. (c) **N-(Methanesulfonyl)cyclopropanesulfonanilide (18)**, from methanesulfonanilide (0.8 g, 4.7 mmol), Et_3N (0.8 g, 8 mmol), 1 (0.5 g, 3.6 mmol) in CH_2Cl_2 (10 mL), in 61% yield: mp 153–154 °C (ethanol); IR ν_{max} 1347, 1154 cm^{-1}; ^{1}H NMR δ 1.2 (m, 4 H), 3.2 (m, 1 H), 3.4 (s, 3 H), 7.4 (m, 5 H); ^{13}C NMR δ 6.5, 32.9, 42.8, 129.5, 130.4, 131.0, 134.1; exact mass calcd for $C_{10}H_{13}S_2O_4N$ 275.0286, found 275.0280.

Potassium Cyclopropanesulfonate-1-d (8a). To a stirred solution of D_2O (30 mL) and Et_3N (8.0 g, 79.2 mmol) in DME (30 mL) was added 1 (5.0 g, 35.6 mmol), and the mixture was stirred at room temperature for 24 h. Aqueous KOH (3.98 g, 71.2 mmol, in 5 mL of water) was added and the solution washed with ether. Evaporation of the water under reduced pressure gave potassium cyclopropanesulfonate-1-d (8a) (5.16 g, 90% yield): ^{1}H NMR δ 0.8, 1.0 (AB quartet, J = 10 Hz); ^{13}C NMR δ 7.8, 32.0 (t, J = 26 Hz) (est. >99% α-D).

Sodium Cyclopropanesulfonate-1-d (8b). A solution of sodium deuteroxide in D_2O (from Na, 2.4 g and D_2O, 10 mL) was added to a stirred, ice-cooled solution of 1 (5.0 g, 35.6 mmol) in DME (10 mL) and the mixture stirred at room temperature for 30 min. Dilute HCl was added to bring the pH to 7, and evaporation of the solvent gave sodium cyclopropanesulfonate-1-d (8b) (est. >99% α-D).

Cyclopropanesulfonyl-1-d Chloride (9). A solution of sodium or potassium cyclopropanesulfonate-1-d (8), thionyl chloride, and DMF (1%) was refluxed for 10 h, and after the

(27) (a) Zimmerman, H. E.; Thyagarajan, B. S. *J. Am. Chem. Soc.* **1960**, *82*, 2505–2511. (b) Ratajczak, A.; Anet, F. A. L.; Cram, D. J. *J. Am. Chem. Soc.* **1967**, *87*, 2072–2077. Jeffery, S. M.; Niedoba, S.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1992**, 650–652.

(28) Bordwell, F. G.; Vanier, N. R.; Matthews, W. S.; Hendrickson, J. B.; Skipper, P. L. *J. Am. Chem. Soc.* **1975**, *97*, 7160–7162.

usual workup gave cyclopropanesulfonyl-*1-d* chloride: IR ν_{max} 1368, 1173 cm^{-1}; ^{1}H NMR δ 1.3–1.6 (m, major signals at 1.4, 1.6); ^{13}C NMR δ 9.05, 42.87 (1:1:1 t, J = 28 Hz) (est. >99% α-D).

2-Propyl Cyclopropanesulfonate-*1-d*. Butyllithium (1.6 M, 8.0 mL) was added to a stirred dry ice–acetone cooled solution of 2-propyl cyclopropanesulfonate (0.5 g, 3.0 mmol) in THF (100 mL) and the mixture stirred for 10 min. The mixture, after addition of D_2O (5 mL), was allowed to warm to room temperature, the solvent was evaporated, and the residue was extracted with CH_2Cl_2 (50 mL) which was washed with water and dried ($MgSO_4$). Removal of solvent and distillation of the residue under reduced pressure gave 2-propyl cyclopropanesulfonate-*1-d* (0.3 g, 60% yield): bp 100 °C (0.01 Torr); IR ν_{max} 1175, 1343, 2988 cm^{-1}; ^{1}H NMR δ 1.0 (t, 2 H), 1.2 (t, 2 H), 1.4 (d, 6 H), 4.9 (septet, 1 H); ^{13}C NMR δ 5.6, 23.2, 28.2 (1:1:1 t, J = 27 Hz), 76.8 (est. >99% α-D). Similarly prepared was ***N,N*-diethylcyclopropanesulfonamide-*1-d***, from butyllithium (1.6 M, 9 mL), *N,N*-diethyl-3-chloropropanesulfonamide (1.2 g, 5.6 mmol) in 90% yield: bp 160 °C (0.05 Torr); ^{1}H NMR δ 0.9–1.1 (m, major signals at 0.9 and 1.1, 4 H), 1.2 (t, 6 H), 3.2 (q, 4 H); ^{13}C NMR δ 4.9, 14.2, 29.2 (1:1:1 t, J = 27 Hz), 41.4.

Kinetics. (a) Aqueous Medium. The pH-stat apparatus and procedure have been described.[10] The initial concentrations of the cyclopropanesulfonyl chloride and cyclopropanesulfonyl-*1-d* chloride varied from 3×10^{-4} to 5×10^{-4} M (added in DME) in 50 mL of 0.1 M aqueous KCl at 25.0 °C, with the reaction followed by titration with NaOH (0.1 M). With 2-chlorophenol (0.26 mL in 50 mL of aqueous KCl solution) as the added nucleophile, the initial concentration of 1 varied from 8×10^{-4} to 9×10^{-4} M; the 2-chlorophenoxide concentration was calculated from $[ArO^-] = [ArOH]_T/(1 + [H^+]/K_a)$, where $[ArOH]_T = [ArOH] + [ArO^-]$. The reactions were followed by titration with NaOH (0.1 M) and the end point determined by the infinity titre.

(b) In Dichloromethane. The general method is that previously described.[29] All stock solutions were precooled in a water bath kept at 20.0 °C by a Thermomix 1420 (B. Braun Melsungen AG). The sulfonyl chlorides (1×10^{-3} M), Et_3N, and 2-propanol were mixed at time t = 0. Aliquots of 25 mL were removed at intervals and quenched in aqueous HNO_3 (0.2 M). The chloride ion content determined potentiometrically by titration with 0.005 M $AgNO_3$ solution using a Sargent-Welch, pH 6000, digital display pH meter (on the mV operating mode) equipped with a silver electrode connected to the reference and an all range combination electrode (pH 1–14, Fisher). The second-order rate constant was obtained from $k_2 = k_{obsd}/[Et_3N]$.

Deuterium Substitution Experiments. (a) Hydrolysis. (i) A solution of cyclopropanesulfonyl-*1-d* chloride (**9**) (>97% α-D, 0.2 g, 1.4 mmol) in DME (1 mL) was injected into water (500 mL), and the mixture was stirred for 72 h with occasional addition of aqueous NaOH to maintain pH at 5 ± 1. The pH was then adjusted to 7 with aqueous NaOH. The water was evaporated, and the residue dried in oven (60 °C) for 24 h to give **8b**: ^{1}H NMR δ 0.8, 1.0 (AB quartet, J = 10 Hz); ^{13}C NMR δ 6.9, 30.8 (t, J = 27 Hz) (est. >97% α-D). In water (500 mL) at pH 10 (kept constant by adding aqueous NaOH), **9** (0.2 g, 1.4 mmol) in DME (1 mL) gave **7b**: ^{1}H NMR δ 0.9–1.0 (m, 4 H), 2.4 (tt, 1 H); ^{13}C NMR δ 6.9, 31.1 (est. <1% α-D). (ii) A solution of **1** (0.2 g, 1.4 mmol) in DME (0.5 mL) was injected into a solution of NaOD in D_2O (1 M, 5 mL) and DME (0.5 mL). The reaction mixture was quenched (aqueous H_2SO_4) after 10 s and extracted with CH_2Cl_2. The organic extract was dried ($MgSO_4$) and evaporated to give unreacted **1** (0.05 g, 25% yield): ^{1}H NMR δ 1.4 (m, 2 H), 1.6 (m, 2 H), 3.3 (tt, 1 H); ^{13}C NMR δ 9.2, 43.2 (est. <1% α-D). The aqueous portion was neutralized (aqueous NaOH) and evaporated. The white solid residue was triturated with absolute ethanol, the ethanol was evaporated, and the residue was dried (60 °C oven) to give **8b**: ^{1}H NMR δ 0.8, 1.0 (AB quartet, J = 10 Hz); ^{13}C NMR δ 7.8, 32.0 (1:1:1 t, J = 26 Hz) (est. >99% α-D).

(b) With an Added Nucleophile. Cyclopropanesulfonyl chloride (**1**) (0.1 g, 0.7 mmol) was added to a stirred solution of methanesulfonanilide (0.8 g, 4.7 mmol) and NaOD in D_2O (10 mL, pD = 11.4, maintained by pH-stat), and stirring was continued for 10 min. The reaction mixture was extracted with CH_2Cl_2 (50 mL), the organic extract was washed (10% NaOH) and dried ($MgSO_4$), and the solvent was evaporated to give *N*-(methanesulfonyl)cyclopropanesulfonanilide-*1-d* (0.11 g, 56% yield) as a white solid: ^{1}H NMR δ 1.1, 1.2 (AB quartet, J = 11 Hz, 4 H), 3.4 (s, 3 H), 7.4–7.5 (m, 5 H); ^{13}C NMR δ 6.4, 32.6 (1:1:1 t, J = 28 Hz), 42.8, 129.5, 130.4, 131.0, 134.1 (est. >97% α-D).

Reaction of Cyclopropanesulfonyl-*1-d* Chloride (9) with 2-Propanol in the Presence of Triethylamine. A solution of **9** (74.0 mg, 0.52 mmol, 0.0026 M) in CH_2Cl_2 (10 mL) was added to a stirred solution of Et_3N (10.0 g, 0.5 M) and 2-propanol (12.0 g, 1.0 M) in CH_2Cl_2 (190 mL) and stirred at 25 °C for 8 h. The reaction mixture was washed (dilute H_2SO_4, then water) and dried ($MgSO_4$), and the solvent was removed to give a brown oil (65 mg; ^{1}H NMR showing **9**:**10**:**11** in the ratio 2:7:1). It was distilled in vacuum to give pale yellow oil: ^{1}H NMR δ (a) **9**, 1.3 (t, 2 H), 1.6 (t, 2 H) (16.7% yield) (90% α-D); (b) **10**, 1.0–1.2 (m, 4 H), 1.4 (d, 6 H), 2.4 (tt, 1 H), 4.9 (septet, 1 H) (58.3% yield) (<1% α-D); (c) **11**, 1.0–1.2 (m, 4 H), 2.2 (tt, 1 H), 3.3 (q, 4 H) (8.3% yield) (<1% α-D); ^{13}C NMR δ (a) **9**, 5.7, 23.1, 28.5, 76.6; (b) **10**, 9.0, 42.8 (1:1:1 t, J = 28 Hz); (c) **11**, 5.0, 14.2, 29.5, 41.5.

Reaction of Cyclopropanesulfonyl-*1-d* Chloride with 2-Propanol in the Presence of Trimethylamine. A solution of **9** (0.2 g, 1.4 mmol, 0.0057 M) in CH_2Cl_2 (10 mL) was added to a stirred solution of 2-propanol (1.2 g, 20 mmol, 0.08 M) and Me_3N (1.2 g, 20 mmol, 0.08 M) in CH_2Cl_2 (240 mL), and stirring was continued at 25 °C for 36 h. The usual workup gave a brown oil (0.18 g; ^{1}H NMR showing **9**:**10**:**12** in the ratio 25:6:14): ^{1}H NMR δ (a) **9**, 1.3 (t, 2 H), 1.5 (t, 2 H) (48.9% yield) (96% α-D); (b) **10**, 1.0 (m, 2 H), 1.2 (m, 2 H), 1.4 (d, 6 H), 2.4 (tt, 1 H), 4.9 (septet, 1 H) (11.7% yield) (<1% α-D); (c) **12**, 0.9 (t, 2 H), 1.1 (t, 2 H), 2.8 (s, 6 H) (27.4% yield) (97% α-D); ^{13}C NMR δ (a) **9**, 9.0, 42.8 (1:1:1 t, J = 28 Hz); (b) **10**, 5.6, 9.1, 28.4, 76.8; (c) **12**, 3.9, 24.3 (1:1:1 t, J = 27 Hz), 37.9. The aqueous portion was evaporated and was dried (60 °C oven) to give a white salt: ^{1}H NMR δ 3.2 (s, $Me_4N^+Cl^-$), 2.9 (s, $Me_3NH^+Cl^-$); ^{13}C NMR δ 57.6 ($Me_4N^+Cl^-$), 47.1 ($Me_3NH^+Cl^-$).

Reaction of Ethanesulfonyl-*1,1-d*$_2$ Chloride with 2-Propanol in the Presence of Triethylamine. A solution of $CH_3CD_2SO_2Cl$ (0.1 g, 0.8 mmol) in CH_2Cl_2 was added to a stirred solution of 2-propanol (9.6 g, 0.16 mol), Et_3N (0.4 g, 4.0 mmol) in CH_2Cl_2 (400 mL), and stirring was continued for 12 h. The usual workup gave $CH_3CHDSO_2OPr^i$ (0.1 g, 85% yield) as a yellow oil: ^{1}H NMR δ 1.4 (d, 9 H), 3.0 (quartet of 1:1:1 triplets, 1 H), 4.9 (septet, 1 H); ^{13}C NMR δ 8.1, 23.1, 45.5 (1:1:1 t, J = 21 Hz), 76.3 (est. >99% mono D at C-1).

Reaction of 2-Propanesulfonyl-*1-d* Chloride with 2-Propanol in the Presence of Triethylamine. A solution of $(CH_3)_2CDSO_2Cl$ (0.12 g, 0.8 mmol) in CH_2Cl_2 (425 mL) was added to a stirred solution of NEt_3 (3.4 g, 0.03 mol) and 2-propanol (51 g, 0.85 mol) in CH_2Cl_2 (425 mL), and stirring was continued for 12 h. The reaction mixture was washed (dilute H_2SO_4) and dried ($MgSO_4$), and the solvent was evaporated to give 2-propyl 2-propanesulfonate ester (0.13 g, 94% yield) as a pale brown oil. A sample was distilled in a cold-finger apparatus to yield a colorless oil: bp 90 °C (0.05 Torr); IR ν_{max} 1159, 1343, 2988 cm^{-1}; ^{1}H NMR δ 1.4 (d, 12 H), 3.2 (septet, 1 H), 5.0 (septet, 1 H); ^{13}C NMR δ 16.6, 23.1, 52.5, 75.9 (est. <1% α-D).

H/D Exchange Control Experiments. (a) 2-Propyl Cyclopropanesulfonate-*1-d*. A solution of 2-propyl cyclopropanesulfonate-*1-d* (70 mg, 0.5 mmol, 0.000 25 M), triethylamine (10 g, 0.05 M), 2-propanol (12 g, 0.1 M), and triethylamine hydrochloride (0.1 g, 0.000 33 M) in CH_2Cl_2 (200 mL) was stirred at 25 °C for 8 h. The usual workup gave a yellow oil: ^{1}H NMR δ 1.0 (t, 2 H), 1.2 (t, 2 H), 1.4 (d, 6 H), 4.9 (septet, H); ^{13}C NMR δ 5.5, 23.1, 28.2 (1:1:1 t, J = 29 Hz), 76.8 (no sign of H/D exchange). **(b) *N,N*-Diethylcyclopropanesulfonamide-*1-d*.** A solution of *N,N*-diethylcyclopropanesulfonamide-*1-d* (0.05 g, 0.3 mmol), triethylamine (10 g, 0.05 M), 2-propanol (12 g, 0.1 M), and triethylamine hydrochloride (0.1 g, 0.000 33 M) in CH_2Cl_2 (200 mL) was stirred at 25 °C for 8 h. The usual workup gave a pale brown oil: ^{1}H NMR δ 0.9–1.2 (m, major signals at 0.96 and 1.15, 4 H), 1.2 (t, 6 H), 3.3 (q, 4 H); ^{13}C NMR δ 4.9, 14.2, 29.2 (1:1:1 t, J = 27 Hz), 41.4 (no sign of any H/D exchange).

Reaction of Cyclopropanesulfonyl Chloride with 1-(2-Methylpropenyl)pyrrolidine in the Presence of Trieth-

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ylamine. A solution of 1 (0.21 g, 1.5 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of Et_3N (0.46 g, 4.6 mmol) and 1-(2-methylpropenyl)pyrrolidine (0.19 g, 1.5 mmol) in CH_2Cl_2 (40 mL), and stirring was continued for 24 h. The reaction mixture was washed (diluted H_2SO_4) and dried ($MgSO_4$), and the solvent was evaporated. The residue was then chromatographed on Kieselgel 60 GF_{254} (eluent, ether) to give a mixture of **23** (0.14 g, 52% yield) and **24** (0.03 g, 13% yield) as a pale yellow oil. **23**: ^1H NMR δ 0.9–1.2 (m, 4 H), 1.9 (t, 4 H), 2.3 (tt, 1 H), 3.4 (t, 4 H); ^{13}C NMR δ 4.4, 25.7, 26.2, 47.9. **24**: ^1H NMR δ 0.9–1.2 (m, 4 H), 1.6 (s, 6 H), 2.3 (tt, 1 H), 9.7 (s, 1 H); ^{13}C NMR δ 5.0, 16.4, 26.6, 70.3, 189.5. The mixture of **23**, **24** (0.3 g, 1.7 mmol) in methanol (1 mL) was added to a solution of (2,4-dinitrophenyl)-hydrazine (0.1 g, 0.5 mmol) and concd HCl (7 drops) in methanol (10 mL), and the reaction mixture was placed on the steam bath for 2 min and allowed to stand at room temperature for 2 min. Water (10 mL) was added and the mixture cooled (ice bath) and filtered to give reddish yellow solid which was eluted through a microcolumn of neutral aluminum oxide with benzene. The eluate was evaporated and recrystallized (methanol) to give $(CH_2)_2CHSO_2C(CH_3)_2CH{=}NNHC_6H_3(2,4\text{-}(NO_2)_2)$ (0.05 g, 41% yield) as a yellow-orange solid: mp 180–181 °C; IR ν_{max} 1333, 1619, 1310, 1285, 3297, 3110 cm^{-1}; ^1H NMR δ 1.0–1.3 (m, 4 H), 1.7 (s, 6 H), 2.4 (tt, 1 H), 7.6 (s, HC=N), 7.9 (d, 1 H), 8.4 (d, 1 H), 9.1 (s, 1 H), 11.3 (1 H, N-H); ^{13}C NMR δ 5.0, 19.6, 25.4, 65.4, 116.5, 123.4, 130.1, 130.2, 138.9, 144.7, 147.9; exact mass (M + 1) calculated 357.0869, found 357.0870 (CI, isobutane).

Reaction of Cyclopropanesulfonyl Chloride with 1-(2-Methylpropenyl)pyrrolidine in Aqueous Solution. Solutions of 1-(2-methylpropenyl)pyrrolidine (1.0 g, 8.0 mmol) in DME (5 mL) and of aqueous NaOH (40 mL, pH 10.5) were added simultaneously to a stirred solution of 1 (0.5 g, 3.6 mmol) in DME (5 mL), and stirring was continued for 10 min. The reaction mixture was acidified (aqueous H_2SO_4) and extracted (CH_2Cl_2, 50 mL). The organic extract was dried ($MgSO_4$) and evaporated to give a mixture shown by NMR to consist of **23**, **24**, and cyclopropyl isopropyl sulfone ($(CH_2)_2CHSO_2CH(CH_3)_2$) (0.12 g, 20% total yield) as a yellow oil. **23** (11% yield): ^1H NMR δ 1.0 (m, 4 H), 2.0 (t, 4 H), 2.4 (tt, 1 H), 3.4 (t, 4 H); ^{13}C NMR δ 4.2, 25.5, 25.9, 47.7. **24** (3% yield): ^1H NMR δ 1.0 (m, 4 H), 1.6 (s, 6 H), 2.4 (tt, 1 H), 9.7 (s, H); ^{13}C NMR δ 4.8, 16.2, 26.4, 70.1, 196.5. $(CH_2)_2CHSO_2CH(CH_3)_2$ (6% yield): ^1H NMR δ 1.0 (m, 4 H), 1.4 (d, 6 H), 3.2 (septet, 1 H); ^{13}C NMR δ 4.2, 15.4, 26.1, 53.8.

pH–Product Ratio Profiles. The procedure has been described.[2] Cyclopropanesulfonyl chloride (50 μL, 67.3 mg, 4.792×10^{-4} mol) was injected into a solution (500 mL) of the nucleophile (either $[2\text{-chlorophenol}]_T = [ArO^-] + [ArOH] = 0.05$ M or $[CH_3SO_2N^-Ph] = 0.05$ M). The results are shown in Figure 2.

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Supplementary Material Available: ^1H NMR spectra for all compounds listed in the Experimental Section (30 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.