Thermolytic Rearrangements of 1,1-Cyclopropanedimethanol Disulfonates: Cyclopropylcarbinyl Cations Revisited

Peter A. Wade* and Paul A. Kondracki

Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104

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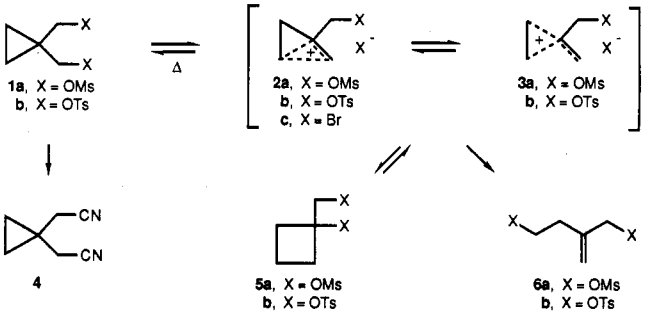
1,1-Cyclopropanedimethanol dimethanesulfonate (**1a**) and the corresponding ditosylate **1b** underwent thermal rearrangement at 110–140 °C after melting. Short reaction time resulted in the formation of mixtures containing 1-(sulfonyloxy)cyclobutanemethanol sulfonates **5a,b** (major), starting material, and 2-methylene-1,4-butanediol disulfonates **6a,b**. Longer reaction times afforded complete conversion to disulfonates **6a,b**, isolated in 49 and 62% yield, respectively. These reactions are postulated to proceed via initial carbocation formation, presumably interconverting bicylobutonium and cyclopropylcarbinyl cations, which exist as ion pairs in the melt. Crossover experiments with dimesylate **1a** and ditosylate **1b** offer support for the presence of ion pairs in the melt: internal return competed with external trapping of the intermediate cations. Reaction of **1a** and 2-methylene-1,4-butanediol ditosylate (**6b**) gave a mixture in which 2-methylene-1,4-butanediol 1-mesylate 4-tosylate (**8**) predominated over the isomeric 4-mesylate 1-tosylate **7** by a 5:1 ratio. Crossover experiments with **6a** and **6b** indicated that partial allylic substitution was occurring for the open-chain products under the thermolysis conditions. Reaction of **1a** with excess tetrabutylammonium tosylate at 114–15 °C afforded mixed 1-(sulfonyloxy)cyclobutanemethanol sulfonates and 2-methylene-1,4-butanediol disulfonates formed competitively by internal return and tosylate interception. Acetolysis of **1a** at 42–43 °C afforded predominately products of internal return early on the reaction profile. Longer reaction times afforded predominately monoacetates while reactions run at 108–10 °C afforded substantial amounts of diacetates. Acetolysis of 1-acetoxycyclobutanemethanol mesylate (**12a**) resulted in the substitution of the mesyloxy group with substantial rearrangement.

The rearrangement of cyclopropylcarbinyl and cyclobutyl substrates has been studied extensively by many of the leading research groups in organic chemistry, beginning in the late 1940's and continuing into the 1990's.[1,2] In one early study, Applequist and Roberts[3] examined the reaction products obtained from methylenecyclobutane and bromine: a mixture consisting of 1-(bromomethyl)-1-bromocyclobutane, 1,1-bis(bromomethyl)cyclopropane, and 2-(bromomethyl)-4-bromo-1-butene was obtained and the bicyclobutonium cation **2c** was postulated as a common intermediate. Recent evidence for the parent cation $C_4H_7^+$ has indicated that it exists as an interconverting mixture of bicyclobutonium and cyclopropylcarbinyl species.[2a] Evidence for ion pairing of cyclopropylcarbinyl cations and concomitant internal return has also been reported.[2b]

1,1-Cyclopropanedimethanol dimethanesulfonate (**1a**) and 1,1-cyclopropanedimethanol bis(4-methylbenzenesulfonate) (**1b**) have been known for some time and have been employed in a variety of substitution reactions *without* rearrangement. For example, ditosylate **1b** is reported to react with sodium cyanide at 90 °C to afford the corresponding dinitrile **4**, isolated after 100 h.[4]

When we prepared dimesylate **1a**, we were surprised to find that its melting point (119.5–120 °C[5]) differed markedly from the reported[6] melting point of 58–60 °C. Examination of the melted sample resulted in the identification of two new products, 1-[(methylsulfonyl)oxy]-cyclobutanemethanol methanesulfonate (**5a**) and 2-methylene-1,4-butanediol dimethanesulfonate (**6a**) (Scheme I). The open-chain dimesylate **6a** could be made the sole isomer on prolonged heating. This system, then, provides a convenient opportunity to reexamine the cyclopropylcarbinyl cation rearrangement with emphasis on the ring-opened products. The environment, a melt, might be expected to differ from the typically studied solution phase. Finally, the juxtaposition of two leaving groups might be expected to permit additional possibilities for cation formation.

Scheme I



Results

The disulfonates **1a,b** were prepared by literature procedures from 1,1-cyclopropanedimethanol.[6,4] Heating

(1) (a) For extensive reviews of early work, see: Wiberg, K. B.; Hess, B. A., Jr.; Ashe, A. J., III. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, pp 1295–1346. Richey, H. G., Jr. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, pp 1201–1294. (b) For more recent reviews, see: Saunders, M.; Jiménez-Vázquez, H. A. *Chem. Rev.* **1991**, *91*, 375–97. Tidwell, T. T. In *The Chemistry of the Cyclopropyl Group*; Rapoport, H., Ed.; Wiley: New York, 1987; Part I, pp 565–632.

(2) Recent studies include: (a) Myhre, P. C.; Webb, G. G.; Yannoni, C. S. *J. Am. Chem. Soc.* **1990**, *112*, 8892. (b) Roberts, D. D. *J. Org. Chem.* **1991**, *56*, 5661.

(3) Applequist, D. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 874.

(4) (a) Chamboux, B.; Étienne, Y.; Pallaud, R. *C. R. Hebd. Seances Acad. Sci.* **1962**, *254*, 313. (b) Foos, J.; Steel, F.; Rizvi, S. Q. A.; Fraenkel, G. *J. Org. Chem.* **1979**, *44*, 2522.

(5) Wade, P. A.; Kondracki, P. A.; Carroll, P. J. *J. Am. Chem. Soc.* **1991**, *113*, 8807.

(6) Newman, M. S.; Busch, D. H.; Cheney, G. E.; Gustafson, C. R. *Inorg. Chem.* **1972**, *12*, 2890.

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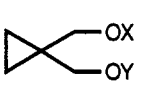
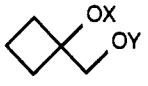
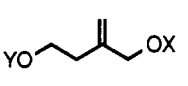
Table I. Product Ratios for Mesylate–Tosylate Crossover Experiments[a]

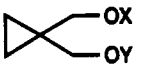
1st reactant	2nd reactant	temp, °C	time, min	recovery,[b] %	 (1a:2a:11a)	 (5a:5b:9:10)	 (6a:6b:7:8)
1a	**1b**	127–28	4.5	73	31 (42:43:15)	53 (40:40:8:11)	15 (27:44:14:15)
1a	**1b**	126–27	5	73	20 (33:45:22)	57 (39:40:10:11)	24 (34:38:13:15)
1a	**1b**	128–29	7	68	7 (36:37:27)	16 (20:33:23:24)	77 (26:33:20:21)
1a	**1b**	128–29	7.5	77	4 (19:27:54)	14 (17:31:24:28)	82 (27:29:22:22)
6a	**6b**	123–24	25	97	0	0	100 (42:42:08:08)
1a	**6b**	118–23	12	84	7 (87:00:13)	19 (90:00:3.8:6.3)	74 (25:68:1.1:5.7)
1b	**6a**	127–28	8	82	6 (00:87:13)	24 (00:86:9.6:3.9)	70 (62:25:11:1.2)
1a	Bu_4N^+ OTs^- (8 mol equiv)	115–16[c]	4	58[d]	32 (36:09:55)	59 (37:09:12:42)	08 (29:17:21:34)

[a] Molar ratios; an equimolar mixture of reactants, unless otherwise stated. [b] Based on the number of moles of both starting materials. [c] Premelted by heating at 127–29 °C for 57 s. [d] Based on starting **1a** only; salts produced in the reaction were not examined.

Table II. Product Ratios for Solvolysis of 1,1-Cyclopropanedimethanol Dimethanesulfonate (1a) in Acetic Acid

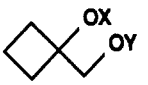
			dimesylates			mesylate acetates				diacetates		
time, min	temp, °C	recovery, %[a]	**1a**	**5a**	**6a**	**12a**	**13a**	**13b**	mesylate **12e**	**12c**	**13c**	**14a**
210	42–3	62	20	44	2.5	19	0.1[b]	1.3	10	2	0	1.5
360	42–3	63	9	43	3.2	26	0.3	1.6	15	1.2	0.1	0.7
780	42–4	62	2.1	18	4.5	41[c]	1.9	6.4	12	5.6	1.1	2.1
7	108–10	45	1.1	8	14	44	4.7	10	3	8	2.6	4.8
15	110–12	41	0	0.3	15	8.3	11	6.4	0	40	7	12

[a] Reisolated **1a** and products. [b] Also present was 0.1% of **14b**. [c] The acetate **12d** was present in mesylate acetate fractions for this run: **12d**/**12a**, 5.3:41.

Table III. ^{1}H-NMR Spectra[a] for 

compd	α-CH_2, s	OMs, s	OTs methyl, s	OTs aryl, d (*J*)	OAc, s	CH_2CH_2, s or m
1a	4.17[b]	3.06				0.84 (s)
1b	3.86[b]		2.46	7.73, 7.34 (8.1 Hz)		0.61 (s)
11a	4.09,[b] 3.96	2.99	2.46	7.79, 7.36 (8.3 Hz)		0.77 (m), 0.70 (m)
14a	3.98[b]				2.08	0.62 (s)
14b	4.14, 4.03[b]	3.04			2.09	0.73 (s)

[a] Spectral values (δ) are for purified compounds. [b] Integration of this band in mixtures was used for quantitation.

Table IV. ^{1}H-NMR Spectra[a] for 

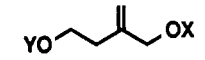
compd	α-CH_2, s	OMs, s	OTs methyl, s	OTs aryl, d (*J*)	OAc, s	$CH_2CH_2CH_2$, m	$CH_2CH_2CH_2$, m
5a	4.56[b]	3.10, 3.07				2.72, 2.35	2.02, 1.73
5b	4.33[b]		2.46, 2.44	7.76, 7.35 (8.3 Hz); 7.70, 7.30 (8 Hz)		2.64, 2.21	1.93, 1.59
9	4.36[b]	2.98	2.47	7.82, 7.38 (8.1 Hz)		2.68, 2.27	1.97, 1.63
10	4.56[b]	3.03	2.45	7.80, 7.35 (8.3 Hz)		2.65, 2.30	1.95, 1.67
12a	4.57[b,c]	3.03			2.04	2.33	1.93, 1.73
12b	4.48	3.03			2.13	2.70, 2.29	1.98, 1.71
12c	4.45[b]				2.08, 2.0	2.29	1.86, 1.70
12d[d]	4.16[b]				2.11	2.08	1.78, 1.57
12e[e]	4.27[b]	3.08				2.14	1.82, 1.61

[a] Spectral values (δ) are for purified compounds. [b] Integration of this band in mixtures was used for quantitation. [c] The band overlapped with the CH_2 of **13a**. To quantitate **12a**, the amount of **13a** was determined from its δ 4.36 signal and was subtracted from the δ 4.57 signal. [d] OH at δ 2.25. [e] OH at δ 1.96.

solid dimesylate **1a** at temperatures in the range of 110–140 °C resulted in melting followed by conversion to mixtures of the cyclobutyl dimesylate **5a**, the open-chain dimesylate **6a**, and starting **1a**. The results, however, were somewhat variable from run to run. At either high temperature in short runs or at lower temperature in long runs, low yields (<20%) of the identified products were obtained. It was found advantageous to melt **1a** in a bath preheated to 130 °C and then to continue heating in a second bath at 112–14 °C. In a typical experiment, the predominant product after 2.5 min at 112–14 °C was cyclobutyl dimesylate **5a** (**1a**/**5a**/**6a**, 20:51:29). Product ratios were determined by integration of the ^{1}H NMR spectrum of the mixture using singlets at δ 4.17, 4.56, and 4.71 for **1a**, **5a**, and **6a**, respectively (Tables III–V). After 6.5 min at 112–14 °C in another experiment, the only dimesylate present was the open-chain isomer **6a**, isolated in 49% yield by chromatography.

The ditosylate **1b** (mp 111–12 °C) also rearranged at temperatures from 110–140 °C. Here the rearrangement was slower and the products less sensitive to prolonged heating so that continued heating at 130–32 °C was most effective. Ratios were again determined by integration of the ^{1}H NMR spectrum of the mixture using singlets at δ

Table V. ^{1}H-NMR Spectra[a] for



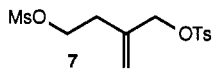
compd	=CH$_2$, s	CH$_2$OX, s	CH$_2$CH$_2$, t (J)	OMs, s	OTs methyl, s	OTs aryl, d (J)	OAc, s
6a	5.36, 5.24	4.71[b] (2 H, s)	4.38, 2.61 (6.4 Hz)	3.03			
6b	5.13, 5.01	4.39[b] (2 H, s)	4.06, 2.36 (6.5 Hz)		2.45	7.76, 7.35 (8.1 Hz)	
7	5.21, 5.13	4.49[b] (2 H, s)	4.28, 2.49[c] (6.5 Hz)	2.99	2.46[c]	7.79, 7.37 (8.3 Hz)	
8	5.29, 5.13	4.61[b] (2 H, s)	4.17, 2.50[c] (6.4 Hz)	3.01	2.46[c]	7.78, 7.36 (8.3 Hz)	
13a	5.28, 5.15	4.56 (2 H, s)	4.36,[b] 2.53 (6.7 Hz)	3.02			2.10
13b	5.14, 5.02	4.70[b] (2 H, s)	4.22, 2.47 (6.6 Hz)	3.04			2.05
13c		4.55[b] (2 H, s)	4.20, 2.41 (6.7 Hz)				2.10, 2.05

[a] Spectral values (δ) are for purified compounds. [b] Integration of this band in mixtures was used for quantitation. [c] These signals overlapped for the pure compounds.

3.86, 4.33, and 4.39 for **1b**, **5b**, and **6b**, respectively. Thus, heating ditosylate **1b** at 131–32 °C for 8.5 min gave a mixture of unrearranged **1b** and cyclobutyl ditosylate **5b** as the major products (**1b**/**5b**/**6b**, 46:43:12). These results were obtained somewhat earlier on the reaction profile then those reported above for **1a**: from other experiments there was no discernible difference in product spread for **1a** and **1b**, assuming the same extent of rearrangement. Heating **1b** for a longer time (15 min) gave the open-chain ditosylate **6b** as the sole isomer, isolated in 62% yield.

The crude rearranged mixtures were strongly acidic (pH 1–3). Furthermore, these rearrangements were subject to acid catalysis. Addition of 9 mol % *p*-toluenesulfonic acid to ditosylate **1b** followed by heating for 8 min at 114–15 °C afforded mostly open-chain distosylate **6b** (**1b**/**5b**/**6b**, 3:7:90). Under the same conditions in the absence of added acid, there was only 6% reaction. One month-old samples of **1b** rearranged more rapidly and at lower temperature than freshly recrystallized samples. Similar observations were made for the dimesylate **1a**.

Substantial crossover was noted when equimolar mixtures of the cyclopropylcarbinyl dimesylate **1a** and the ditosylate **1b** were heated at 126–29 °C (Table I). At 4.5–7.5 min the products consisted of a gross mixture of **1a,b**, **5a,b**, **6a,b** and mesylate tosylates **7–11a**. These products were partially separated into dimesylate (**1a**, **5a**, and **6a**), ditosylate (**1b**, **5b**, and **6b**), and mesylate tosylate (**7–11a**) fractions. The ratio of cyclopropylcarbinyl, cylobutyl, and



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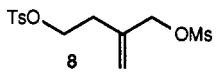

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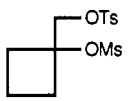

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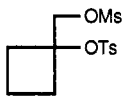

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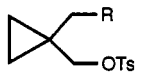


11a, R = OMs
b, R = H

open-chain products was determined from NMR integration and weight data for the three fractions. After a 15-min reaction time, only the open-chain products **6a,b** and **7** and **8** were present. These were partially separated to provide pure **6a**, pure **6b**, and a mixture of **7** and **8**. Conversely, when the open-chain diesters **6a** and **6b** were heated at 123–24 °C for 25 min, relatively little crossover was observed and no cyclobutyl or cyclopropylcarbinyl products were evident.

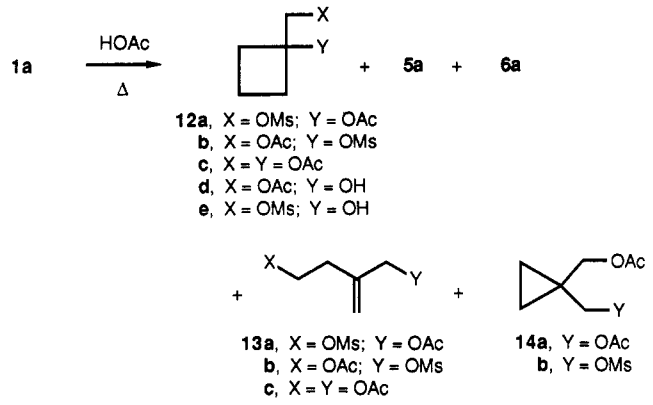
Isomer assignments for **7**, **8** and **9**, **10** are based on ^{1}H NMR data. The methylene protons for a (mesyloxy)-methylene group resonate downfield while the methylene protons for a (tosyloxy)methylene group resonate upfield. The isomer **7** had a triplet at δ 4.28 attributed to the homoallylic (mesyloxy)methylene protons and a singlet at δ 4.49 attributed to the allylic (tosyloxy)methylene protons. For isomer **8** the signal at δ 4.17 is attributed to homoallylic (tosyloxy)methylene protons and the signal at δ 4.61 is attributed to allylic (mesyloxy)methylene protons. The cyclobutyl isomers **9** and **10** had singlets at δ 4.36 and 4.56, respectively.

Heating a mixture of cyclopropylcarbinyl dimesylate **1a** and open-chain ditosylate **6b** at 118–23 °C for 12 min gave a mixture of cyclobutyl, cyclopropylcarbinyl, and open-chain products (Table I). The crossover product 2-methylene-1,4-butanediol 1-mesylate 4-tosylate (**8**) strongly predominated over isomeric 4-mesylate 1-tosylate **7** (**8**/**7**, 5:1) in this mixture. The cyclobutyl mesylate tosylate **10** predominated over **9** (**10**/**9**, 1.7:1) but the regioselectivity was markedly less than for the open-chain crossover products. The reverse experiment, similar heating of cyclopropylcarbinyl ditosylate **1b** with open-chain dimesylate **6a**, gave reversed preferences: (**8**/**7**, 1:9 and **10**/**9**, 1:2.5). Here, too, open-chain crossover products were formed with higher regioselectivity than the cyclobutyl crossover products.

Dimesylate **1a** was heated at 127–28 °C with 8 mol equiv of tetrabutylammonium tosylate, affording a homogeneous melt from which a complex mixture of products was obtained (Table I). The products were separated into three fractions, dimesylates (**1a**, **5a**, **6a**), ditosylates (**1b**, **5b**, **6b**), and mesylate tosylates (**7–11a**), and ratios were determined from weight and NMR data as in preceding experiments.

Solvolysis of **1a** in glacial acetic acid was examined. At 42–43 °C after 3.5 h the major product present was the rearranged cyclobutyl dimesylate **5a**, present in 27% yield (Table II). Also present and isolated by preparative thin-layer chromatography in 11% yield was the mesylate acetate **12a**. The hydrolysis product 1-hydroxycyclobutanemethanol methanesulfonate (**12e**) was formed in varying amounts from run to run. Acetolysis at 42–44 °C for 13 h afforded a more complex product spread. Here the mesylate acetate **12a** was the major component and was isolated in 25% yield, contaminated by the hydrolysis product **12d** (**12a**/**12d**, 89:11). Acetolysis of **1a** at 108–12 °C gave a complex mixture of products including significant quantities of diacetates **12c**, **13c**, and **14a**, mesylate acetates **12a** and **13a,b**, and dimesylates **5a** and **6a**. The ratio of the open-chain mesylate acetates **13a,b** was altered markedly as a function of reaction time: short reaction time favored **13b** while longer reaction time favored **13a**.

Standard samples of mesylate acetate **13a** and diacetate **13c** were prepared by reaction of sodium acetate with dimesylate **6a** in DMSO solution. Standard samples of



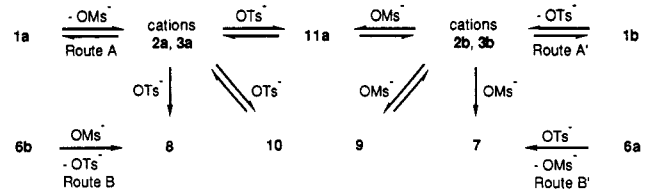
the acetate **12d**, diacetates **12c** and **14a**, mesylate **12e**, and mesylate acetates **12b** and **14b** were prepared from the known corresponding diols.

Discussion

The formation of cyclobutyl products **5a,b** and open-chain products **6a,b** from the cyclopropylcarbinyl disulfonates **1a,b** clearly proceeded via cation rearrangement. The observed catalytic effect of acid supports the intermediacy of carbocation, rather then free radical, intermediates. From work on the parent cyclopropylcarbinyl system,[2a] it seems likely that both the bicyclobutonium cations **2a,b** and cyclopropylcarbinyl cations **3a,b** are involved. Thermal reaction to give the open-chain, cyclobutyl, and cyclopropylcarbinyl products could then involve either **2a,b** or **3a,b** or both as direct precursors to the different products. The evidence obtained here, however, does not dispute a common cation precursor to all three products. Since this is the simplest sequence of events, our interpretations are based on a common cation precursor.

1-Methylcyclopropanemethanol 4-methylbenzenesulfonate (**11b**) is a previously studied tertiary substrate closely related to **1a,b**.[7] In acetic acid, **11b** was solvolyzed to afford exclusively 1-(1-methyl)cyclobutyl acetate, identified after base-catalyzed hydrolysis to the free alcohol. Product selectivity was attributed to localization of charge at the methyl-substituted carbon of the intermediate cation. Conversely, thermolysis of **1a,b** always afforded a mixture of cyclobutyl **5a,b**, cyclopropylcarbinyl **1a,b**, and open-chain isomers **6a,b** until such time as only **6a,b** remained. The ratio of **5a** to **1a** was 76:24 in a typical melt-phase reaction where **6a** was the major product and this ratio should be very close to the equilibrium ratio. A slightly higher equilibrium ratio (88:12) was apparent in acetic acid solution. The melt-phase equilibrium ratio of the ditosylates was similar (72:28). The ratio of crossover products (**9** + **10**/**11a**), obtained for thermolyses of **1a** and **1b** where open-chain products were major, was 80:20, again showing a marked preference for cyclobutyl products. Nonexclusion of **1a,b** from thermolytic product mixtures is likely due to an electronic effect: (sulfonyloxy)methyl substituents, unlike the methyl substituent, would not significantly stabilize adjacent positive charge.[8] Positive charge would not then be localized as strongly at the (sulfonyloxy)methyl-substituted carbon as at the methyl-substituted carbon of the cation derived from **11b**.

Scheme II



Complete conversion of **1a,b** to **6a,b** after long reaction time indicates that the open-chain products are strongly favored thermodynamically. Heating a mixture of **6a** and **6b** gave no cyclopropylcarbinyl or cyclobutyl products so that isomerization was clearly irreversible. However, mixed mesylate tosylates **7** and **8** (16% of products) were formed from **6a** and **6b**. The absence of any added nucleophile requires that **6a** and **6b** form cations. The complete absence of cyclopropylcarbinyl and cyclobutyl products indicates that cation formation was at the *allylic* rather than homoallylic site. It should also be noted that formation of **7** and **8** from heating **6a** with **6b** shows that allylic substitution must be occurring during thermolysis of **1a** and **1b**.

Heating **1a** and open-chain ditosylate **6b** gave open-chain crossover products **8** and **7** in a 5:1 ratio. The cyclobutyl crossover products **9** and **10** were also formed but with lower regioselectivity (1:1.7). These results can be explained by assuming that the open-chain crossover products are formed by two competing routes, one of which is highly regioselective (route B, Scheme II) and one which is less regioselective (route A), while the cyclobutyl products are formed only by the less regioselective route. It is likely that the highly regioselective route is simple allylic displacement and involves only reaction of **6b** with generated mesylate ion. It is clear that replacement of the allylic tosyloxy group of **6b** must occur since this is the only viable source of tosylate ion leading to crossover. Here allylic substitution is proceeding at a faster rate than for simple heating of **6a** with **6b**. Presumably the faster rate arises owing to an increased ion concentration from route A. Route A begins with thermolysis of **1a** to an intermediate cation (**2a** or **3a**). The cation would then be expected to give **10** rapidly and **8** more slowly. The modest regioselectivity for **10** is interpreted to mean that substantial leakage from **2a** (or **3a**) to **2b** (or **3b**) must occur. The relatively higher regioselectivity for **8** means that most of **8** must arise from route B. Leakage in route A likely occurs through cyclopropylcarbinyl mesylate tosylate **11a**. Similar considerations apply to crossover in the other direction, i.e., reaction of **1b** with **6a**, routes A′ and B′. Here regioselectivity was somewhat greater for both the open-chain products (**7**/**8**, 9:1) and the cyclobutyl products (**9**/**10**, 2.5:1) compared to the reaction of **1a** with **6b**. Presumably there is less leakage in route A′ than in route A (i.e., fewer toyloxy cations convert to mesyloxy cations than in the other direction).

There is abundant evidence that the cation intermediates present in the melt phase and in acetic acid solution exist as ion pairs. A significant degree of internal return was observed for melt-phase reactions, melt-phase reactions with tetrabutylammonium tosylate, and solution-phase reactions in acetic acid. Similar ion pairing of cations derived from cyclopropylcarbinyl substrates has been

(7) Roberts, D. D. *J. Org. Chem.* **1966**, *31*, 2000.
(8) The inductive effect of (methylsulfonyl)oxy and [(4-methylphenyl)-sulfonyl]oxy substituents can be ascertained from σ_I values. These are +0.58 and +0.59, respectively: Exner, O. In *Correlation Analysis in Chemistry*, Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; pp 439–540.

documented by others in the case of solution-phase reactions.[2b]

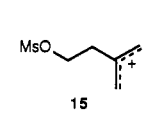
Crossover experiments between disulfonates **1a** and **1b** proceeded with substantial, but far from complete, internal return. Early on the reaction profile the cyclobutyl products predominated. For random cation capture, a 25:25:25:25 ratio of **5a,b**, **9**, and **10** would be anticipated. However, as can be seen for the first three entries in Table I, the dimesylate and ditosylate products **5a,b** were favored at the expense of mixed disulfonates. The extent of internal return was calculated to be 58–62% for reactions run 4.5–5 min falling to nil by 7.5 min. A somewhat lower, less variable degree of internal return for the open-chain products was observed. For reactions run 4.5–5 min, 42–44% internal return was calculated. Later on the reaction profile (after 7.5 min), there was still a small preference for **6a,b** over **7** and **8**, 12% internal return being calculated. Since **6a,b** are slower to form than **5a,b**, the initial extent of internal return is lower: a common cation intermediate must be generated and regenerated many times on average before conversion to **6a,b**, resulting in increased opportunity for external trapping. Conversely, formation of **6a,b** is irreversible so that the degree of internal return does not rapidly fall to zero. However, at very long reaction time equal quantities of **6a,b**, and **7**, and **8** were obtained presumably owing to allylic substitution.

Results for cyclopropylcarbinyl products are complicated by nonreaction of a portion of the starting material early on the reaction profile. After 4.5 min, cyclopropylcarbinyl products amounted to 31% of isolated material but there was very little mixed disulfonate **11a** (**1a**/**1b**/**11a**, 42:43:15).[9] After 7 min, cyclopropylcarbinyl products amounted to only 7% of isolated material and there was still little **11a**, consistent with substantial internal return. However, after 7.5 min a ratio experimentally indistinguishable from the random formation ratio (**1a**/**1b**/**11a**, 25:25:50) was observed.

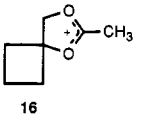
The melt-phase reaction of **1a** with tetrabutylammonium tosylate occurred with substantial internal return: dimesylate **5a** amounted to fully 37% of the cyclobutyl products. Since the molar ratio of tetrabutylammonium tosylate/**1a** was 8:1, random product formation should have given less than 5% of **5a**. Thus, approximately one-third of the cyclobutyl product was formed via internal return, necessitating ion pair intermediates. The dimesylate **6a** made up 29% of the open-chain products. Here, too, more than one-fourth of the product arose from internal return.

Solvolysis of **1a** in acetic acid occurred at a significant rate even at 42–44 °C. Here, too, internal return was prevalent, accounting for the bulk of the product at early stages. Thus, after 3.5 h the major product present was **5a**. After 6 h the cyclobutyl mesylate acetate **12a** was major, presumably arising from repetitive ion pair formation followed by eventual solvent capture. At 108–112 °C, mesylate acetate **12a** was initially the major product but fell to a minor product after 15 min, indicating a secondary reaction. A small amount of the open-chain mesylate acetates **13a** and **13b** accompanied **12a** in these reactions. At 42–44 °C, the ratio of **13b** to **13a** dropped from 11:1 at 3.5 h to 3.5:1 at 13 h. At 108–12 °C, the preference for **13b** first diminished and then altered to a preference for **13a**. Thus, **13b** is a primary reaction product while **13a** appears to be a secondary product. Acetolysis of **6a** might be expected to afford **13a**. Furthermore, it was later demonstrated that acetolysis of **12a** affords a small amount of **13a** (vide infra). Diacetates were also formed increasingly with heating at 108–12 °C: after 15 min cyclobutyl diacetate **12c** was the major reaction product. The mesylate acetates **12b** and **14b** were not significant products in any of the reactions.

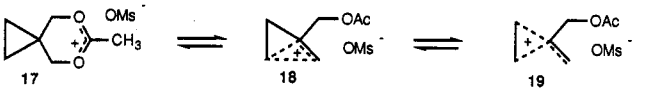
The possibility of direct rearrangement from the cyclic cations **2** (or **3**) to an open-chain allylic cation **15** was considered but rejected based on the acetolysis results.



15



16



17 18 19

Solvolysis of **1a** initially gave **13b** preferentially to **13a** (**13b**/**13a**, 11:1), indicating a strong preference for substitution at the homoallylic site. The opposite preference would have been expected in a pathway involving **2** (or **3**) → **15** → products. Other results, namely the last three entries in Table I, are also inconsistent with a direct cation → cation rearrangement.

Acetolysis of mesylate acetate **12a** at 109–11 °C was investigated to determine what secondary reactions might be taking place. Unreacted **12a**, diacetates **12c**, **14a**, and **13c**, and open-chain mesylate acetate **13a** were obtained after 10 min reaction time (**12a**/**12c**/**14a**/**13c**/**13a**, 32:46:12:6:4). Thus, **12a** does undergo cation formation, although it is slower to do so than **5a** or **1a**. Furthermore, cation formation led to replacement of the mesyloxy group: quite possibly neighboring group participation from the adjacent acetoxy group to form cation **16** occurred. Other 1,2-acetoxy-bridged cations are well-documented[10] providing some precedence for **16**. Isomerization of **16** paired with mesylate ion to **18** (or **19**) and subsequent internal return would then explain formation of the minor product **13a**. When glacial acetic acid was used without drying, the diol monoacetate **12d** was obtained as a major product. This result in particular suggests either a 1,2-acetoxy-bridged cation or a cation in which acetoxy has migrated to the cyclobutylcarbinyl position.

Cyclopropylcarbinyl mesylate acetate **14b** was a particularly sensitive compound. During chromatography on silica gel, **14b** partially isomerized to cyclobutyl mesylate acetate **12a**. It seems that the acetoxy group may provide anchimeric assistance to the loss of mesylate ion, rapidly affording the ion pair **17**. Isomerization of **17** to **18** (or **19**) and subsequent internal return could then give **12a**.

In summary, disulfonates **1a,b** showed a rich cation chemistry on either melting or heating in acetic acid solution. Cation rearrangement initially afforded predominately cyclobutyl products in these reactions but reversion to the cation provided increasing amounts of open-chain products as reaction time increased. The observed extent of internal return provided strong evidence

(9) An S_N2 displacement does not appear to operate here. On the basis of ^{14}C-labeling studies, it was proposed that an S_N2 displacement process competes with cyclopropylcarbinyl cation formation in the nitrosation of cyclopropylmethanamine: Mazur, R. H.; White, W. N.; Semenow, D. A.; Lee, C. C.; Silver, M. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1959**, *81*, 4390.

(10) Winstein, S.; Hanson, C.; Grunwald, E. *J. Am. Chem. Soc.* **1948**, *70*, 812. Winstein, S.; Grunwald, E.; Buckles, R. E.; Hanson, C. *J. Am. Chem. Soc.* **1948**, *70*, 816.

for appreciable ion pairing both in the melt phase and in acetic acid solution. The open-chain disulfonates were not inert to thermolysis conditions: they underwent substitution at the allylic site. The mesylate acetate **12a** was not inert to vigorous solvolysis conditions, undergoing substitution of the mesyloxy group accompanied by substantial rearrangement.

Experimental Section

General. All reactions were run under argon and all thermolyses were conducted in a Pyrex 25-mL round-bottom flask. Powdered reactants were obtained by grinding with a mortar and pestle. Dried HOAc was obtained by distillation of glacial HOAc from P_2O_5. Reactions were typically worked up by rapidly cooling the crude reaction mixture to room temperature and partitioning it between CH_2Cl_2 (25 mL) and 6% Na_2CO_3 (15 mL). The aqueous layer was extracted with CH_2Cl_2 (25 mL) and the organic layers were combined, washed with water (10 mL), dried using anhydrous Na_2SO_4, and concentrated at water aspirator pressure using a rotary evaporator. Crude products were purified by preparative TLC (elution solvent) on 0.25- and 1.0-mm Analtech silica gel GF plates. ^1H NMR spectra (Tables III–V) and ^{13}C NMR spectra were determined in $CDCl_3$ (TMS internal standard) on a Bruker WM-250 instrument. Disulfonates **1a**[5] (mp 119.5–20 °C; lit.[5] mp 119.5–20 °C) and **1b**[10] (mp 111–12 °C; lit.[10] mp 112–14 °C) were prepared according to the published procedures. Other routine procedures have been previously published.[5]

Rearrangement of 1,1-Cyclopropanedimethanol Dimethanesulfonate (1a). A: Isolation of 6a. Powdered dimesylate **1a** (25 mg; 0.1 mmol) was stirred and heated using a preheated oil bath at 130 °C until the solid melted (2–2.5 min). The melt was then stirred and heated for 6.5 min using a second preheated oil bath kept at 112–114 °C. The reaction was worked up and the relatively clean (but black) crude product was purified by preparative TLC (CH_2Cl_2–MeOH, 99:1) affording 12.1 mg (49% yield) of **6a** as a colorless oil: IR (neat) 1655 (C=C), 1350 and 1171 (SO_2) cm^{-1}; ^{13}C NMR δ 137.09, 119.17, 71.86, 67.30, 37.93, 37.55, 32.47; MS m/z 258 (M^+). Anal. Calcd for $C_7H_{14}O_6S_2$: C, 32.56; H, 5.42. Found: C, 32.79; H, 5.58.

B: Isolation of 5a. Powdered **1a** (52.2 mg; 0.2 mmol) was heated as in run A at 126–28 °C with stirring for 2.5 min. Workup gave crude products which were purified by preparative TLC (EtOAc–hexanes, 40:60). Two fractions, one containing 15.1 mg (29% yield) of predominantly **5a** (**5a/1a/6a**, 96:2:2) and a second fraction containing 17.8 mg (34% yield) of a gross mixture (**6a/1a/5a**, 66:28:6) were obtained. The first fraction was rechromatographed then recrystallized twice from benzene–hexanes to give 7.4 mg (14% yield) of pure **5a** as a white solid: mp 51.5–52.5 °C; IR (KBr) 1336 and 1174 (SO_2); ^{13}C NMR δ 84.75, 70.31, 40.38, 37.73, 31.53, 13.71; MS m/z 258 (M^+). Anal. Calcd for $C_7H_{14}O_6S_2$: C, 32.56; H, 5.42. Found: C, 32.68; H, 5.46.

C: Isomer Ratios. Powdered **1a** (25 mg; 0.1 mmol) was melted and thermolyzed as in run A but time and temperature were varied. Workup and subsequent preparative TLC afforded a mixture of the three isomeric dimesylates **1a**, **5a**, and **6a**. In a typical experiment, the melt was heated at 112–114 °C for 2.5 min to afford a black oil which by ^1H NMR consisted of a clean mixture of dimesylates (**1a/5a/6a**, 20:51:29).

Rearrangement of 1,1-Cyclopropanedimethanol Bis(4-methylbenzenesulfonate) (1b). A: Isolation of 6b. Powdered ditosylate **1b** (24.7 mg; 0.06 mmol) was stirred and heated using a preheated oil bath at 130–31 °C for 15 min. The reaction was worked up according to the general procedure and the product was purified by preparative TLC (CH_2Cl_2) to give 15.3 mg (62% yield) of **6b** as an oil. An analytical sample was obtained by crystallization from aqueous MeOH: mp 41–42 °C; IR (neat) 1657 (C=C), 1597 (aryl), 1358 and 1176 (SO_2); ^{13}C NMR δ 144.93, 144.81, 136.76, 132.73, 129.82, 127.76, 118.49, 72.32, 67.69, 31.97, 21.70; MS m/z 410 (M^+). Anal. Calcd for $C_{19}H_{22}O_6S_2$: C, 55.59; H, 5.40. Found: C, 55.35; H, 5.25.

B: Isolation of 5b. Powdered **1b** (53.7 mg; 0.13 mmol) was heated for 12.2 min as in run A at 125–27 °C. Workup followed by repetitive preparative TLC (HOAc–EtOAc–hexanes, 2:20:78) on the crude product gave an oily white solid. This was recrystallized from benzene–hexanes to give 9.8 mg (18% yield) of predominantly **5b** (**5b/1b**, 97:3) as a white solid: mp 101–102 °C; IR (KBr) 1596 (aryl), 1357 and 1172 (SO_2); ^{13}C NMR 144.96, 144.43, 135.45, 132.54, 129.81, 129.57, 127.87, 127.22, 84.99, 70.74, 31.30, 21.75, 13.68; MS m/z 410 (M^+). Anal. Calcd for $C_{19}H_{22}O_6S_2$: C, 55.59; H, 5.40. Found: C, 55.57; H, 5.52.

Also isolated from a more polar TLC fraction was 11.6 mg (21% yield) of a mixture of ditosylates (**1b/5b/6b**, 21:10:69).

C: Isomer Ratios. Powdered **1b** (25 mg; 0.06 mmol) was thermolyzed as in run A but reaction time and temperature were varied. Workup and subsequent preparative TLC afforded a mixture of the three isomeric ditosylates **1b**, **5b**, and **6b**. In a typical experiment, the melt was heated at 131–32 °C for 8.5 min to give an oil which by ^1H NMR consisted of a clean mixture of ditosylates (**1b/5b/6b**, 46:43:12).

D: Effect of Added *p*-Toluenesulfonic Acid. A powdered mixture containing **1b** (24.9 mg; 0.06 mmol) and *p*-TsOH·H_2O (1 mg; 0.005 mmol) was heated at 114–15 °C for 8 min and then the reaction was worked up. The ^1H NMR spectrum showed predominant conversion to **6b** (**1b/5b/6b**, 3:7:90). A control experiment run in the absence of added acid afforded little reaction (**1b/5b/6b**, 95:05:01).

Thermolyses of 1a,b Mixtures. Powdered mixtures of dimesylate **1a** (20.1 mg; 0.08 mmol) and ditosylate **1b** (31.7 mg; 0.08 mmol) were stirred and heated for various times (Table I) in a preheated bath typically kept at 127–28 °C. Workup followed by preparative TLC (CH_2Cl_2–MeOH, 99:1) gave three fractions: ditosylates (R_f = 0.85); mesylate tosylates (R_f = 0.65); dimesylates (R_f = 0.4).

The fraction R_f = 0.65 from one run conducted at 140 °C for 8 min consisted of a 46:54 inseparable mixture of the mesylate tosylates **7** and **8**, obtained as an oil: IR and MS data for the individual compounds; ^{13}C NMR δ 144.98, 144.90, 137.02, 136.85, 132.70, 129.85, 127.78, 118.90, 118.85, 72.47, 71.80, 67.83, 67.21, 37.88, 37.49, 32.36, 32.12, 21.70. Anal. Calcd for $C_{13}H_{18}O_6S_2$: C, 46.69; H, 5.42. Found: C, 46.75; H, 5.56.

The fraction R_f = 0.65 obtained from a reaction heated only 3 min was rechromatographed (HOAc–EtOAc–hexanes, 1:40:59) to afford 1,1-cyclopropanedimethanol methanesulfonate 4-methylbenzenesulfonate (**11a**) as an impure oil (**11a/8/7/9/10**, 72:10:4:8:6, respectively): IR (neat) 1359 and 1174 cm^{-1} (SO_2); MS m/z 334 (M^+).

The fraction R_f = 0.65 (5.1 mg) obtained from a reaction heated 6.3 min was rechromatographed (EtOAc–hexanes, 40:60) to afford 3 mg of an oil enriched in 1-[[(4-methylphenyl)sulfonyl]oxy]-cyclobutanemethanol methanesulfonate (**10**) (**10/9/11a** 82:16:2): IR (neat) 1599 (aryl), 1354 and 1176 cm^{-1} (SO_2); MS m/z 334 (M^+).

The fraction R_f = 0.65 (5 mg) obtained from a reaction heated 6.3 min was rechromatographed (EtOAc–hexanes, 40:60) to afford 2.8 mg of slightly impure 1-[(methylsulfonyl)oxy]cyclobutanemethanol 4-methylbenzenesulfonate (**9**) (containing a trace of an unidentified tosylate): IR (neat) 1600 (aryl), 1366, 1326, 1190 and 1174 cm^{-1} (SO_2); ^{13}C NMR δ 145.17, 129.92, 127.87, 84.72, 70.63, 40.26, 31.57, 21.76, 13.71; MS m/z 334 (M^+).

Thermolysis of a Mixture of 6a and 6b. Dimesylate **6a** (13.5 mg; 0.055 mmol) and ditosylate **6b** (22.2 mg; 0.055 mmol) were dissolved in CH_2Cl_2 (5 mL) and the solvent was removed under reduced pressure (0.05 mm). The resulting oil was heated at 123–24 °C for 25 min. The reaction was worked up to afford 34.8 mg of crude product which by ^1H NMR consisted of **6a,b** and the crossover products **7** and **8** (**6a/6b/7/8**, 42:42:8:8).

Thermolysis of a Mixture of 1b and 6a. Ditosylate **1b** (36.5 mg; 0.09 mmol) and dimesylate **6a** (23.1 mg; 0.09 mmol) were dissolved in CH_2Cl_2 (5 mL), and the solvent was removed under reduced pressure (0.05 mm). The resulting mixture was stirred and heated using a preheated bath kept at 127–28 °C for 8 min. Workup followed by preparative TLC (CH_2Cl_2–MeOH, 99:1) gave three fractions: 25.9 mg of ditosylates (**1b/5b/6b**, 12:47:41), 13.7 mg of mesylate tosylates (**7/8/11a/10/9**, 62:7:6:18:7), and 16.4 mg of **6a**. Isomer ratios (Table I) were determined from the weight data and ^1H NMR data.

Rechromatography (EtOAc–hexanes, 40:60) of a mesylate tosylate fraction (8.7 mg) gave 5 mg of impure **7** (**7/8/11a/10**,

84:9:4:3) as an oil: IR (neat) 1654 (C=C), 1354 and 1174 (SO_2) cm^{-1}; ^{13}C NMR and elemental analysis were determined for a mixture (7/8, 46:54, vide supra); MS m/z 334 (M^+).

Thermolysis of a Mixture of 1a and 6b. A mixture of dimesylate **1a** (19.1 mg; 0.08 mmol) and ditosylate **6b** (31.5 mg; 0.08 mmol) was prepared similarly to the mixture of **1b** and **6a**. This mixture was heated at 118–23 °C for 12 min. Workup followed by preparative TLC gave three fractions: 26.5 mg of **6b**, 3.3 mg of mesylate tosylates (**7/8/11a/10/9**, 11:54:11:9:15), and 13.4 mg of dimesylates (**1a/5a/6a**, 14:41:45). Isomer ratios (Table I) were determined from the weight data and ^1H NMR data.

Rechromatography (EtOAc–hexanes, 40:60) of a mesylate tosylate fraction (3.8 mg) gave 1.2 mg of impure **8** (**8/7/11a**, 78: 15:7) as an oil: IR (neat) 1658 (C=C), 1351 and 1171 (SO_2) cm^{-1}; ^{13}C NMR and elemental analysis were determined for a mixture (7/8, 46:54, vide supra); MS m/z 334 (M^+).

Thermolyses of Dimesylate 1a and Tetrabutylammonium *p*-Toluenesulfonate. Powdered mixtures of dimesylate **1a** (38 mg; 0.15 mmol) and $(n\text{-Bu})_4N^+OTs^-$ (484 mg; 1.17 mmol) were melted using a preheated bath kept at 129–30 °C (ca. 1 min) and then heated in a second bath at 115–19 °C. In a typical experiment, heating at 115–16 °C was carried out for 4 min. The cooled reaction mixture was partitioned between water (30 mL) and CH_2Cl_2 (30 mL). The aqueous layer was further extracted with CH_2Cl_2 (two 30-mL portions). The combined organic layers were washed with water (40 mL), dried, and evaporated. Preparative TLC (CH_2Cl_2–MeOH, 99:1) gave three fractions: 3.4 mg of ditosylates (**1b/5b/6b**, 30:55:15), 15.5 mg of mesylate tosylates (**7/8/11a/10/9**, 3:4:33:47:13), and 8 mg of dimesylates (**1a/5a/6a**, 32:61:7). Isomer ratios (Table I) were determined from the weight data and ^1H NMR data.

Solvolysis of 1a in Acetic Acid. A: 42–43 °C. Solutions of dimesylate **1a** (77 mg, 0.3 mmol) in glacial HOAc (5 mL) were heated in a bath kept at 42–44 °C for various times (Table II). The cooled reaction mixtures were diluted with water (35 mL) and extracted with CH_2Cl_2 (four 15-mL portions). The combined extracts were washed with 6% Na_2CO_3 (30 mL) followed by water (30 mL), dried, and concentrated. Purification by preparative TLC (HOAc–EtOAc–hexanes, 2:30:68) of the residue obtained in a typical experiment heated for 3.5 h gave five fractions: 1.2 mg of diacetates (**12c/14a**, 56:44, R_f = 0.65); 7.2 mg of mesylate acetate **12a** (R_f = 0.47); 1 mg of mesylate acetates (**13b/12a/13a**, 52:43:5; R_f = 0.39); 19 mg of dimesylates and **12e** (**5a/12e/1a**, 88:7:5; R_f = 0.26); 16.1 mg of dimesylates and **12e** (**1a/5a/12e/6a**, 50:22:21:7; R_f = 0.12).

The mesylate acetate **12a** was obtained as an oil which solidified overnight in the freezer: mp 32.5–33.5 °C; IR (neat) 1730 (C=O), 1355 and 1175 (SO_2) cm^{-1}; ^{13}C NMR δ 169.79, 78.76, 69.72, 37.61, 30.99, 21.58, 13.89; MS m/z 222 (M^+). Anal. Calcd for $C_8H_{14}O_5S$: C, 43.23; H, 6.35. Found: C, 43.41; H, 6.34.

When dry HOAc was employed, **12e** was not present in the products. The fraction containing **12a** was contaminated (**12a/12d**, 88:12) in one long run (13 h) performed in glacial HOAc.

B: 108–11 °C. These reactions were run similar to the low-temperature runs except that the flask was fitted with a reflux condenser and the bath temperature was kept at 108–11 °C. A typical reaction was run using **1a** (50 mg, 0.19 mmol) and HOAc (3.2 mL) with stirring for 15 min at 110–11 °C. Workup followed by preparative TLC gave four fractions: 8.7 mg of diacetates (**12c/14a/13c**, 68:20:12); 1.3 mg of **12a**; 3.2 mg of mesylate acetates (**13a/13b/12a**, 60:35:5); 3.1 mg of **6a**.

The diacetate fraction was rechromatographed (HOAc–EtOAc–hexanes, 2:20:78, R_f = 0.6) to afford 3.2 mg of pure **12c**.

Preparation of 1-Hydroxycyclobutanemethanol.[11] Methylenecyclobutane (0.37 g; 5.4 mmol) was oxidized with a cold (0–5 °C) mixture of 88% formic acid (4.29 g; 82 mmol) and 50% hydrogen peroxide (0.67 g; 9.8 mmol of H_2O_2) according to the published procedure. Kugelrohr distillation (57–65 °C, 0.05 mmHg) of the crude product gave 350 mg (63% yield) of a colorless oil which by ^1H NMR contained 1-hydroxycyclobutanemethanol and 1,1-cyclopropanedimethanol (95:5, respectively).

Preparation of 1-[(Methylsulfonyl)oxy]cyclobutanemethanol Acetate (12b). Mesyl chloride (0.03 mL; 0.4 mmol) was added to a cold (0–5 °C) solution of **12d** (17.6 mg; 0.12 mmol) in pyridine (1.5 mL) containing DMAP (3 mg). The solution was stirred at 0–5 °C for 6 h and then volatiles were removed in vacuo (0.05 mmHg). The residue was taken up in CH_2Cl_2 (20 mL) and the solution was washed (water, 10 mL), dried, and concentrated to afford crude product (11.4 mg). Preparative TLC (EtOAc–hexanes, 40:60) gave 7.3 mg (27% yield) of pure **12b** (R_f = 0.85) as an oil: IR (neat) 1740 (C=O), 1350 and 1176 (SO_2) cm^{-1}; ^{13}C NMR δ 170.55, 86.07, 65.61, 40.37, 31.97, 20.87, 13.83, MS m/z 222 (M^+).

Preparation of 1-(Acetyloxy)cyclobutanemethanol Acetate (12c). Acetic anhydride (0.33 mL; 3.5 mmol) was added dropwise over 5 min to a cold (0–5 °C) stirred solution of 1-hydroxycyclobutanemethanol (35.6 mg; 0.35 mmol), pyridine (0.27 mL; 3.4 mmol), and 4-(dimethylamino)pyridine (10 mg) in CH_2Cl_2 (2 mL). The reaction mixture was stirred at 0–5 °C for 3 h and at ambient temperature overnight. Methylene chloride (25 mL) was added and the resulting solution was washed with 1.2 N HCl (20 mL), saturated aqueous $NaHCO_3$ (20 mL), and brine (20 mL). The organic layer was dried, concentrated, and the residue purified by preparative TLC (HOAc–EtOAc–hexanes, 2:20:78) followed by Kugelrohr distillation to afford 43.4 mg (67% yield) of **12c**: bp 50–60 °C at 7.6 mmHg (lit.[12] bp 106–110 °C at 35 mmHg); IR (neat) 1740 (C=O); ^{13}C NMR 170.83, 169.76, 79.51, 64.79, 31.36, 21.67, 20.88, 14.03, 9.42; MS (CI, CH_4) m/z 187 (M^+ + 1).

Preparation of 1-Hydroxycyclobutanemethanol Acetate (12d). Acetic anhydride (0.07 mL; 0.7 mmol) was added dropwise over 1 min to a cold (0–5 °C) solution of 1-hydroxycyclobutanemethanol (50 mg; 0.5 mmol) and pyridine (0.12 mL; 1.5 mmol) in dry CH_2Cl_2 (7 mL) containing a few crystals of DMAP. After 80 min of stirring, the reaction solution was diluted with CH_2Cl_2 (25 mL) and water (25 mL). The organic layer was separated, washed with 10% HCl in brine, dried, and concentrated. Purification by preparative TLC (EtOAc–hexanes, 40:60) gave 60 mg (85% yield) of a colorless oil: IR (neat) 3428 (OH), 1729 (C=O) cm^{-1}; ^{13}C NMR δ 171.41, 73.30, 69.19, 32.94, 20.90, 12.01; MS (CI, CH_4) m/z 145 (M^+ + 1).

Preparation of 1-Hydroxycyclobutanemethanol Methanesulfonate (12e). Mesyl chloride (0.045 mL; 0.6 mmol) was added dropwise over 1 min to a cold (0–5 °C) solution of 1-hydroxycyclobutanemethanol (30 mg; 0.3 mmol) and pyridine (0.1 mL) in dry CH_2Cl_2 (4 mL). After stirring for 2 h, the cold reaction solution was diluted with CH_2Cl_2 (25 mL), washed with 1.2 N HCl (10 mL) followed by water (10 mL), dried, and concentrated. Purification by preparative TLC (CH_2Cl_2–MeOH, 98:2) gave 17 mg (32% yield) of pure **12e** as an oil which solidified after cooling: mp 33–35 °C; IR (neat) 3511 (OH), 1350 and 1171 (SO_2) cm^{-1}; ^{13}C NMR δ 74.04, 73.04, 37.65, 32.62, 12.00; MS (CI, CH_4) m/z 187 (M^+ + 1).

Preparation of 2-Methylene-1,4-butanediol 1-Acetate 4-Methanesulfonate (13a). A mixture containing **6a** (89 mg; 0.35 mmol), powdered $NaOAc{\cdot}3H_2O$ (0.47 g; 3.45 mmol), and DMSO (25 mL) was stirred for 2 h and added to cold water (50 mL). The resulting mixture was extracted with CH_2Cl_2 (four 15-mL portions) and the combined extracts were washed with water (three 70-mL portions) followed by brine (50 mL), dried, and concentrated. Purification by preparative TLC (HOAc–EtOAc–hexanes, 2:20:78) gave 48.4 mg (63% yield) of **13a** as a slightly yellow oil. Kugelrohr distillation (bp 76–83 °C at 0.05 mmHg) afforded an analytical sample: IR (neat) 1737 (C=O), 1657 (C=C), 1351 and 1172 (SO_2) cm^{-1}; ^{13}C NMR δ 170.59, 138.78, 116.28, 67.65, 66.65, 37.60, 32.92, 20.93; MS (CI, CH_4) m/z 223 (M^+ + 1). Anal. Calcd for $C_8H_{14}O_5S$: C, 43.23; H, 6.35. Found: C, 42.93; H, 6.20.

Preparation of 2-Methylene-1,4-butanediol Diacetate (13c). Powdered $NaOAc{\cdot}3H_2O$ (200 mg; 1.52 mmol) was added to a solution of **6b** (62.7 mg; 0.15 mmol) in DMSO (7 mL) and the mixture was stirred overnight. Cold water (20 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (three 20-mL portions). The combined organic layers were washed with brine (three 30-mL portions), dried, and concentrated. Preparative TLC (HOAc–EtOAc–hexanes, 2:20:78) of the residue

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afforded 9 mg (32% yield) of **13c** with IR and ^1H NMR spectra matching the literature.[13]

Preparation of 1,1-Cyclopropanedimethanol Diacetate (14a). Acetic anhydride (0.51 g; 5 mmol) was added dropwise over 10 min to a cold (0–5 °C) solution of 1,1-cyclopropanedimethanol (0.17 g; 1.65 mmol) in pyridine (2 mL) containing a few crystals of DMAP. After 3 h stirring, the cold reaction mixture was poured into cold water (30 mL) and the resulting solution was then extracted with CH_2Cl_2 (four 15-mL portions). The combined extracts were washed with 5% H_2SO_4 (50 mL) followed by brine (30 mL), dried, and concentrated. Preparative TLC (CH_2Cl_2) followed by Kugelrohr distillation of the residue gave 0.23 g (74% yield) of the diacetate **14a** as a clear oil: bp 35–40 °C at 0.5 mmHg (lit.[14] bp 115 °C at 15 mmHg); IR (neat) 1740 (C=O) cm^{-1}; ^{13}C NMR δ 170.89, 67.72, 20.93, 19.41, 9.36; MS m/z 186 (M^+).

Preparation of 1,1-Cyclopropanedimethanol Acetate Methanesulfonate (14b). Acetic anhydride (0.36 mL; 3.8 mmol) was added dropwise over 5 min to a cold (0–5 °C) solution of 1,1-cyclopropanedimethanol (0.39 g; 3.8 mmol) in pyridine (3 mL) and the resulting mixture was stirred for 1.5 h. Volatiles were removed at reduced pressure (1 mmHg). Purification by preparative TLC (HOAc–EtOAc–hexanes, 2:30:68) gave 153 mg (28% yield) of pure 1,1-cyclopropanedimethanol monoacetate as an oil: IR (neat) 3427 (OH), 1736 (C=O) cm^{-1}; ^1H NMR δ 4.05 (2 H, s), 3.45 (2 H, s), 2.10 (3 H, s), 0.55 (4 H, m); ^{13}C NMR δ 171.45, 68.25, 66.37, 22.20, 20.91, 8.84; MS (CI, CH_4) m/z 145 ($M^+ + 1$).

Mesyl chloride (0.05 mL; 0.65 mmol) was added dropwise over 5 min to a cold (0–5 °C) solution of 1,1-cyclopropanedimethanol monoacetate (36.5 mg; 0.25 mmol) in dry pyridine (1 mL). The cold reaction solution was stirred for 2 h and volatiles were removed at reduced pressure (1 mmHg). The residue was taken up in CH_2Cl_2 (25 mL) and the solution was washed with H_2O (10 mL), dried, and concentrated. The crude **14b** was free of isomeric **12a**. However, purification by preparative TLC (EtOAc–hexanes, 40:60) gave 29 mg (52% yield) of impure **14b** (**14b**/**12a**, 86:14) as an oil: IR (neat) 1738 (C=O), 1355 and 1175 (SO_2) cm^{-1}; ^{13}C NMR δ 170.78, 73.65, 66.87, 37.62, 19.85, 20.94, 9.98; MS m/z 222 (M^+).

Solvolysis of 1-(Acetyloxy)cyclobutanemethanol Methanesulfonate (12a) in Acetic Acid. Dry HOAc (0.3 mL) and **12a** (4 mg; 0.02 mmol) were heated for 10 min at 109–11 °C. The reaction mixture was cooled and diluted with ice–water (10 mL) and then extracted with CH_2Cl_2 (four 10-mL portions). The combined extracts were washed with 6% Na_2CO_3 (two 10-mL portions), dried, and concentrated to afford 2.3 mg (64% recovery) of crude products which contained starting material **12a**, diacetates **12c**, **14a**, and **13c**, and mesylate acetate **13a** (**12a**/**12c**/**14a**/**13c**/**13a**, 32:46:12:6:4). Preparative TLC (HOAc–EtOAc–hexanes, 2:20:78) gave mesylate acetate and diacetate fractions in accordance with structure assignments. When glacial HOAc was used without drying, diol monoacetate **12d** was obtained as a major product.

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