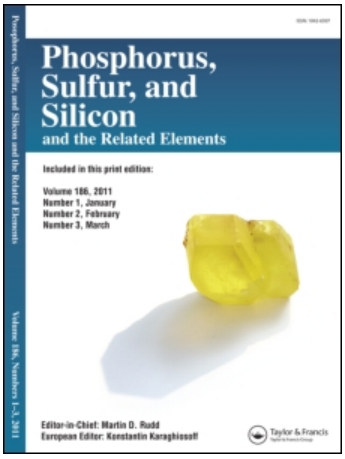

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HYDROXYALKANESULFONYL CHLORIDES FROM CHLORINATION OF HYDROXYALKANESULFINATE SALTS IN A NONPOLAR MEDIUM: 3-HYDROXY-1-PROPANESULFONYL AND 4-HYDROXY-1-BUTANESULFONYL CHLORIDES[1]

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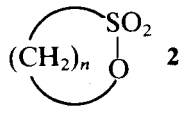
3-Hydroxy-1-propanesulfonyl chloride (**1b**) was obtained for the first time (admixed with 10% of propane sultone, **2b**) by chlorination of a dichloromethane suspension of sodium 3-hydroxy-1-propanesulfinate (**3b**). 4-Hydroxy-1-butanesulfonyl chloride (**1c**) containing 13% butane sultone (**2c**) was prepared similarly from **3c**. The cyclizations of **1b** and **1c** in $CDCl_3$ containing 1-butanol (0.9 M) showed first order rate constants of 1.4×10^{-4} and $6.4 \times 10^{-5}\ s^{-1}$, corresponding to effective concentrations of 4.5×10^2 and 2.1×10^2 M, respectively. Reaction of triethylamine in ethanol-*d* (**a**) with **1b** gave exclusively the undeuterated sultone (**2b**), evidently by a direct cyclization, and (**b**) with **1c** produced mainly ethyl 4-hydroxy-1-butanesulfonate largely monodeuterated at the α-position, and presumably formed by way of the sulfene (**6c**).

We have recently shown[2–4] that aqueous chlorination of ω-hydroxythiols or ω-hydroxythiouronium salts is a serviceable general procedure for preparing ω-hydroxy-1-alkanesulfonyl chlorides (**1**). Whereas the 2-, 5-, and 6-carbon hydroxysulfonyl chlorides (**1a**, **1d**, and **1e**) were prepared in reasonably pure form (>95%), 4-hydroxy-1-butanesulfonyl chloride (**1c**) was obtained only as the major component (~75%) of a reaction product, and 3-hydroxy-1-propanesulfonyl chloride (**1b**) was not observed directly at all, though its formation as a transitory species giving propane sultone (**2b**) was adduced from oxygen-labelling studies.[5]

$HO(CH_2)_nSO_2Cl$ **1**



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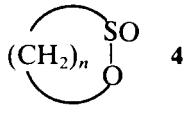
$HO(CH_2)_nSO_2^-Na^+$ **3**



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a) $n = 2$ **b)** $n = 3$ **c)** $n = 4$ **d)** $n = 5$ **e)** $n = 6$

In the course of this work we noted that the cyclization of 4-hydroxy-1-butanesulfonyl chloride to butane sultone (**1c** → **2c**) occurred much faster in water than in chloroform-*d*. This suggested that the likelihood of preparing a purer

specimen of **1c** and of directly observing **1b**, might well be enhanced by carrying out the reaction in nonpolar media. Accordingly we turned to the chlorination of the corresponding sulfinate salts in chloroform or methylene chloride[6] as an appropriate procedure. In this paper we report the outcome of these efforts.

PREPARATION OF ω-HYDROXY-1-ALKANESULFONYL CHLORIDES **1b** AND **1c**

Sodium 4-hydroxy-1-butanesulfinate (**3c**) was readily obtained by treating the sultine (**4c**) with one equivalent of aqueous sodium hydroxide. Peaks at 1011 and 965 cm^{-1} in the infrared spectrum[7] taken with a simple four-signal ^{13}Cmr spectrum and an appropriate ^{1}Hmr spectrum (see Experimental) showed the reaction product to be essentially pure **3c**. Addition of a solution of chlorine in dichloromethane to **3c**, followed by removal of the NaCl and the solvent, gave a liquid product which showed the characteristic signals in the ^{1}H and ^{13}Cmr spectra already assigned[2] to **1c** (~87%) along with small peaks indicating the presence of about 13% of the sultone (**2c**).

Similar reaction of **4b** to give **3b** followed by chlorination, gave a product showing a ^{13}Cmr spectrum consisting of three major peaks clearly assignable to 3-hydroxy-1-propanesulfonyl chloride (**1b**) plus three small signals (at δ 23.6, 44.1, and 68.9) due to about 10% of **2b**. The ^{1}Hmr spectrum was in full accord with this assignment: in addition to the three small absorptions at δ 2.60–2.72, 3.25, and 4.49 from **2b**, there were an approximate quintet at 2.2–2.35 ppm and a multiplet formed by superposition of the triplet at δ 3.85 due to the —CH_2OH and the characteristic "near triplet" at δ 3.89 commonly found with the —CH_2SO_2— grouping. The data collected in Table I, which lists the proton and

TABLE I

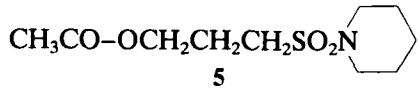
Chemical shifts[a] for the simple ω-hydroxy-1-alkanesulfonyl chlorides, $HO(CH_2)_nSO_2Cl$

	n	^{1}Hmr (δ)	^{13}Cmr (δ)	Ref.
1a	2	2.98 (s, 1H), 3.98 ("t", 2H), 4.28 ("t", 2H)	56.9, 67.6	4
1b	3	2.2 (s, 1H), 2.2–2.35 ("quint", 2H), 3.85 (t, 2H), 3.89 ("t", 2H)	27.2, 59.4, 62.4	b
1c	4	1.7–1.9 (m, 2H), 2.15–2.25 (m, 2H), 3.73 (t, 2H), 3.79 ("t", 2H), 4.3 (br s, 1H)	21.6, 30.1, 61.8, 65.4	2
1d	5	1.18–2.56 (m, 6H), 2.86 (s, 1H), 3.65 (t, 2H), 3.71 ("t", 2H)	23.9, 24.1, 31.7, 62.1, 65.3	2
1e	6	1.3–1.8 (m, 6H), 1.8–2.3 (m, 2H), 3.63, (t, 2H), 3.70 ("t", 2H), 5.13 (s, 1H)	24.2, 25.1, 27.2, 32.0, 62.3, 65.3	2

[a] From $CDCl_3$ solutions at room temperature; values for the OH singlets are variable.
[b] This study.

carbon nmr signals of the five simple ω-hydroxy-1-alkanesulfonyl chlorides (**1a–e**) that we have prepared to date,[8] clearly show the similarity expected in such an homologous series.

Chemical characterization of 3-hydroxy-1-propanesulfonyl chloride (**1b**) was carried out by treating a freshly prepared sample with acetyl chloride to give the 3-acetoxy–1-propanesulfonyl chloride followed by reaction of the crude product with piperidine to give the crystalline piperidide (**5**), which showed the correct exact mass and appropriate infrared, ^{1}Hmr, and ^{13}Cmr spectra. The identity of the 3-acetoxy-1-propanesulfonyl chloride was confirmed by preparing it from 3-mercapto-1-propanol 1,3-diacetate by aqueous chlorination.



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These results encouraged us to see if any 3-hydroxy-1-propanesulfonyl chloride (**1b**) could be observed in the product of the aqueous chlorination of 3-mercapto-1-propanol. Indeed we found that rapid workup after 2 min reaction gave a mixture the ^{1}Hmr and ^{13}Cmr spectra of which clearly showed the presence of 40% of **1b** along with propane sultone (**2b**) (20%) and 3-chloro-1-propanesulfonyl chloride (40%).

SPONTANEOUS AND BASE-INDUCED REACTIONS OF SULFONYL CHLORIDES **1b** AND **1c**

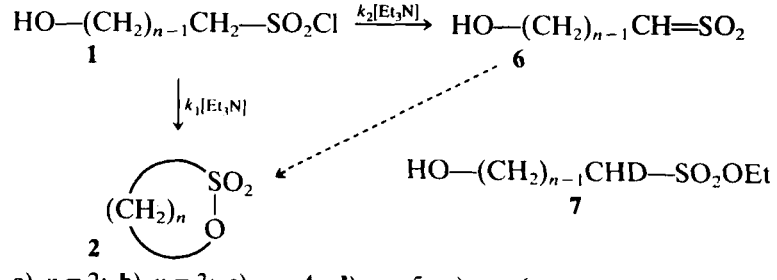
A sample consisting of 3-hydroxy-1-propanesulfonyl chloride (**1b**) (90%) and propane sultone (**2b**) (10%) was dissolved in $CDCl_3$ containing 1-butanol (0.9 M) and was found to be smoothly converted entirely to the sultone (**2b**) on standing at room temperature. The reaction was followed by ^{1}Hmr and showed acceptable first order kinetics to >75% reaction with a half-life around 80 to 85 min, corresponding to $k = (1.4 \pm 0.1) \times 10^{-4}\,s^{-1}$. We have previously reported a rate constant of $8.7 \times 10^{-5}\,s^{-1}$ for 4-hydroxy-1-butanesulfonyl chloride.[2] Repetition with the material prepared as in this paper leads to a slightly modified average value of $(6.4 \pm 1) \times 10^{-5}\,s^{-1}$. When compared with the second order rate constant ($3.1 \times 10^{-7}\,M^{-1}\,s^{-1}$) reported earlier[2] for the model reaction of 1-butanesulfonyl chloride and 1-butanol (also 0.9 M in $CDCl_3$), we obtain effective concentrations[9,10] (C_{eff}) of 4.5×10^2 and 2.1×10^2 M, respectively, for the uncatalyzed cyclizations **1b**→**2b** and **1c**→**2c** (in $CDCl_3$—0.9 M BuOH at 22°C). The C_{eff} for the latter reaction is in good accord with those reported for other 6-exo-tet processes[10] (e.g. 280 M for cyclization of ^-O–$(CH_2)_5Cl$ and 100 M for that of $NH_2(CH_2)_5Br$), but that for the five-membered ring formation (450 M) seems low in comparison with those of analogous 5-exo-tet reactions,[10] e.g. 6×10^4 M for ^-O–$(CH_2)_4Cl$→tetrahydrofuran and $\sim 7 \times 10^3$ M for $NH_2(CH_2)_4Br$→pyrrolidine. A possible explanation for the slow cyclization of **1b** to **2b** under these conditions is that there is relatively greater ring strain in its transition state; this would be a part of the strain present in five-membered

sultones and cyclic sulfates and which is believed to contribute to their remarkable ease of ring opening.[11]

As was noted in the introduction these cyclizations become slower as the solvent polarity decreases. In $CDCl_3$ without any 1-butanol, we have observed a half-life for the reaction **1b**→**2b** of 52 h, and for **1c**→**2c** of about 66 h. We had previously reported $t_{1/2}$ for **1c**→**2c** of 15 h, and on further investigation found that the rate varied erratically from one sample to another. It seems likely that the variation arises from a sensitivity of the reaction to small amounts of water and perhaps other adventitious materials. The sample prepared in the earlier study, which was obtained by extraction from an aqueous medium, almost certainly contained water which may have accelerated the reaction by acting as a general base catalyst and (or) simply by increasing the solvent polarity. In the cyclizations in $CDCl_3$ containing 1-butanol, the rates are evidently reproduceable. hence it would appear that the effect of any variation in adventitious impurities is swamped by that of the much larger amount of the alcohol.

In $CDCl_3$ solution **1b** was instantly converted by addition of triethylamine to propane sultone (**2b**) with no sign of any polymer. When the reaction of **1b** with triethylamine was carried out in ethanol-*d* solution, again the only product was the fully-protonated sultone (**2b**) with no evidence of any ethyl 3-hydroxy-1-propanesulfonate or polymer. Reaction of **1c** (containing ~15% **2c**), however, with triethylamine in ethanol-*d* gave the ethyl ester (**7**) as the major product (~90%), along with what appeared to be a small proportion (~10%) of butane sultone (**2c**) in addition to that present in the starting material. The ester was largely (~70 ± 20%) monodeuterated (i.e. $HOCH_2CH_2CH_2CHDSO_2OEt$) but the sultone (**2c**) showed no sign of deuterium incorporation. These observations are consistent with the reactions shown in Scheme 1. With 3-hydroxy-1-propanesulfonyl chloride (**1b**) k_1 is larger than k_2 (by more than 20 times), and the only observed reaction is the formation of undeuterated propane sultone (**2b**), presumably by general-base assisted direct cyclization of **1b**. With 4-hydroxy-1-butanesulfonyl chloride (**1c**), on the other hand, k_2 is apparently ten (or more) times k_1. These reactions may be compared to those reported[4] for 2-hydroxyethanesulfonyl chloride (**1a**), which reacts with tertiary amines and alcohols (in CH_2Cl_2) to give some of the ester (corresponding to **7**) but mainly products derived from further reaction of the sultone (**2a**), i.e. k_1 is about twice k_2 (with triethylamine).

Sulfene **6c**, once formed appears to be trapped largely by the solvent (ethanol)



a) $n = 2$; **b**) $n = 3$; **c**) $n = 4$; **d**) $n = 5$; **e**) $n = 6$

SCHEME 1

without any sizeable fraction cyclizing to form butane sultone. The presence of **2c** in the starting material, however, makes it difficult to see if any of the relatively small amount of sultone (**2c**) that may have been formed in the reaction is deuterated and hence produced from the sulfene (**6c**). It may be recalled[2] that the sultones **2d** and **2e** are largely monodeuterated when formed in the presence of ethanol-*d* and are therefore formed (largely) by the route **1**→**6**→**2**.

In concluding, we may briefly sum up the present and earlier work[2,4] on the mode of reaction of the known ω-hydroxy-1-alkane-sulfonyl chlorides (**1**) with triethylamine in the presence of an excess of an alcohol as follows: direct cyclization (**1**→**2**) is the principal reaction with the entropically favored cases, **1a** and **1b**, whereas the normal sulfene process (**1**→**6**→**2** and (or) **7**) is the chief reaction with the higher homologues (**1c–1e**).

EXPERIMENTAL

Magnetic resonance spectra were obtained using Varian T60, XL200 (^{1}H) and XL300 (^{13}C) instruments, with all reported chemical shift values (relative to tetramethylsilane for organic solution and DSS for aqueous solutions) from the high field instruments. Infrared (ir) spectra were recorded with an IR/32 FTIR IBM spectrometer. Melting points were obtained with a Kofler Hot Stage apparatus and are uncorrected. Rate measurements were carried out by integration of ^{1}Hmr signals as previously described.[2]

4-Hydroxy-1-butanesulfonyl Chloride (**1c**)

A solution of NaOH (40 mg, 1 mmol) in H_2O (10 mL) was added to butane sultine (**4c**) (120 mg, 1 mmol). After the resulting solution was allowed to stand at room temperature for 2 h, the water was removed under reduced pressure to yield **3c** (160 mg, ~100%), ir (KBr) ν_{max}: 3382 (vs), 2945 (vs), 1655 (s), 1560 (s), 1456 (s), 1401 (s), 1312 (s), 1046 (s), 1011 (vs), 965 (vs) cm^{-1}; ^{1}Hmr (D_2O) δ: 1.57–1.65 (m, 4H), 2.37 (t, 2H), 3.61 (t, 2H); ^{13}Cmr (D_2O) δ: 20.8, 33.3, 62.9, 63.8. Chlorine was bubbled into dichloromethane (10 mL) until the solution turned yellowish-green. The solution was quickly added to **3c** (160 mg). The resulting suspension was immediately dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure to yield a (87:13) mixture of **1c** and **2c** in quantitative yield; ir (neat) ν_{max}: 3314 (s), 2957 (s), 1360 (vs), 1304 (s), 1190 (s), 1167 (vs), 999 (s), 914 (s) cm^{-1}; ^{1}Hmr ($CDCl_3$) δ: 1.74–1.84 (m, 2H), 2.08–2.23 (m, 2H), 3.73 (t, 2H), 3.79 (t, 2H), 4.3 (br s, 1H), plus small signals at 3.18 (t, 2H), 4.56 (t, 2H) assigned to 13% **2c**; ^{13}Cmr ($CDCl_3$) δ: 21.3, 29.8, 61.5, 65.1, plus the small signals at 22.8, 23.5, 48.2, 74.2 characteristic of **2c**.

3-Hydroxy-1-propanesulfonyl Chloride (**1b**)

Reaction of propane sultine (**4b**) (106 mg, 1 mmol), NaOH (40 mg) and water (5 mL) as above gave **3b** in quantitative yield (146 mg); ir (KBr): 3399 (vs), 2953 (vs), 1676 (s), 1466 (s), 1424 (s), 1308 (s), 1009 (s), 963 (s) cm^{-1}; ^{1}Hmr (D_2O) δ: 1.80 (quintet, 2H), 2.39 (t, 2H), 3.66 (t, 2H); ^{13}Cmr (D_2O) δ: 27.1, 59.9, 63.5. Chlorination of **3b** (146 mg) as above gave a mixture **1b** and **2b** (90:10) in quantitative yield; ^{1}Hmr ($CDCl_3$) δ: 2.2 (s, 1H), 2.2–2.35 (m, 2H), 2.08 (s, 1H), 3.8–3.95 (m, 4H), plus small signals at 2.6–2.7 (m, 2H), 3.25 (t, 2H), 4.49 (t, 2H) assigned to 10% of **2b**; ^{13}Cmr ($CDCl_3$) δ: 27.2, 59.4, 62.4 (plus small signals at 23.6, 44.1, 68.9 due to **2b**).

A freshly prepared sample of **1b** (containing 10% **2b**) (100 mg) was immediately treated with excess acetyl chloride (2 mL) and the mixture allowed to stand at room temperature for 2 h and worked up as before[2] to give a colorless oil (115 mg) shown by ^{1}Hmr and ^{13}Cmr spectra to be chiefly 3-acetoxy-1-propanesulfonyl chloride (δ_C 20.7, 24.2, 61.0, 62.2, 170.4) (115 mg). The piperidide, prepared from the acetoxy-sulfonyl chloride mixture as before[2], followed by chromatography on silica gel, formed white crystals, m.p. 72–73°C, from cyclohexane; ir (KBr) ν_{max}: 1738 (vs), 1389 (m), 1360 (m), 1333 (vs), 1277 (s), 1242 (vs), 1159 (s), 1140 (vs), 939 (vs), 1069 (m), 1053 (s), 1037 (s), 939 (vs), 590 (m) cm^{-1}; ^{1}Hmr ($CDCl_3$) δ: 1.55–1.65 (m, 6H), 2.03 (s, 3H), 2.03–2.29 (m, 2H), 2.92 (t, 2H), 3.21 (t, 4H), 4.18 (t, 2H); ^{13}Cmr ($CDCl_3$) δ: 20.9, 22.9, 23.8, 25.6, 46.1, 46.6, 62.3, 170.6. Calc'd. exact mass for $C_{10}H_{19}O_4SN$: 249.1034. Found: 249.1035.

ω-Acetoxy-1-alkanesulfonyl Chlorides from ω-Mercapto-1-alkanols

The ω-mercapto-1-alkanol was converted to the diacetate by adding 2.2 equivalents of acetyl chloride dropwise and with stirring, then heating the mixture[12] at 50°C for 0.5 h, and distilling the diacetate. To prepare the sulfonyl chloride, Cl_2 was bubbled into water (100 mL) cooled in an ice-salt bath until the solution turned yellow-green. The diacetate (~0.5 mmol) was added and the mixture stirred vigorously for 5 min and then worked up by thorough extraction with CH_2Cl_2, drying of the extract with $MgSO_4$ and evaporation of the solvent. The following were thus obtained in >90% yields. 4-Acetylthio-1-butyl acetate: bp 84–86°C (0.3 torr), ir (neat) ν_{max}: 3366 (m), 1740 (vs), 1694 (vs), 1387 (s), 1368 (s), 1239 (vs), 1134 (vs), 1046 (vs), 956 (m) cm^{-1}; ^{1}Hmr ($CDCl_3$) δ: 1.75–1.66 (m, 4H), 2.05 (s, 3H), 2.34 (s, 3H), 2.90 (t, 2H), 4.06 (t, 2H); ^{13}Cmr ($CDCl_3$) δ: 20.8, 26.9, 27.6, 28.5, 30.5, 63.63, 170.7, 195.2. 4-Acetoxy-1-butanesulfonyl chloride, colorless oil, ^{1}H and ^{13}Cmr spectra identical to those reported previously.[2] 3-Acetylthio-1-propyl acetate: ir (neat) ν_{max}: 1742 (vs), 1694 (vs), 1366 (s), 1242 (vs), 1136 (s), 1040 (s), 959 (m), 625 (s); ^{1}Hmr ($CDCl_3$) δ: 1.91 (quintet, 2H), 2.06 (s, 3H), 2.34 (s, 3H), 2.94 (t, 2H), 4.11 (t, 2H); ^{13}Cmr ($CDCl_3$) δ: 20.8, 25.5, 28.6, 30.5, 62.6, 170.6, 195.0. 4-Acetoxy-1-propanesulfonyl chloride: ir (neat) ν_{max}: 1742 (vs), 1443 (s), 1375 (vs), 1244 (vs), 1165 (vs), 1044 (s), 739 (s), 698 (s), 637 (s) cm^{-1}; ^{1}Hmr ($CDCl_3$) δ: 2.09 (s, 3H), 2.45–2.31 (m, 2H), 3.81 (t, 2H), 4.24 (t, 2H); ^{13}Cmr ($CDCl_3$) δ: 20.7, 24.0, 60.9, 62.1, 170.4; converted to the crystalline piperidide with spectra as above.

Reaction of the Hydroxyalkanesulfonyl Chlorides **1b** *and* **1c** *with Triethylamine*

To a mixture (50 mg) of 4-hydroxy-1-butanesulfonyl chloride (**1c**) (85%) and butane sultone (**2c**) (15%) was added a solution of triethylamine (~40 mg) in ethanol-*d* (1 mL). After 5 min the ethanol-*d* and excess amine were removed under reduced pressure; the ^{1}Hmr spectrum of the crude product indicated a mixture of ethyl 4-hydroxy-1-butanesulfonate, butane sultone (**2c**), and triethylammonium cation, with the first two in the ratio of 77:23 (from the integrals of the signals at δ 4.30 and 4.56) and with the Et_3NH^+ peaks around δ 3.2 obscuring the signals due to the protons α to the sulfonyl groups. Workup by washing with aqueous HCl and water gave an oil (45 mg), the ^{1}Hmr and ^{13}Cmr spectra ($CDCl_3$) showed signals due to **2c** (at 1.86 (m), 2.26 (m), 3.17 ("t"), 4.56 (t), and 22.8, 23.6, 48.2, 73.9 ppm, respectively) and peaks at 1.72 (m), 1.96 (m), 3.17 ("t", superimposed on that due to **2c**), 3.70 (t), 4.30 (q), and 15.1, 20.2, 30.7, 49.9 (1:1:1 t, *J* 23 Hz, plus superimposed singlet at 50.1), 61.8, 65.9 ppm clearly assignable to the ethyl ester with about 70% $CHDSO_2$ (and 30% CH_2SO_2); the sulfur-bearing carbon in **2c** (at 48.2) showed no sign of splitting due to the presence of deuteration. In an experiment the same except for the use of ordinary ethanol, the nmr peaks were similar except that the CH_2SO_2 signal appeared as a singlet at 50.1 ppm.

3-Hydroxy-1-propanesulfonyl chloride (**1b**) (90%) plus **2b** (10%) (total 50 mg) was treated with EtOD and Et_3N and worked up as above to give an oil (40 mg) the ^{1}H and ^{13}C nmr spectra of which (except for small solvent peaks) were identical to those of authentic **2b**. A similar reaction of **1b** (90%) (50 mg) in $CDCl_3$ instead of EtOD gave only **2b** (35 mg), again as shown by the ^{1}H and ^{13}C nmr spectra.

ACKNOWLEDGMENTS

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8. For reasons detailed elsewhere[4] it seems likely that hydroxymethanesulfonyl chloride, $HOCH_2SO_2Cl$, the first member of this series, will prove unstable at room temperature, and hence that the compounds listed in Table I represent the first five accessible members of the set.
9. Also known as "effective molarities" (EM), and defined as $C_{eff} = k_1/k_2$ where k_1 is the first order rate constant for the cyclization and k_2 the second order rate constant for an appropriate model reaction.
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