Reinvestigation of the S_Ni Reaction. The Ionization of Chlorosulfites

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The decomposition of alkyl chlorosulfites (ROSOCl) has been investigated both computationally and experimentally. Semiempirical (AM1 and PM3) as well as ab initio (HF/3-21G(*), HF/6-31G*, and MP2(full)/6-31G*//MP2(full)/6-31G*) methods were employed, and the results were confirmed experimentally by NMR spectroscopy. The computations indicated that certain alkyl sulfinyl cations ($ROSO^+$) are stable and might be involved in the decomposition of chlorosulfites. Detection of these ions by ^1H and ^{13}C NMR spectroscopy in polar solvents such as acetone-d_6 and acetonitrile-d_3 as well as kinetic studies allowed important conclusions to be drawn about the mechanistic details of the S_Ni reaction. We conclude that primary alkyl chlorosulfites ionize to yield a sulfinyl cation ($ROSO^+$) and Cl^-, whereas tertiary chlorosulfites preferentially give a carbenium ion and a chlorosulfinyl anion ($OSOCl^-$). The generation of these ion pairs is facilitated in polar solvents where the rates of decomposition of chlorosulfites are largely accelerated. The decomposition of neopentyl chlorosulfite without rearrangement and the substitution at the bridgehead position of 7,7-dimethylbicyclo[2.2.1]-heptyl 1-chlorosulfite show that the loss of SO_2 from $ROSO^+$ must be accompanied by the attack of the chloride ion from the *front side*.

Introduction

Organic cations which are detectable at room temperature in conventional solvents by methods such as nuclear magnetic resonance are rare. Nevertheless, these important intermediates explain reaction mechanisms.[2,3] The well known S_Ni reaction,[4-9] in which an alcohol reacts with thionyl chloride to yield a chloride which retains the configuration of the starting material, has been described in terms of an ion pair mechanism.[10-14] This conclusion was simply drawn from the observation that the decomposition of chlorosulfites, which were established as intermediates in the S_Ni reaction, is strongly accelerated in more polar solvents.[10-12] However, no direct detection of the intermediate ions specifically involved in this reaction has been reported.

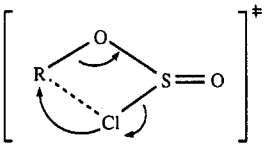
Lewis and Boozer[11] proposed a multistep ionization mechanism (1) to explain the formation of the various products. Since only the inverted product is obtained in

$$ROSOCl \rightleftharpoons R^+OSOCl^- \rightleftharpoons R^+SO_2\,Cl^- \rightarrow RCl + SO_2 \quad (1)$$

the presence of, e.g., a tertiary amine, Coppinger, Lewis, and Boozer[13,14] modified their ionization mechanism and proposed that the sulfur–chlorine bond breaks first (2), due to the attack of the base at sulfur.

$$ROSOCl \rightleftharpoons ROSO^+Cl^- \rightleftharpoons R^+SO_2\,Cl^- \rightarrow RCl + SO_2 \quad (2)$$

On the other hand, a concerted four-center process, termed the S_Ni reaction, was proposed[10a] although this is an orbitally forbidden reaction according to the Woodward–Hoffmann rules.[10b]



Cram[12] investigated the influence of a neighboring phenyl group adjacent to the reacting center by studying the decomposition of secondary phenyl alkyl alcohols and concluded that bridged phenonium ion pairs might be involved in the transition state. Overall, the decomposition was described as an "ion pair, multi-stage substitution reaction".

To date, no unambiguous explanation has been given why the stereochemistry of the S_Ni reaction is so predictable. Lewis and Boozer[11-13] determined, by using UV spectroscopy, that the decomposition of chlorosulfites followed first-order kinetics in most cases, although some runs, which were not further specified, fit only second-order kinetics. The rates increased in more polar solvents, confirming the suggestion that an ion pair or a highly ionic intermediate is involved. Interestingly, only the inverted product was obtained when PCl_5 was used,[9] probably due to its easy ionization.

It has not been clearly established whether or not ion pairs are involved or, if so, which ions are present. Several mechanisms might account for the variety of products formed under different reaction conditions. Attention must be paid to the quite different stabilities of primary, secondary, and tertiary carbenium ions which determine which set of ion pairs, R^+ and $OSOCl^-$ or $ROSO^+$ and Cl^-, is actually generated. Frequently, very significant amounts of olefin are formed during the decomposition.[12] This has never been taken into account adequately. These con-

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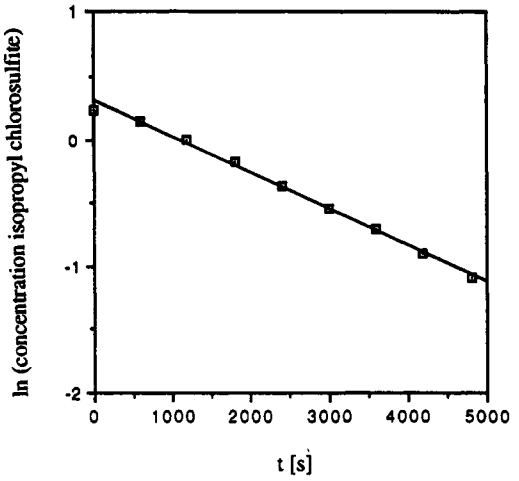

Figure 1. Decomposition of isopropyl chlorosulfite in acetone-d_6 at 308 K.

siderations are addressed theoretically and experimentally in the present paper.

Methods

Computations. All computations were performed using either the semiempirical methods AM1[15] and PM3[16] included in the MOPAC 6.0 program package (QCPE no. 455), installed on a DEC 3100[17] computer, or the ab initio program GAUSSIAN 90,[18] running on a CONVEX-220[19] computer. Geometries were minimized with respect to all geometrical parameters using the standard BFGS algorithm.[20] Finally, a force calculation was carried out to determine the number of imaginary frequencies (NIMAG). Generally, the optimized geometries at the semiempirical level were taken as starting points for ab initio calculations. Minima were determined at the Hartree-Fock HF/3-21G(*), HF/6-31G*, and the correlated MP2(full)/6-31G*//MP2(full)/6-31G* levels of theory.[21,22] Zero-point energies were obtained from the harmonic frequencies calculated at the HF/6-31G* level.

NMR Spectroscopy. The rates of decomposition and the low-temperature experiments were monitored using a Bruker AC 300 NMR spectrophotometer. Temperatures were measured with an accuracy of ±1 °C by a Bruker variable-temperature unit. For the kinetic runs, the time between acquisitions was controlled by a self-written microprogram. The concentrations employed were approximately 10^{-2} mol L^{-1}. The NMR tubes were filled under a nitrogen atmosphere and sealed. Chloroform-d, acetone-d_6, and acetonitrile-d_3 were chosen as solvents to ascertain the influence of solvent polarities upon the rates of decomposition. Rate constants were calculated from the slope of $\ln_{relconcn}$ vs time plots, assuming first order (for example, Figure 1). The low-temperature experiments were interpreted following the treatment of Martin et al.[23,24] based on a line-shape analysis.

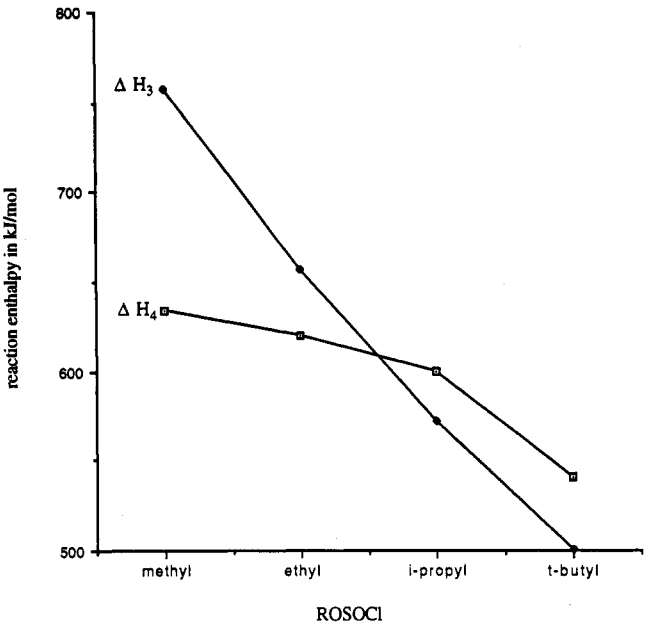

Figure 2. Reaction enthalpies ΔH_3 and ΔH_4 for ionization of chlorosulfites at the HF/6-31G* level of theory (cf. Tables I and II).

Results and Discussion

Computations. Semiempirical (AM1 and PM3) and ab initio HF/3-21G(*), HF/6-31G*, and MP2(full)/6-31G*//MP2(full)/6-31G* computations were used to examine the two different alkyl chlorosulfite ionization possibilities. The enthalpies of the following reactions (3 and 4) were considered:

$$ROSOCl \rightarrow R^+ + OSOCl^- \quad \Delta H_3 \qquad (3)$$

$$ROSOCl \rightarrow ROSO^+ + Cl^- \quad \Delta H_4 \qquad (4)$$

The reaction enthalpies were derived from the heats of formation (semiempirical) or the absolute electronic energies (ab initio) computed by full geometry optimizations of stationary points along the energy hypersurface. Methyl (**1**), ethyl (**2**), isopropyl (**3**), and *tert*-butyl (**4**) chlorosulfite were used to probe the effect of the different stabilities of the corresponding carbenium and chlorosulfinyl ions. The results are summarized in Tables I–III and Figure 2.

Our computations show that primary chlorosulfites ionize more easily at the sulfur–chlorine bond to yield $ROSO^+$ and Cl^- whereas tertiary derivatives preferably give R^+ and $OSOCl^-$. Secondary compounds might ionize either way, depending upon the substrate. The alkyl chlorosulfinyl cation is not unusual; the ionization of methyl chlorosulfite on treatment with SbF_5 to form $CH_3OSO^+SbF_5Cl^-$ was observed in Olah's laboratory.[25] Christie, Lewis, and Casserly[26] suggested that certain methyl transfer reactions probably involve the CH_3OSO^+ (**5**) intermediate, produced by reaction of methyl chlorosulfite with antimony pentachloride. Finally, an X-ray structure of $CH_3OSO^+Sb_2F_{11}^-$, reported by Gillespie,

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Table I. Heats of Formation (AM1 and PM3 in kJ mol^{-1}) and Absolute Electronic Energies (ab Initio, in au) of Alkyl Chlorosulfites and Corresponding Chlorosulfinyl Cations at Different Levels of Theory. Zero Point Energies (ZPE) kJ mol^{-1}

	AM1	PM3	HF/3-21G(*)	HF/6-31G*	MP2/6-31G*// MP2/6-31G*	ZPE (HF/6-31G*)
CH_3OSO^+ [a]	544.21	586.35	−583.61153	−586.47721	−587.13170	132.16553
$C_2H_5OSO^+$ [a]	506.81	545.64	−622.44337	−625.52459	−626.31494	211.04941
$C_3H_7OSO^+$ [a]	478.11	514.76	−661.27573	−664.57106	−665.49942	287.22713
$C_4H_9OSO^+$ [a]	460.74	489.82	−700.10192	−703.62782	−704.67922	354.38782
CH_3OSOCl [b]	−424.26	−375.10	−1041.29323	−1046.24469	−1047.04097	137.86061
C_2H_5OSOCl [b]	−448.19	−393.76	−1080.11904	−1085.28576	−1086.21816	217.58113
C_3H_7OSOCl [b]	−467.39	−418.15	−1118.94427	−1124.32462	−1125.35355	295.53956
C_4H_9OSOCl [b]	−471.66	−433.92	−1157.76666	−1163.35865	−1164.57120	373.07138
Cl^-	−157.68	−214.35	−457.44412	−459.52510	−459.65210	
$OSOCl^-$ [c]	−577.68	−582.04	−1001.98281	−1006.72554	−1007.39359	23.97880

[a] Point group = C_s. [b] Point group = C_1. [c] Point group = C_{2v}.

Table II. Reaction Enthalpies (ΔH_3) for ROSOCl → R^+ [a] + $OSOCl^-$ in kJ mol^{-1} at Different Levels of Theory, Including Zero-Point Vibrational Energy Corrections

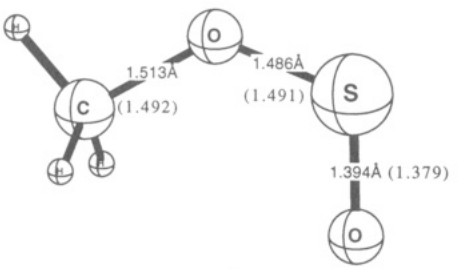
R	AM1	PM3	HF/ 3-21G(*)	HF/ 6-31G*	MP2/6-31G*// MP2/6-31G*
methyl	902.41	866.59	765.93	732.37	809.67
ethyl	777.55	742.53	699.58	632.24	665.97
isopropyl	692.49	665.80	595.72	550.07	500.91
tert-butyl	621.58	594.97	533.91	479.96	372.11

[a] Energies taken from archived standard geometry optimizations at the same levels of theory.

Table III. Reaction Enthalpies (ΔH_4) for ROSOCl → $ROSO^+$ + Cl^- in kJ mol^{-1} at Different Levels of Theory, Including Zero-Point Vibrational Energy Corrections

R	AM1	PM3	HF/ 3-21G(*)	HF/ 6-31G*	MP2/6-31G*// MP2/6-31G*
methyl	810.90	747.10	618.27	628.52	669.72
ethyl	797.43	725.05	601.63	613.47	653.00
isopropyl	787.93	681.91	582.22	591.70	522.02
tert-butyl	774.83	680.32	560.72	521.63	610.99

Riddell, and Skim,[27] allows a comparison with the calculated structure (level shown: HF/6-31G*, X-ray measurements in parentheses).



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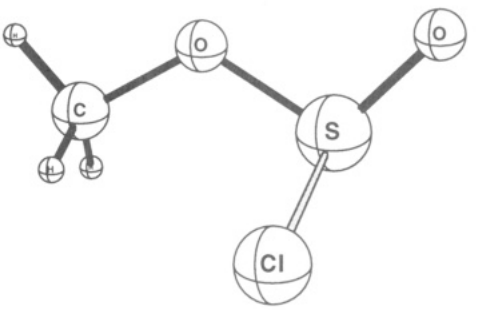
As expected, the syn form of **5** is more stable (Table IV) due to more favorable electrostatic interactions. Moreover, *anti*-**5** was characterized as a transition state (NIMAG = 1) for rotation around the S–O bond.

The nonplanar optimized geometry of the chlorosulfite group is chiral as demonstrated below (at the HF/6-31G* level) for the methyl derivative **1**. Consequently, adjacent methylene protons, e.g., in RCH_2OSOCl, will be diastereotopic and distinguishable in an NMR experiment.

NMR Experiments in Different Solvents and at Various Temperatures. The influence of the chiral chlorosulfite group is demonstrated for *n*-propyl-, neopenyl-, and apocamphanyl chlorosulfite (7,7-dimethylbicyclo[2.2.1]heptyl 1-chlorosulfite) (**9**), which were chosen



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to investigate the effect of different solvents upon the degree of ionization.

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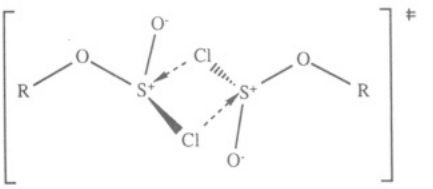
As reported,[28] neopentyl chlorosulfite shows an ABX_9 proton spectrum (δ 4.26, 3.97, 1.02) with a geminal coupling constant J = 9.43 Hz at 300 MHz in $CDCl_3$ at room temperature. The diastereotopicity is lost on heating to more than 100 °C in the neat state or by adding trace amounts of chloride ion, e.g., pyridinium hydrochloride (10^{-5} mol L^{-1}). The latter conditions lead to rapid exchange of chloride at sulfur and fast inversion of configuration. On the other hand, Hudson[28] attributed the appearance of a simple A_2X_9 pattern to a bimolecular chlorine exchange.



The ^1H NMR spectrum of *n*-propyl chlorosulfite does not give the expected $ABMNX_3$ pattern, but is better described as an $ABMM'X_3$ spectrum, where the AM, AM′ and BM, BM′ coupling constants and the chemical shifts of the β-methylene protons are degenerate. The α-methylene protons appear at 4.52 and 4.37 ppm as two doublets of triplets with coupling constants of J(AM) =

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Table IV. Absolute Energies (in au) and Energy Differences (in kJ mol^{-1}) of Syn and Anti Forms of the Methyl Sulfinyl Cation at Different Levels of Theory

	HF/3-21G(*)	HF/6-31G*	MP2/6-31G*// MP2/6-31G*	ZPE[a]
5, syn	−583.61153	−586.47721	−587.13170	132.16538
5, anti	−583.60119	−586.46794	−587.12189	131.10300
ΔE	27.16	24.35	25.76	

[a] HF/6-31G*.

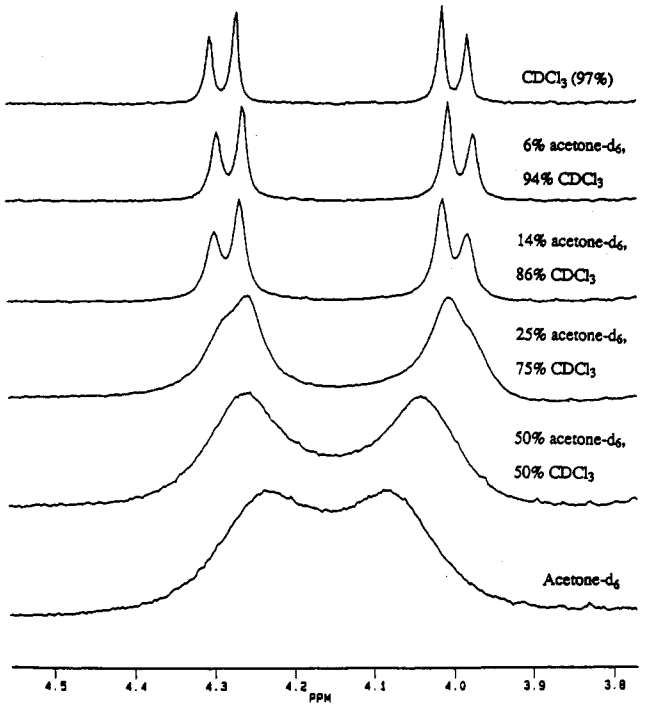


Figure 3. Proton NMR spectrum (300 MHz) of neopentyl chlorosulfite in variable mixtures of chloroform-*d* and acetone-d_6 at 25 °C.

6.56 Hz and J(AB) = 9.86 Hz, recorded at 400 MHz in $CDCl_3$ at 25 °C. Surprisingly, the adjacent methylene group shows simple first order splitting (six peaks). The effect of the chiral group seems to be ameliorated due to the equivalence of the chemical shifts and coupling constants.

The changes in spectra with different solvents were confusing at first, but then illuminating. The spectra of solutions of *n*-propyl chlorosulfite in acetone-d_6 and acetonitrile-d_3 did not show the expected diastereotopicity of the adjacent methylene protons. Instead, these appeared as a simple triplet, centered between the separated peak groups observed in chloroform-*d*. The proton NMR spectrum of a solution of neopentyl chlorosulfite in acetone-d_6 consisted of a broad doublet (δ 4.24 and 4.09 ppm) and a sharp singlet (1.03 ppm), suggesting a chemical exchange process rather than a complex with the solvent. In order to obtain further evidence, spectra were taken in mixed solvents (acetone-d_6 and chloroform-*d*). The bottom spectrum in Figures 3 and 4 was obtained using pure acetone-d_6. Spectra above were subsequently recorded after dilution with chloroform-*d*. The chlorosulfite was obviously still present, while the nonequivalence was lost in polar solvents due to the equilibrium between the alkyl chlorosulfite and the alkyl chlorosulfinyl cation.

Apocamphanyl chlorosulfite was studied to access the loss of nonequivalence of carbon atoms (Table V). As nine ^{13}C peaks were observed in $CDCl_3$, the remote methyl

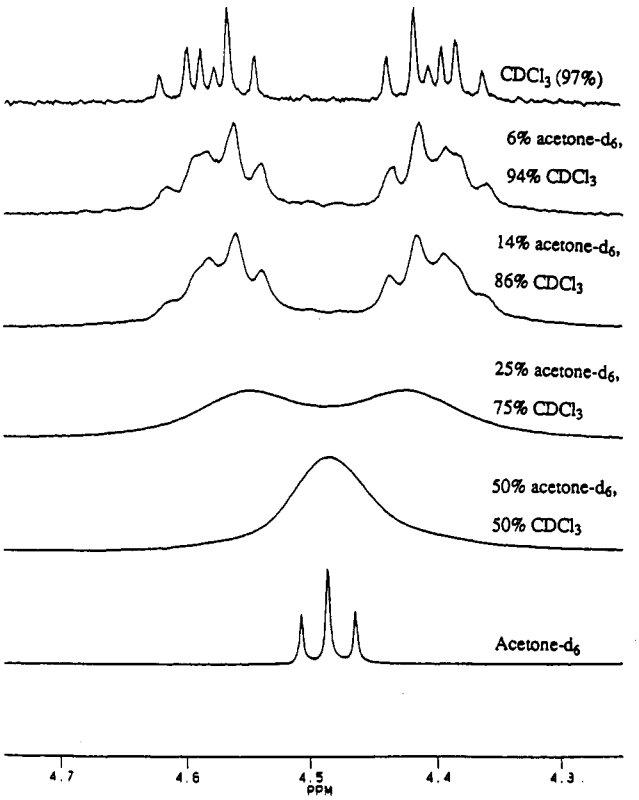
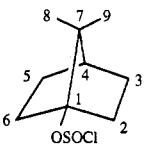


Figure 4. Proton NMR spectrum (300 MHz) of *n*-propyl chlorosulfite in variable mixtures of chloroform-*d* and acetone-d_6 at 25 °C.

Table V. ^{13}C NMR Chemical Shifts of l-Apocamphanyl Chlorosulfite in Chloroform-*d* and Acetonitrile-d_3 at 25 °C

atom no.[a]	1	2	3	4	5	6	7	8	9
$CDCl_3$	98.67	32.13	28.13	38.77	27.77	31.18	47.92	18.20	18.15
CD_3CN	99.65	32.68	28.97	40.08	as 3	as 2	49.07	18.99	as 8

[a] Numbering:



groups are influenced by the chiral substituent. This effect vanished in the polar solvent acetonitrile-d_3; only six peaks were observed.

In order to ascertain whether an ionization or an inversion at sulfur takes place, thermodynamic data were determined by studying the equilibration process at various temperatures. The temperature dependence is illustrated in Figures 5 and 6.

The relatively small values for the enthalpy of activation (1.05 and 3.74 kJ mol^{-1} for neopentyl- and *n*-propyl chlorosulfite, respectively) and the large negative entropy changes (−224.86 J K^{-1} mol^{-1} and −187.31 J K^{-1} mol^{-1}) are consistent with an ionization rather than an inversion. The ions involved *must* be $ROSO^+$ and Cl^-.

The rates of decomposition of *n*-propyl-, *n*-pentyl-, neopentyl-, isopropyl-, 2-butyl-, and cyclohexyl chlorosulfite were determined at 308 and 322 K in chloroform-*d*, acetone-d_6, and acetonitrile-d_3. The dynamic spectra (examples are given in Figures 7 and 8) showed the formation of chloride, olefin (in the case of a secondary derivative), and an approximately constant amount of dialkyl sulfite which is in equilibrium with alkyl chloro-

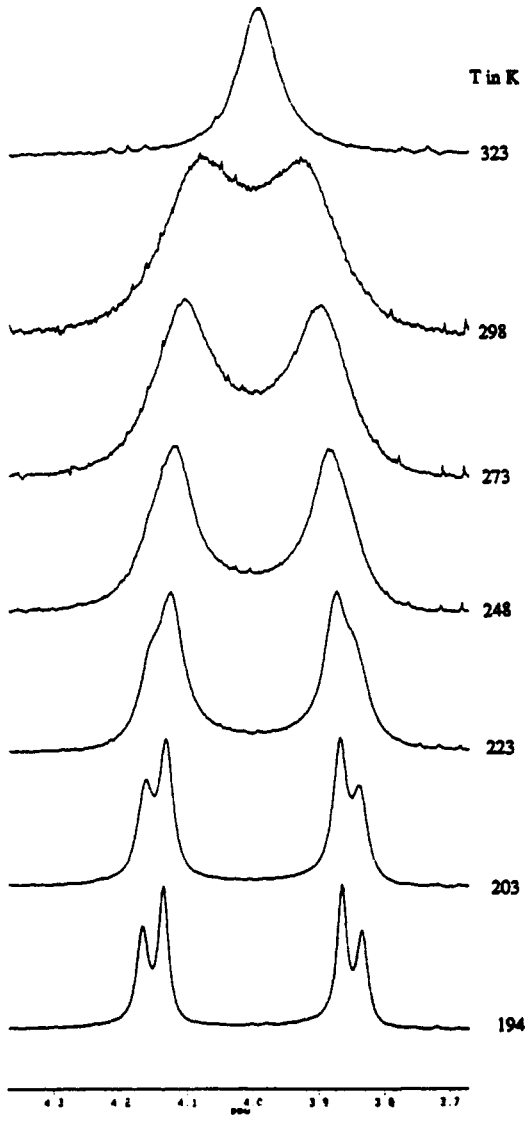
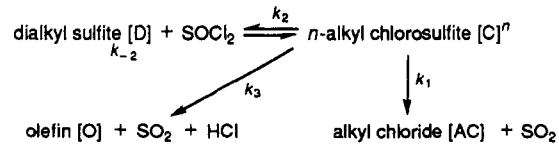


Figure 5. Proton NMR spectrum (300 MHz) of neopentyl chlorosulfite at various temperatures in acetone-d_6.

sulfite and thionyl chloride. Although olefin formation is significant, it has not been taken into account for the determination of the rate constants in earlier work. This is probably due to the low boiling points of the olefins formed. For the first time, the two individual rates and not the composite of the two rates were determined for cyclohexyl chlorosulfite. The rate law was based on the following:



Since [D] is small and remains approximately constant, we assumed that $K_2 = k_2/k_{-2}$ is much smaller than k_1 or k_3; k_1 has the same order of magnitude as k_3. Moreover, [D] = [$SOCl_2$], [AC] = [SO_2], from chloride formation and [O] = [SO_2], from olefin formation.

Thus, the rate of disappearance of [C]

$$\frac{d[C]}{dt} = -k_2[C]^2 + k_{-2}[D]^2 - k_1[C] - k_3[C] \qquad (5)$$

simplifies to

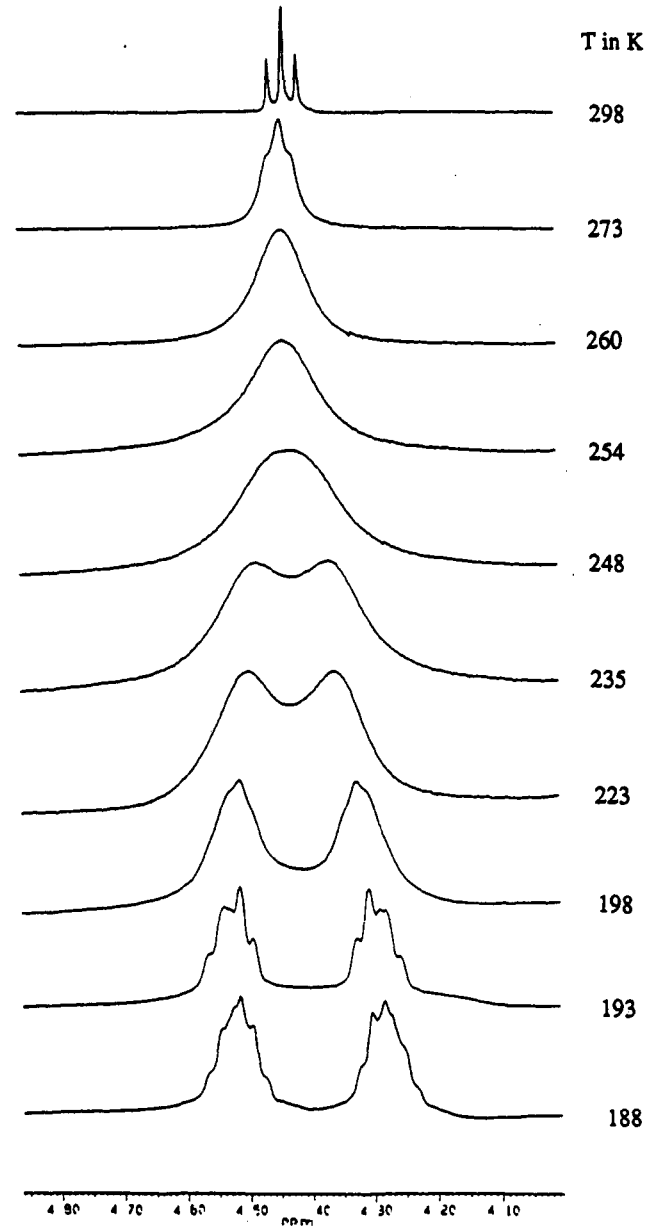


Figure 6. Proton NMR spectrum (300 MHz) of *n*-propyl chlorosulfite at various temperatures in acetone-d_6.

$$\frac{d[C]}{dt} = -(k_1 + k_3)[C] \qquad (6)$$

which means overall first order for $k_\Sigma = k_1 + k_3$ for the chloride and olefin formation. If the concentration of olefin is known, the rates can be separated:

$$[O]_0 - [O] = \frac{k_3}{k_1 + k_3}\{[C]_0 - [C]\} \qquad (7)$$

The rates were determined graphically and are summarized in Table VI.

Conclusions

The most probable ionization pathways of alkyl chlorosulfites computed by semiempirical and ab initio MO methods were supported by NMR investigations. Computations indicated that primary chlorosulfites should ionize to give preferentially an alkyl sulfinyl cation ($ROSO^+$) and Cl^-, whereas tertiary chlorosulfites should yield a carbenium ion and a chlorosulfinyl anion ($OSOCl^-$).

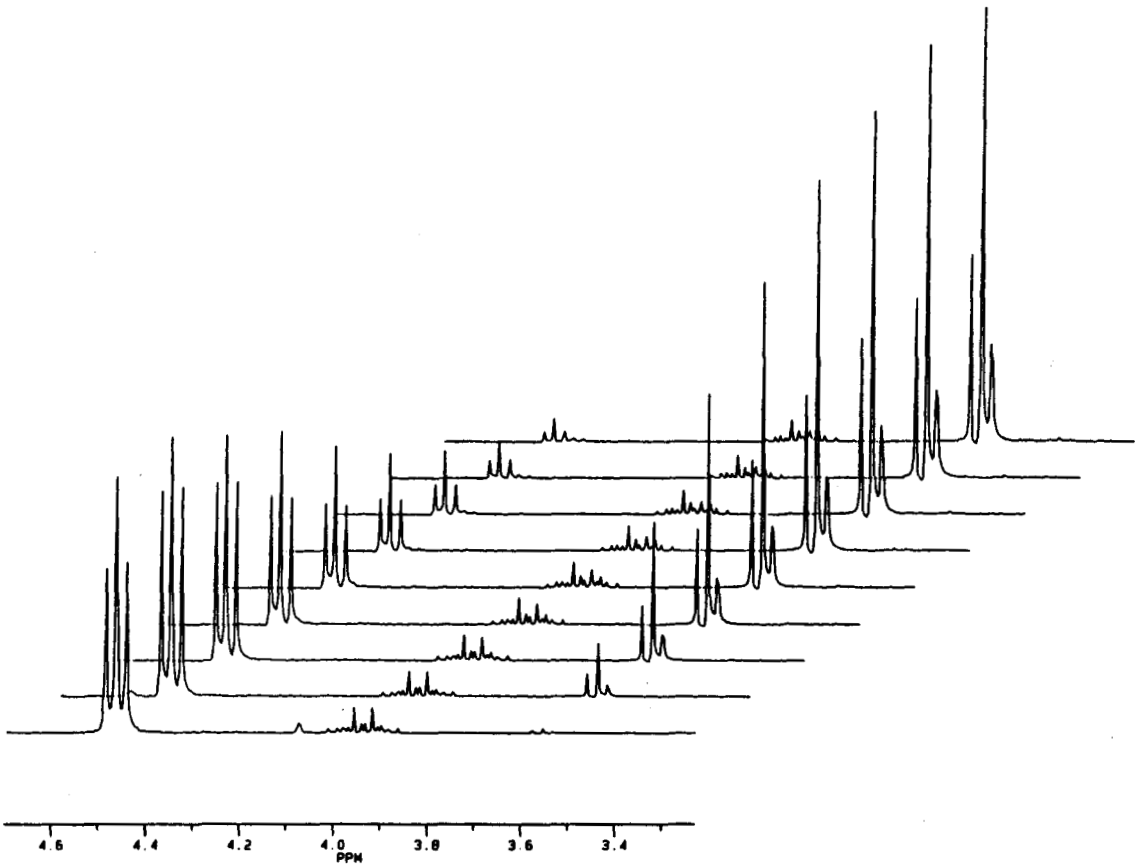


Figure 7. Spectrum of *n*-propyl chlorosulfite in acetonitrile-d_3 during decomposition: time between acquisitions, 3600 s; temperature, 322 K; left triplet, chlorosulfite, right triplet, chloride.

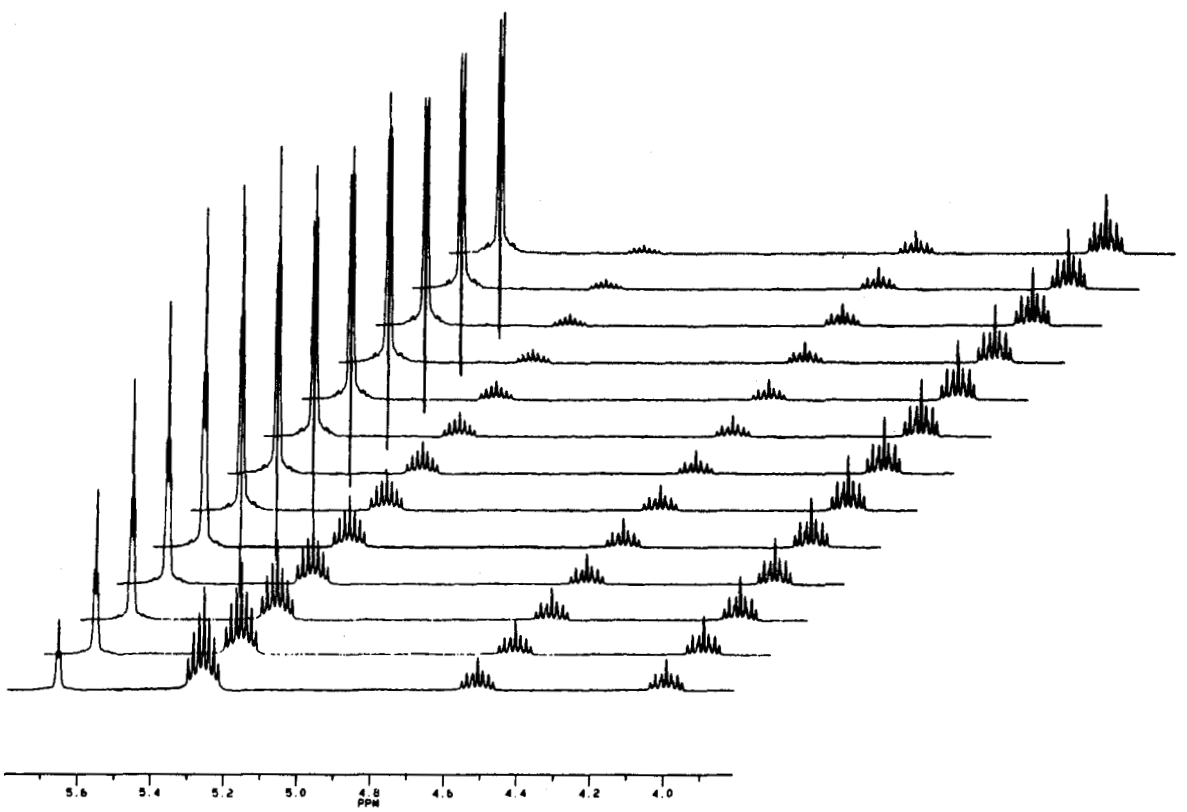


Figure 8. Spectrum of cyclohexyl chlorosulfite in acetonitrile-d_3 during decomposition: time between acquistions, 3600 s; temperature, 322 K. Peak groups from left to right: olefin, chlorosulfite, dialkyl sulfite, chloride.

Alkyl sulfinyl cations are known to be relatively stable. The syn structure of the methyl sulfinyl cation (CH_3OSO^+) revealed by X-ray crystallography also is more stable according to ab initio calculations. Ionization of primary

Table VI. Rate Constants for the Decomposition of Primary and Secondary Alkyl Chlorosulfites in $s^{-1} \times 10^{-5}$

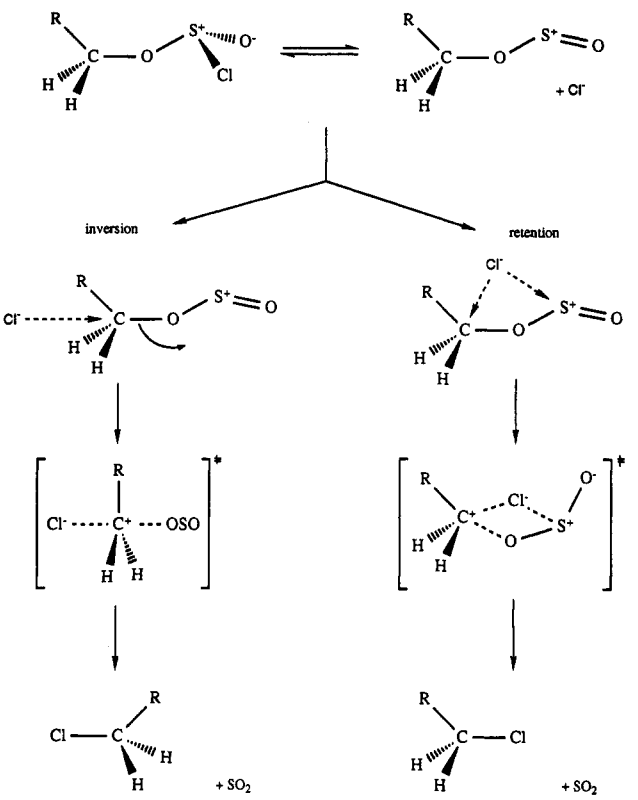
ROSOCl	chloroform-*d*	acetone-d_6	acetonitrile-d_3	*T* (K)
n-propyl	$<10^{-2}$	8.00	1.43	308
	0.18	17.5	8.25	322
n-pentyl	$<10^{-2}$	5.28	1.39	308
	0.22	12.5	8.35	322
neopentyl	$<10^{-4}$	2.63		308
	$<10^{-4}$	6.96	2.61	322
isopropyl, k_Σ[a]	0.26	29.0	71.0	308
	0.87	108.0	479.0	322
sec-butyl, k_Σ[a]	0.70	24.0	36.0	308
	0.95	56.0	124.0	322
cyclohexyl, k_Σ[a]	0.39	21.0	41.0	308
	0.82	79.0	307.0	322
k_1[b]			-11.6	308
		-46.8		322
k_3[b]			-29.4	308
		-32.2		322

[a] $k_\Sigma = k_1 + k_2$. [b] Rates were only calculated where deviations from straight lines were small.

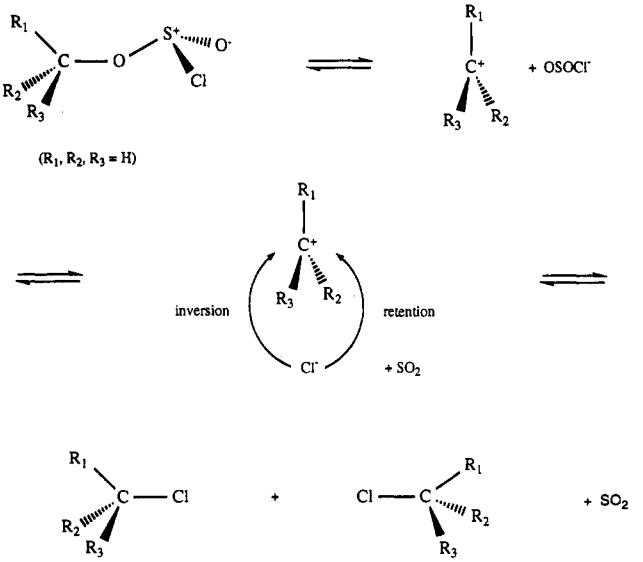
and bridged tertiary chlorosulfites was observed and examined by mixed solvent and low-temperature NMR techniques.

The formation of $ROSO^+ Cl^-$ explains why the rates of decomposition of chlorosulfites are accelerated in highly polar solvents. Ion pair formation precedes the loss of SO_2 and is a key step in the S_Ni reaction. Moreover, the formation of pure neopentyl chloride without rearrangement excludes the intermediate formation of a primary carbenium ion and suggests an S_N2-like mechanism, which is inhibited in neopentyl chlorosulfite due to the bulky *tert*-butyl group. A reasonable pathway involves an ion pair return (Cl^- to $ROSO^+$) to the *front side* of the substrate. The formation of apocamphanyl chloride from apocamphanol (where backside attack is a priori impossible) on treatment with thionyl chloride on prolonged standing (longer than 1 month at room temperature) supports this possibility. Attempts to isolate *tert*-butyl or 1-adamantyl chlorosulfite failed although the NMR spectra were observed in solution.[29] This is due to the increased stability of the *tert*-butyl and 1-adamantyl cations. For further work it appears to be useful to differentiate between S_Ni mechanisms which are S_N2-like or S_N1-like. Scheme I represents the S_N2-like S_Ni mechanism which could be termed the "S_N2i mechanism". Since *tert*-butyl and 1-adamantyl chlorosulfite are more likely to decompose through a carbenium ion intermediate, the mechanism is termed "S_N1i" (Scheme II).

Scheme I



Scheme II



Experimental Section

NMR spectra (δ) were recorded at 250, 300, or 400 MHz with Bruker AC 250, AC 300, and AMX 400 high-field instruments, temperature calibrated with a Bruker variable-temperature unit. Solvents of commercial grade were purified by common procedures and stored over the appropriate drying agent. IR spectra were obtained on a Perkin-Elmer 1600 Series FT/IR spectrophotometer.

Materials. General Procedure for Primary and Secondary Chlorosulfites. A 50-mL two-necked round-bottomed flask with a gas inlet tube was filled with 20 mL of methylene chloride and placed in an ice–water/salt bath (-10 °C). A stream of nitrogen was bubbled through the solution at a rate of 2 bubbles per s. Four portions of 2.2 mL (30 mmol) of thionyl chloride were added over a period of 30 min, always followed by a 25 mmol portion of the chosen alcohol. The solution was allowed to stand at room temperature for another 30 min, and the solvent and excess $SOCl_2$ were removed under reduced pressure. The remaining solution was distilled under reduced pressure to give 31–88% chlorosulfite, which was stored under nitrogen and kept in the refrigerator.

***n*-Propyl Chlorosulfite.** Yield: 12.5 g (79%). Bp: 37–39 °C (3.2 Torr). IR: 2959.2, 2932.2, 2894.1, 1466.4, 1384.3, 1221.6, 1120.0, 1039.8, 1016.2, 924.3, 893.3 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): 4.51 (dt, 1 H, J(AB) = 6.56 Hz, J(AA') = 9.86 Hz), 4.37 (dt, 1 H, J(AB) = 6.56 Hz, J(AA') = 9.86 Hz), 1.85 (m, 2 H, J = 7.23 Hz), 1.03 (t, 3 H, J = 8.83 Hz). ^{1}H-NMR (300 MHz, $(CD_3)_2$-CO): 4.47 (br t, 2 H), 1.86 (m, 2 H), 1.02 (t, 3 H, J = 7.38 Hz). ^{1}H-NMR (300 MHz, CD_3CN): 4.46 (t, 2 H, J = 6.00 Hz), 1.86 (m, 2 H), 1.01 (t, 3 H, J = 8.13 Hz). ^{13}C-NMR (400 MHz, $CDCl_3$): 68.93, 22.11, 10.07.

***n*-Pentyl Chlorosulfite.** Yield: 14.9 g (88%). Bp: 51–52 °C (4.5 Torr). IR: 2959.4, 2932.8, 2873.1, 1465.9, 1380.3, 1221.8, 1119.7, 1038.9, 1012.6, 923.4, 893.7, 807.7, 788.2 cm^{-1}. ^{1}H-NMR

(29) Schreiner, P. R. Masters Thesis, Department of Chemistry, University of Georgia, 1991.

(250 MHz, $CDCl_3$): 4.55 (m, 1 H), 4.40 (m, 1 H), 1.81 (m, 2 H), 1.39 (m, 4 H), 0.97 (t, 3 H). ^{1}H-NMR (300 MHz, CD_3CN): 4.49 (t, 2 H, J = 6.28 Hz), 1.82 (m, 2 H), 1.41 (m, 4 H), 0.93 (t, 3 H, J = 6.80 Hz).

Neopentyl Chlorosulfite. Yield: 15.2 g (81%). Bp: 46–47 °C (3.2 Torr). IR: 2925.2, 2891.0, 1471.7, 1452.4, 1220.1, 1179.1, 1085.2, 878.2 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.26 (d, 1 H, J = 9.43 Hz), 3.97 (d, 1 H, J = 9.43 Hz), 1.02 (s, 9 H). ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 4.16 (br d, 2 H), 1.03 (s, 9 H). ^{1}H-NMR (300 MHz, CD_3CN): 4.17 (s, 2 H), 1.03 (s, 9 H).

Isopropyl Chlorosulfite. Yield: 10.6 g (67%). Bp: 33–34 °C (4.5 Torr). IR: 2986.3, 2939.5, 1586.6, 1468.7, 1453.4, 1387.7, 1376.9, 1220.4, 1181.8, 1091.6, 874.0 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.47 (m, 1 H, J = 4.96 Hz), 1.52 (d, 3 H, J = 5.00 Hz), 1.47 (d, 3 H, J = 5.00 Hz). ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 5.47 (m, 1 H, J = 6.35 Hz), 1.48 (d, 6 H, J = 6.38 Hz). ^{1}H-NMR (300 MHz, CD_3CN): 5.45 (m, 1 H, J = 5.81 Hz), 1.47 (d, 6 H, J = 6.62 Hz).

2-Butyl Chlorosulfite. Yield: 12.4 g (72%). Bp 36–37 °C (4.5 Torr). IR: 2977.4, 2939.4, 2882.4, 1458.9, 1340.9, 1222.8, 1174.8, 1022.3, 879.7 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.26 (m, 1 H, J = 6.24 Hz), 1.78 (dq, 2 H), 1.50 (d, 3 H, J = 6.40 Hz), 1.00 (t, 3 H, J = 4.26 Hz). ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 5.41 (m, 1 H, J = 2.59 Hz), 1.72 (m, 2 H), 1.46 (d, 3 H, J = 6.61 Hz), 0.99 (t, 3 H, J = 4.26 Hz).

Cyclohexyl Chlorosulfite. Yield: 6.3 g (35%; note: mixture of chlorosulfite, sulfite and chloride). Bp: 58–60 °C (3.2 Torr). IR: 2939.3, 2860.7, 1450.2, 1334.9, 1219.6, 1157.1, 1031.1, 883.8 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): 5.27 (m, 1 H, J = 5.02 Hz), 2.08–1.27 (br m, 11 H). ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 5.15 (m, 1 H, J = 3.82 Hz), 1.99–1.23 (br m, 11 H). ^{1}H-NMR (300 MHz, CD_3CN): 5.27 (m, 1 H, J = 3.69 Hz), 2.02–1.32 (br m, 11 H).

1-Apocamphanyl Chlorosulfite (7,7-Dimethylbicyclo-[2.2.1]heptyl 1-Chlorosulfite (9)). 1-Apocamphanol (0.1 g, 0.9 mmol) was added to 0.1 mL (0.16 g, 1.35 mmol) thionyl chloride to give 1-apocamphanyl chlorosulfite in essentially quantitative yield. IR (CCl_4): 2963.2, 2888.0, 1561.3, 1441.1, 1221.9, 1178.5, 1023.6, 951.2, 892.1 cm^{-1}. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.13–1.31 (br m, 9 H), 1.06 (s, 6 H). ^{1}H-NMR (300 MHz, $(CD_3)_2CO$): 2.02–1.28 (br m, 9 H), 1.04 (s, 6 H). ^{1}H-NMR (300 MHz, CD_3CN): 2.19–1.37 (br m, 9 H), 1.11 (s, 6 H). ^{13}C-NMR (300 MHz, $CDCl_3$): 98.68, 47.97, 38.77, 31.20, 30.96, 28.04, 27.77, 18.20, 18.15.

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