Table I. Oxidation of Sulfides to Sulfoxides and Sulfones with Peroxytrifluoroacetic Acid[a]

	sulfoxides (1b-10b)				sulfones (1c-10c)			
		mp (bp, mmHg), °C				mp (bp, mmHg), °C		
sulfide	% yield	obsd	lit.	lit. ref[a]	% yield	obsd	lit.	lit. ref[a]
di-*n*-butyl (1a)	83	30-33	32-33	IV, 1, 1561	80[b]	45	44-45	IV, 1, 1561
di-*n*-octyl (2a)	98	68-70	71-72	IV, 1, 1768	89	74-76	76-77	IV, 1, 1768
bis(2-ethylhexyl) (3a)	81	12-15		‡	88	(130-132 0.05 mm)		‡
diphenyl (4a)	80	69-71	71	IV, 6, 1489	99	123-124	128-130	IV, 6, 1490
phenyl benzyl (5a)	84	122-123	124	IV, 6, 2646	99	146-147	148-149	IV, 6, 2647
phenyl phenylethyl (6a)	93	(138, 0.05 mm)		‡	96	53-56	56-58	IV, 6, 3085
benzothiophene (7a)					58	141-142[c]	142-143	III/IV, 17, 485
phenyl allyl (8a)	80	(107-110, 0.5 mm)	(103-104, 0.36 mm)	IV, 6, 1480	77[b]	(122-124, 0.7 mm)	(110-113, 0.5 mm)	IV, 6, 1480
1,2-bis(2-pyridyl)-3,6-dithiaoctane (9a)	89[d]	102-104		‡	81[e]	145 dec		‡
methionine (10a)	61	235 dec	240 dec	III, 4, 1650	81	245 dec	250 dec	III, 4, 1650

[a] All references are the edition, volume, and page of *Beilstein*. Compounds marked with a double dagger have not been previously reported. Satisfactory analytical data (±0.4% for C, H, N, S) were reported for all new compounds listed in this table. [b] CF_3CO_2H removed by a water wash of the benzene solution. [c] Recrystallized from methanol. [d] Di-sulfoxide. [e] Disulfone.

amine functionality (**9a** and **10a**). Sulfides having double bonds (**7a** and **8a**) can be oxidized if stoichiometric amounts of the oxidant are used.[7]

Peroxytrifluoroacetic acid is a quick, convenient, and selective reagent for the oxidation of sulfides to either sulfoxides or sulfones.

Experimental Section

Preparation of Sulfoxides from Sulfides. General Procedure. In a 25-mL, three-necked, round-bottomed flask, outfitted with a magnetic stirrer, thermometer, and addition funnel, was placed trifluoroacetic acid (5 mL) and the sulfide (1.5 g). Peroxytrifluoroacetic acid (1 equiv), from a stock solution prepared by mixing 8.6 mL of 30% hydrogen peroxide and trifluoroacetic acid to a final volume of 25 mL to give a 4 M solution of the peracid, was added dropwise to the stirred, cooled (0 °C, ice–salt bath) sulfide mixture. The reaction was kept at 0 °C until the peroxide was discharged (starch–iodide paper) and the starting material was consumed (TLC, silica gel, dichloromethane or chloroform; 15 min to 3 h). Solvent was removed on a rotary evaporator, and the residue was taken up in benzene (30 mL),[8,9] washed with 10% sodium bicarbonate (2 × 10 mL), dried over anhydrous magnesium sulfate, and stripped of solvent to give the sulfoxide in high purity as evidenced by TLC, GC, HPLC, melting point, IR, and/or ^{1}H NMR. Typical sulfoxide S–O stretches at 1030–1050 cm^{-1} were observed for products **1b–6b** and **8b–10b**.

Preparation of Sulfones from Sulfides. General Procedure. In a 25-mL, three-necked, round-bottomed flask, outfitted with a magnetic stirrer, thermometer, and addition funnel, were placed trifluoroacetic acid (5 mL) and the sulfide (1.5 g). Peroxytrifluoroacetic acid (2 equiv; prepared as above) was added dropwise to the stirred, cooled (0 °C, ice–salt bath) sulfide mixture. The reaction temperature was raised to 30 °C and maintained until the peroxide was discharged (starch–iodide paper; 30 min to 5 h). Solvent was removed by rotary evaporation, benzene (25 mL) was added, and the solvent was again removed on the evaporator. This procedure was repeated three additional times to completely remove residual trifluoroacetic acid. In most cases[8,9] the product needed no further purification as evidenced by TLC, GC, HPLC, melting point, IR, and/or ^{1}H NMR. The typical sulfone S–O stretches at 1125–1160 and 1270–1320 cm^{-1} were observed for products **1c–10c**.

Registry No. **1a**, 544-40-1; **1b**, 2168-93-6; **1c**, 598-04-9; **2a**, 2690-08-6; **2b**, 1986-89-6; **2c**, 7726-20-7; **3a**, 16679-04-2; **3b**, 82374-34-3; **3d**, 82374-35-4; **4a**, 139-66-2; **4b**, 945-51-7; **4c**, 127-63-9; **5a**, 831-91-4; **5b**, 833-82-9; **5c**, 3112-88-7; **6a**, 13865-49-1; **6b**, 34917-41-4; **6c**, 27846-25-9; **7a**, 95-15-8; **7c**, 825-44-5; **8a**, 5296-64-0; **8b**, 19093-37-9; **8c**, 16212-05-8; **9a**, 82374-36-5; **9b**, 82374-37-6; **9c**, 82374-38-7; **10a**, 63-68-3; **10b**, 3226-65-1; **10c**, 7314-32-1; peroxytrifluoroacetic acid, 359-48-8; trifluoroacetic acid, 76-05-1.

Supplementary Material Available: Table II listing infrared S–O bond stretching frequencies and ^{1}H NMR resonances for **1b–6b**, **8b–10b**, and **1c–10c** (1 page). Ordering information is given on any current masthead page.

(7) Durst, T. In "Comprehensive Organic Chemistry"; Jones, D. N., Ed.; Pergamon Press: New York, 1979; Chapter 11.7.

(8) Compounds **9b** and **9c**, which are present as their trifluoroacetate salts, were dissolved in chloroform, washed with 5% sodium hydroxide to liberate the free amines, and then reisolated.

(9) Methionine sulfoxide (**10b**) and methionine sulfone (**10c**) were precipitated from water by the addition of acetonitrile.

Kinetics and Mechanism of the Reaction of Carbon Disulfide with Piperidine in Ethanol

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Introduction

During the study of the aminolysis reactions of bis(ethoxythiocarbonyl) sulfide and other related compounds in ethanolic media, it was found that carbon disulfide (one of the products of the reactions) and the substrate could compete in their reactions toward the amine. In order to obtain the overall scheme, it was thought necessary to study in detail the mechanism of the reactions of carbon disulfide with amines in ethanol.

The reverse reaction of carbon disulfide with amines, i.e., decomposition of dithiocarbamates (eq 1) has been

$$CS_2 + R^1R^2NH \rightleftharpoons R^1R^2NCS_2^- + H^+ \quad (1)$$

subject to study by several authors.[1-4] Nevertheless, the

(1) D. M. Miller and R. A. Latimer, *Can. J. Chem.*, **40**, 246 (1962).
(2) S. J. Joris, K. I. Aspila, and C. L. Chakrabarti, *Anal. Chem.*, **41**, 1441 (1969).
(3) S. J. Joris, K. I. Aspila, and C. L. Chakrabarti, *J. Phys. Chem.*, **74**, 860 (1970).

0022-3263/82/1947-3774$01.25/0

Table I. Experimental Conditions and k_{obsd} for the Reactions of Carbon Disulfide with Piperidine in Ethanol at 25 °C (Ionic Strength 0.0024 M (with Lithium Chloride))

10^3 total amine[a] concn, M	$10^3 k_{obsd}$, s^{-1} [b]		
	0.455[c]	0.591[c]	0.727[c]
1.10		0.89	0.70
1.65	1.23	0.95	0.86
2.20	1.25	1.03	0.99
2.75	1.25		1.19
3.30	1.31	1.21	1.37
3.85	1.31		
4.40	1.42		

[a] A referee has pointed out that this concentration is too small to ensure a constant pH during the reactions. Although it is low, the ratios [piperidinium]/[piperidine] are near unity, and the ratios [total amine]/[CS_2] are 11-90, being 11 in only one case. Furthermore, we have controlled the pH before and after the reactions by means of a pH meter previously standardized at various known ratios of [piperidinium]/[piperidine] in ethanol at the temperature and ionic strength of the reactions. The runs showing pH changes larger than 0.05 were discarded. [b] The above referee has suggested that the increase in k_{obsd} with increase in buffer concentration could be due to a solvent effect. Only the smallest free-amine fraction shows a small increase in k_{obsd} but we do not see how even this could be a solvent effect, since all the solutions are very dilute. On the other hand, we do expect a small increase in k_{obsd} for the lowest fraction and a large one for the highest fraction, according to eq 2. [c] Fraction of free amine.

mechanism of the forward reaction has not been given much attention, its kinetics being followed mainly potentiometrically in aqueous media.[1]

The purpose of this work is to shed more light on the mechanism of the reactions of carbon disulfide with amines in ethanolic media, and we have chosen piperidine as the amine to start this study.

Experimental Section

Materials. Carbon disulfide, piperidine, ethanol, and lithium chloride were reagent grade; however, piperidine and carbon disulfide were freshly distilled prior to use.

Kinetic Measurements. Reaction solutions (3 mL) of the appropriate amine concentration at constant fraction of free amine and ionic strength 0.0024 M (maintained with lithium chloride) in ethanol were introduced into 1-cm cells and placed in the thermostated cell holder of a Pye Unicam SP1800 spectrophotometer. After thermal equilibration at 25 ± 0.1 °C a stock solution (10–30 μL) of the substrate in ethanol was injected into the reaction solution. The reaction was followed by monitoring the increase of absorbance with time at 290 nm. The initial substrate concentration was 0.5–1.5 × 10^{-4} M in all runs.

Pseudo-first-order rate constants were observed (k_{obsd}) in all cases (at least an 11-fold excess of amine concentration over the substrate was employed). These rate constants were determined by the Guggenheim method, in duplicate, the plots remaining linear for at least 3 half-lives.[5] The plots giving correlation coefficients worse than 0.9990 were discarded. The experimental conditions and k_{obsd} for the reactions studied in this work are shown in Table I.

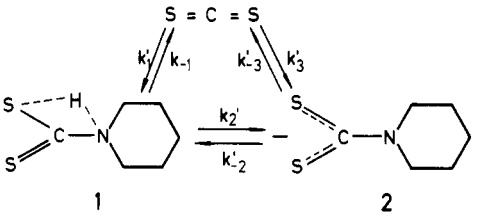
(4) D. De Filippo, P. Deplano, F. Devillanova, E. F. Trogu, and G. Verani, *J. Org. Chem.*, 38, 560 (1973).

(5) Although all the reactions reached the equilibrium and "infinity" absorbances were known, Guggenheim plots were used, which avoid the error in the "infinity" absorbance. The kinetics were in fact followed for 5 half-lives and Guggenheim plots used for 3 half-lives. For assurance that equilibrium was effectively reached and CS_2 neither escaped nor was oxidized, tightly-stoppered Teflon cells (Hellma 110-QS) were used throughout, and some of the slowest reactions were followed for 10 half-lives in the range 190–330 nm. No noticeable changes in absorbances were observed after ca. 6 half-lives.

Table II. Values of k_0 and k_N for the Reactions of Carbon Disulfide with Piperidine in Ethanol at 25 °C, Ionic Strength 0.0024 M (with Lithium Chloride) at Three Fractions of Free Amine

fraction of free amine	$10^3 k_0$, s^{-1}	k_N, s^{-1} M^{-1}
0.455	1.11	0.13
0.591	0.72	0.25
0.727	0.36	0.42

Scheme I



$k'_1 = k_1 [C_5H_{11}N]$
$k'_2 = k_2 [C_5H_{11}N]$
$k'_{-2} = k_{-2} [C_5H_{12}N^+]$
$k'_3 = k_3 [C_5H_{11}N][EtO^-]$
$k'_{-3} = k_{-3} [EtOH]$

Determination of Free Piperidine Concentrations. The three different fractions of piperidine free base employed in the kinetics were prepared by adding the appropriate volumes of a standardized ethanolic solution of HCl to freshly prepared solutions of exactly known concentrations of piperidine in ethanol.

Product Studies. Piperidinium piperidinedithiocarbamate was prepared by a modification of the method used by De Filippo and co-workers[4] and characterized by its IR and NMR spectra. The final product of the kinetic reactions was identified as piperidinedithiocarbamate by comparison of the UV spectra of the reaction samples at equilibrium with authentic samples of piperidinium piperidinedithiocarbamate (prepared as mentioned above) in the same conditions as in the reactions.

The possible product, ethyl xanthate, due to the nucleophilic reaction of carbon disulfide with ethanol or ethoxide ion cannot be detected by UV scannings since it absorbs in the same region as piperidinedithiocarbamate.[6] Its presence was ruled out by the following test: Methyl iodide was added to reaction solutions both during and at the end of the reactions in order to form the possible *S*-methyl *O*-ethyl xanthate. Samples of both were analyzed by GLC (5% SE-30 on chromosorb W) and compared to an authentic sample prepared by reaction of methyl iodide with sodium ethyl xanthate. No ethyl xanthate derivative was detected by these means.

Results and Discussion

The rate law obtained for the reactions of the title compound under the experimental conditions shown in Table I is given by eq 2, where k_{obsd} is the pseudo-first-

$$k_{obsd} = k_0 + k_N F_N [N]_t \quad (2)$$

order rate constant observed, k_N is the second-order rate constant observed (of the form given by eq 5), k_0 is a first-order rate constant in the absence of amine (see eq 6), F_N is the molar fraction of free piperidine, and $[N]_t$ is the total concentration of piperidine (protonated plus free amine concentration). The rate constants k_N were obtained from the slopes (m) of k_{obsd} vs. $[N]_t$ linear plots at constant fraction of free amine, through the equation $k_N = m/F_N$. The rate constants k_0 were obtained as intercepts of the above plots. The values of both rate constants at the different fractions of free amine used are shown in Table II. Plots of k_0 or k_N vs. F_N are not linear, but k_N

(6) We are grateful to a referee for calling this point to our attention.

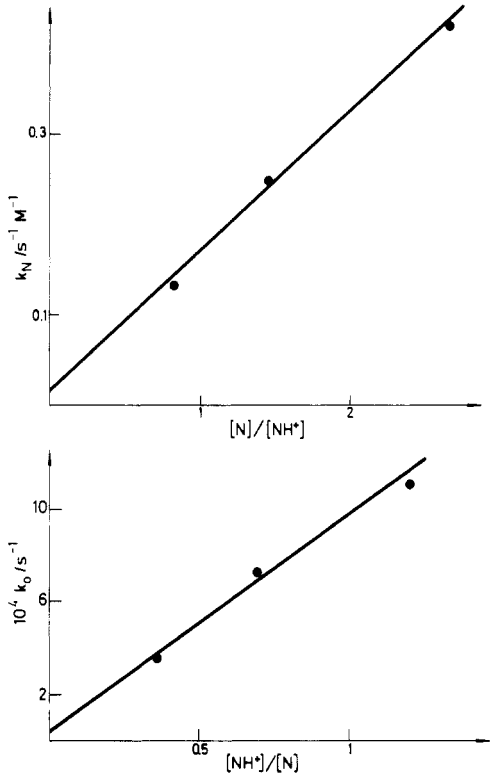


Figure 1. Plots of k_N vs. [N]/[NH$^+$] and k_0 vs. [NH$^+$]/[N] (NH$^+$ and N are the protonated and free-base forms of piperidine) for the reactions of carbon disulfide with piperidine in ethanol at 25 °C, ionic strength 0.0024 M (maintained with lithium chloride).

was found linearly dependent on [N]/[NH$^+$], whereas k_0 has a linear dependence on [NH$^+$]/[N], where N and NH$^+$ represent the free and protonated piperidine, respectively (see Figure 1). These rather unusual forms of k_N and k_0 can be accounted for by the reversible reaction shown in Scheme I. Applying the steady-state treatment to intermediate 1 of the scheme, eq 3 results.[7] Assuming k_{-1}

$$k_{obsd} = \frac{k_1k_2[N]^2 + k_{-1}k_{-2}[NH^+]}{k_{-1} + k_2[N]} + k_3[N][EtO^-] + k_{-3}[EtOH] \quad (3)$$

$\ll k_2[N]$, making $k_{-2}/k_2 = K_{-2}$, and replacing [EtO$^-$] from the basicity constant of piperidine, i.e., $K_b = [NH^+][EtO^-]/[N]$ in eq 3, one gets eq 4, where the ethanol con-

$$k_{obsd} = [k_1 + k_3K_b[N]/[NH^+]][N] + k'_{-3} + k_{-1}K_{-2}[NH^+]/[N] \quad (4)$$

centration has been included in k'_{-3}. Comparison of eq 4 with eq 2 yields eq 5 and 6. The two latter equations account for the plots of Figure 1. As the slopes and intercepts of these plots, the following approximate values can be obtained: $k_1 \approx 0.017$ s^{-1} M^{-1}, $k_3K_b \approx 0.15$ s^{-1} M^{-1}, $k'_{-3} \approx 3.3 \times 10^{-6}$ s^{-1}, and $k_{-1}K_{-2} \approx 9.5 \times 10^{-4}$ s^{-1}.

$$k_N = k_1 + k_3K_b[N]/[NH^+] \quad (5)$$

$$k_0 = k'_{-3} + k_{-1}K_{-2}[NH^+]/[N] \quad (6)$$

The peculiar structure of intermediate 1 of Scheme I, which contains an intramolecular hydrogen bond between the nitrogen and one of the sulfur atoms, has been well established for similar dithiocarbamates.[2,3] The fact that we assumed $k_2[N] \gg k_{-1}$ means that 1 and 2 are effectively at equilibrium during the reaction; therefore, the formation of 1 is the rate-determining step of the left path of Scheme I. This is in complete accord with the work of De Filippo and co-workers on the decomposition of dithiocarbamates.[4]

Further evidence that Scheme I holds for the reactions under study in the present work comes from the shapes of the curves of final absorbance against free-amine concentration obtained at the three fractions of free amine at constant initial substrate concentration. At the wavelength chosen to follow the kinetics, only the final product, 2 of Scheme I absorbs. The equilibrium absorbance of the reaction solution is given by eq 7, where K_1 and K_2 are the

$$A_\infty = \epsilon_2 l[S]_0 \frac{K_1K_2[N]^2/[NH^+]}{K_1K_2[N]^2/[NH^+] + 1} \quad (7)$$

equilibrium constants of steps 1 and 2 of Scheme I, ϵ_2 is the molar absorptivity of 2, l is the cell light path, and $[S]_0$ is the initial concentration of the substrate. An analogous equation can be derived for step 3 of the scheme. Equation 7 gives good account of the experimental curves described above.

Reversibility of step 3 was shown by carrying out the direct reaction of 2 with ethanol in the absence of piperidine. The reaction was followed spectrophotometrically at the same wavelength used for the reactions of carbon disulfide with piperidine, and a decrease in absorbance (due to 2) with time was clearly observed. Under these conditions the kinetics are not simple due to the increase in concentration of free and protonated piperidine as the reaction proceeds toward equilibrium (see Scheme I). This is why the rate constant k'_{-3} could not be measured and compared to the one calculated by plotting eq 6.

We believe that the k_3 step is a nucleophilic attack by piperidine on the substrate, base-catalyzed by ethoxide ion, which partially abstracts a proton from the piperidine molecule in the transition state. Microscopic reversibility implies that ethanol is a general acid in the reverse reaction, i.e., it partially donates a proton to 2 in the transition state of the k_{-3} step. The mechanisms of the k_2 and k_{-2} steps of Scheme I can be described as base-catalyzed and acid-catalyzed by piperidine and piperidinium ion, respectively.

The mechanism proposed for the k_3 step is not known, to our knowledge, for reactions involving dithiocarboxylic acid derivatives, but an analogous mechanism is known for the aminolysis reactions of carboxylic acid derivatives in aqueous solution, viz., the nucleophilic reactions of acetoxime and trifluoroethyl acetates with imidazole, base-catalyzed by hydroxide ion.[8]

Although Jencks and co-workers[9] found no evidence for general acid catalysis of compound 2 in water, the same authors pointed out that other publications have reported both the presence and the absence of general acid catalysis. In spite of the fact that step 3 of Scheme I appears concerted, the possibility of an intermediate with a hydrogen bond between ethanol and 2 can not be ruled out. Although piperidinium ion is a stronger acid than ethanol, a general acid catalysis with formation of an intermediate with a hydrogen bond between piperidinium and 2 is not in agreement with the experimental rate law.[10]

(7) The derivation of eq 3 is given as supplementary material.

(8) J. Kirsh and W. P. Jencks, *J. Am. Chem. Soc.*, **86**, 833 (1964).
(9) S. P. Ewing, D. Lackshon, and W. P. Jencks, *J. Am. Chem. Soc.*, **102**, 3072 (1980).
(10) A referee has suggested the formation of this intermediate. We think this must be highly unstable or perhaps nonexistent due to the higher acidity of piperidinium ion relative to ethanol, which causes the ion to fully donate the proton, thus giving rise to 1. Therefore, we think that catalysis by piperidinium ion would only be observed through the k_{-2} step.

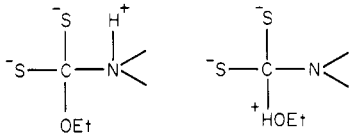
A possible alternative for step 3 of Scheme I could be a reaction of two or more steps involving ethyl xanthate as a reactive intermediate (eq 8). Although it was not

$$CS_2 \underset{k_{-4}}{\overset{k_4[EtO^-]}{\rightleftharpoons}} {}^-SC(S)OEt \underset{k_{-5}}{\overset{k_5[N]}{\rightleftharpoons}} {}^-SC(S)N< \qquad (8)$$

possible to detect its presence during the reactions (see Experimental Section), it might be present as a "steady-state" intermediate. It is known that ethyl xanthate is not stable in ethanol–water mixtures in the presence of acid catalysts even at relatively high pH values.[11] Under the reaction conditions of the present work, the steady state can be applied to the intermediate of eq 8, and with the assumption $k_{-4} \gg k_5[N]$, the resulting rate law is given by eq 9, where K_4 ($=k_4/k_{-4}$) is the equilibrium constant for

$$k_{obsd} = K_4 k_5 [N][EtO^-] + K_{-5} \qquad (9)$$

the first step of eq 8. Equation 9 has the same form as k_{obsd} for step 3 of Scheme I, and both mechanisms are, therefore, kinetically indistinguishable. Step k_5 may comprise two or more steps involving tetrahedral intermediates such as **3** and **4**, which must be highly unstable



3 **4**

or perhaps nonexistent (with lifetimes near that of a molecular vibration). Other alternatives for the k_5 step include acid or base catalysis involving the solvent or piperidine concerted with nucleophilic attack by the amine, but none of them satisfied the rate law given by eq 9 when the principle of microscopic reversibility is taken into account. Therefore, we think that the most likely mechanism for the k_3 step of Scheme I is a nucleophilic reaction of carbon disulfide with piperidine, concerted with proton abstraction from the amine by ethoxide ion.

Acknowledgment. The financial support given to this work by the Dirección de Investigación de la Universidad Católica de Chile (DIUC) is gratefully acknowledged.

Registry No. 1, 98-99-7; piperidine, 110-89-4; carbon disulfide, 75-15-0.

Supplementary Material Available: Detailed derivation of eq 3 from Scheme I (2 pages). Ordering information is given on any current masthead page.

(11) R. J. Millican and C. K. Sauers, *J. Org. Chem.*, **44**, 1664 (1979).

Conformational Stabilities of Substituted Azapropellanes 2-Methyl-1-azoniatricyclo[4.4.4.0^{1,6}]tetradecane Salts[1]

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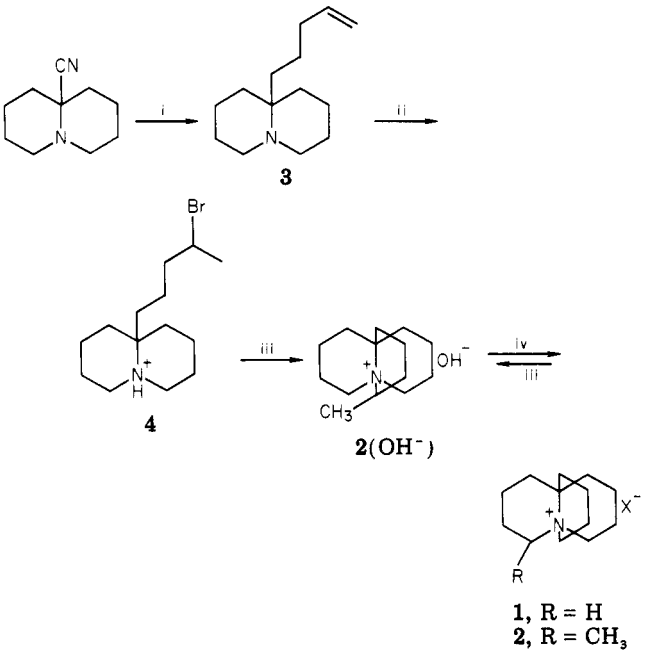
Recently, we reported the synthesis,[2] NMR,[3] and crystal structures[4] of a series of 1-azoniapropellanes containing various combinations of five- and six-membered rings. It was found that the 1-azonia[4.4.4]propellane cation (**1**) exists in a slightly flattened all-chair form which undergoes chair–chair ring inversion of all three rings with a first-order rate constant of 0.7 s^{-1}. Alder has reported[5] that the barrier to this process is 17.6 kcal/mol. Since this process represents the racemization process for this chiral C_3 molecule, it was clear that resolution of **1** was not feasible. However, models indicate that an axially oriented substituent at any position is severely strained, and thus the substituted ring should be constrained to the chair form possessing an equatorial substituent. Models further suggest that, in the presence of one "frozen" ring, sufficient rigidity might be imparted to the entire system to prevent ring inversion of the other two rings, thus making the system optically stable. Since a substituent renders its attached ring carbon chiral, the presence of two diastereomeric pairs of enantiomers is indicated. However, if an axial substituent is forbidden and ring inversion is very slow, the situation simplifies to one enantiomeric pair of ions. Since our objective was the preparation of a resolved ammonium salt whose chirality was centered at nitrogen,[2] we undertook the preparation of **2** to examine if indeed the presence of a single, relatively small substituent would have the desired effect. The ultimate goal of these investigations, viz., the preparation of an effective chiral phase-transfer catalyst, has been fully described previously.[2]

Scheme I[a]



1, R = H
2, R = CH_3

[a] Key: (i), 4-penten-1-ylmagnesium bromide, Et_2O; (ii) 48% hydrobromic acid; (iii) Ag_2O, H_2O; (iv) HX.

The preparation of **2** followed the general route outlined previously and is summarized in Scheme I. Compound **2** was isolated and purified via its iodide salt (mp >300 °C) and reconverted to the hydroxide form (Ag_2O/D_2O) for spectroscopic analysis. It should be noted that, if the preceding stereochemical analysis is valid, the stereo-

(1) Azapropellanes as Phase-Transfer Catalysts. 4. For part 3, see ref 3.
(2) McIntosh, J. M. *Can. J. Chem.* **1980**, *58*, 2604.
(3) McIntosh, J. M. *Tetrahedron.* **1982**, *38*, 261.
(4) McIntosh, J. M.; Delbaere, L. T. J.; Khan, M. A. *Can. J. Chem.* **1982**, *60*, 1073.
(5) Alder, R. W.; Arrowsmith, R. J. *J. Chem Res.* **1980**, 2301.

0022-3263/82/1947-3777$01.25/0