1,3-Diazaallyl radicals must be planar radicals of the π-type since the two nitrogens are equivalent. Molecular models indicate that the radical centers in **2** ($R_nM = CF_3O$) are sterically somewhat less protected than the radical centers in all **1**. It is, therefore, not surprising[20] that although these radicals are stabilized they decay by a bimolecular radical–radical process, presumably a coupling reaction. The small preexponential factor for this reaction ($10^{7\pm1}$ M^{-1} s^{-1}) indicates that these radicals, like certain others,[39] dimerize slowly principally because of a high entropy of activation. That is, for these radicals the duration of an average encounter in solution is not sufficient to ensure that a configuration which would permit reaction is achieved, even though there is no real potential energy barrier to be crossed.

The mechanism by which $(Me_3Si)_2\dot{C}N(SiMe_3)_2$ is formed from $Me_3Si\cdot$ and carbodiimides cannot be unambiguously assigned, since no other radicals were detected during the initial stages of the reaction, even at temperatures as low as −100 °C. However, both for steric and energetic reasons the initial adduct is expected to be a diazaallyl and a possible overall reaction scheme is given in Scheme I. An alternative reaction scheme is shown in Scheme II.[40]

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(1) Issued as NRCC No. 15 427.
(2) NRCC Postdoctorate Fellow, 1974–1975.
(3) NRCC Summer Student.
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(16) See e.g., A. J. Dobbs in "Electron Spin Resonance", Vol. 2, R. O. C. Norman, Ed., Chemical Society, Specialist Report, The Chemical Society, London, 1975, Chapter 10.
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(27) The lifetime of this radical, like that of other presistent radicals, increases with increasing time of irradiation of the sample, presumably because reactive impurities in the medium become consumed.
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(34) The effect of attaching a second sulfur to N_α, as in the $ArS\dot{N}SAr$ radicals,[22] is to further increase g (2.0080–2.0083)[35] and further reduce a^N (11.26–11.45 G).
(35) Comparable g factors have also been reported for N-centered radicals purported to have only one sulfur attached to the nitrogen. See, e.g., U. Schmidt, K. H. Kabitzke, and K. Markau, *Angew. Chem., Int. Ed. Engl.*, **3**, 373 (1964); J. Flood and K. E. Russell, *Can. J. Chem.*, **53**, 1123 (1975).
(36) For example, $\delta^{31}P$ hfs in a nitroxide and in a nitroalkane radical anion are both ca. 1 G.[37] Positions are designated as follows: $Me_\gamma C_\beta \dot{N}_\alpha S_\beta N_\gamma (C_\delta Me_\epsilon)_2 R_\epsilon$.
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(40) Suggested by a referee.

Aminocyclopropyl Sulfoxides. Preparation and Reaction with Acids

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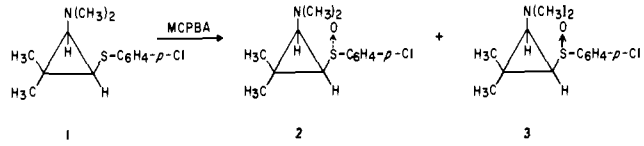
Abstract: The preparation and structural determination of the four isomeric aminocyclopropyl sulfoxides (1*RS*,2*SR*)-2-[(*SR*)-*p*-chlorophenyl)sulfinyl]-*N*,*N*,3,3-tetramethylcyclopropylamine (**2**), (1*RS*,2*SR*)-2-[(*RS*)-(*p*-chlorophenyl)sulfinyl]-*N*,*N*,3,3-tetramethylcyclopropylamine (**3**), (1*RS*,2*RS*)-2-[(*SR*)-*p*-chlorophenyl)sulfinyl]-*N*,*N*,3,3 -tetramethylcyclopropylamine (**4**), and (1*RS*,2*RS*)-2-[(*RS*)-(*p*-chlorophenyl)sulfinyl]-*N*,*N*,3,3-tetramethylcyclopropylamine (**7**) are described. Reaction of **2** with various weak acids ($K_a < 10^{-4}$) in chloroform afforded 3-[(*p*-chlorophenyl)sulfinyl]-1-(*O*-substituted-hydroxy)-*N*,*N*,2,2-tetramethyl-1-propanamines (**8a–d**). Hydrolysis of **8a–d** afforded 2,2-dimethyl-3-[*p*-chlorophenyl)sulfinyl]-propionaldehyde (**9**). Treatment of **2** with various strong acids ($K_a \geq 10^{-4}$) in chloroform afforded stereospecific (>90%) isomerization to **7**. These ring openings and isomerizations are rationalized in terms of zwitterionic intermediates.

We have previously described the preparation of aminocyclopropyl sulfides by the addition of thiocarbenes (or carbenoids) to enamines.[2-4] Oxidation of these aminocyclopropyl sulfides with potassium permanganate in aqueous acetic acid afforded ring-opened sulfone acids and/or ketones.[4,5] It was proposed that these ring openings occurred via aminocyclopropyl sulfone intermediates.[5] We have subsequently prepared an aminocyclopropyl sulfone and have shown that it undergoes a facile hydrolytic ring-opening reaction presumably via a zwitterionic intermediate.[4] This paper describes the preparation of four isomeric aminocyclopropyl sulfoxides and their reactions with weak and strong acids.

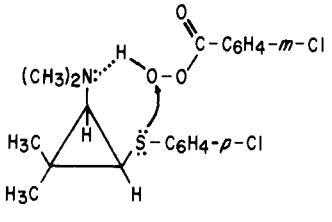
Preparation of Aminocyclopropyl Sulfoxides. Oxidation of *cis*-2-[(*p*-chlorophenyl)thio]-*N*,*N*,3,3-tetramethylcyclopropylamine (**1**)[2-4] with 1 equiv of *m*-chloroperoxybenzoic acid (MCPBA) in methylene chloride at −60 to −70 °C afforded a 90% yield of a mixture of the diastereoisomeric sulfoxides (1*RS*,2*SR*)-2-[(*SR*)-(*p*-chlorophenyl)sulfinyl]-*N*,*N*,3,3-tetramethylcyclopropylamine (**2**) and (1*RS*,2*SR*)-2-[(*RS*)-(*p*-chlorophenyl)sulfinyl]-*N*,*N*,3,3-tetramethylcyclopropylamine (**3**). One recrystallization of this reaction mixture afforded a 70% yield of pure **2**. Laborious column chromatography of the filtrate over acetyl cellulose (elution with 5% acetone in Skelly B[6]) afforded a 0.3% yield of **3**. A ^{1}H NMR spectrum of the reaction mixture before recrystallization showed the ratio of **2**:**3** to be 85:15.



The gross structures of **2** and **3** were determined by elemental analyses,[7] ir, ^{1}H NMR, and mass spectra (see Experimental Section). The configuration of **2** was conclusively established by a single crystal x-ray study. Crystals from Et_2O were large, clear prisms in the orthorhombic system $P2_12_12_1$ with a = 10.536 (5), b = 11.140 (5), c = 12.005 (5) Å, and Z = 4. Intensity data for 1192 reflections were measured using monochromatic Cu radiation on a Syntex $P\bar{1}$ diffractometer controlled by an IBM 1800 computer. The structure was solved by Patterson analysis. Least-squares refinement,[8] with temperature factors isotropic for hydrogens and anisotropic for heavier atoms, converged with an agreement index R = 0.041. Standard deviations for bond lengths are ca. 0.006 Å and for bond angles ca. 0.02°. The configuration of **2** is illustrated in Figure 1.

The chemical shifts ($CDCl_3$) for the dimethylamino groups of **1**, **2**, and **3** are δ 2.29, 2.42, and 2.16, respectively. These data conform to the established principle that protons in the "vicinity" of a S–O bond experience a deshielding effect while protons in the "vicinity" of the lone pair of electrons of a sulfinyl group experience a shielding effect relative to the corresponding sulfide.[9]

The preferential formation of diastereomer **2** was unexpected. Oxidation of a sulfide to a sulfoxide by peracids proceeds by nucleophilic attack of the sulfur atom on the peracid.[10,11] Steric approach control[12] considerations suggest that **3** would be the favored product. The stereoselective formation of **2** can be accounted for by H bonding between the peracid hydrogen atom and the dimethylamino group (I). Cooper and



I

co-workers[13] have suggested that the stereoselective formation of the (*S*)-sulfoxide in the oxidation of phenoxymethyl penicillin is the result of H bonding between an amide hydrogen atom and the carbonyl group of the peracid.

Treatment of **2** with 1 N potassium *tert*-butoxide in refluxing *tert*-butyl alcohol afforded a clean conversion into the trans isomer, (1*RS*,2*RS*)-2-[(*SR*)-(*p*-chlorophenyl)sulfinyl]-*N*,*N*,3,3-tetramethylcyclopropylamine (**4**). That a cis to trans isomerization had occurred was evidenced by their ^{1}H NMR spectra. The vicinal coupling constants for the cyclopropyl hydrogen atoms of compounds **2** and **4** are 6.5 and 3.5 Hz, respectively. It has been established that cis protons on a cyclopropyl ring have larger coupling constants than do trans protons.[14] It is assumed that the configuration about the sulfur atom was unaltered in that Cram and co-workers[15,16] have established that α-sulfinyl carbanions formed under similar conditions maintained their configurations about the sulfur atoms.

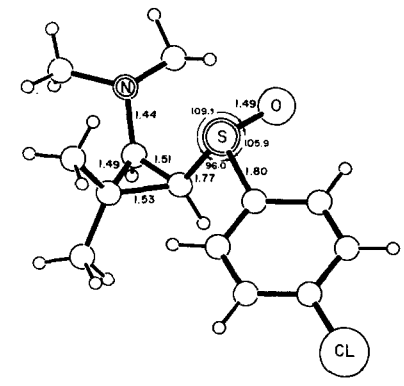
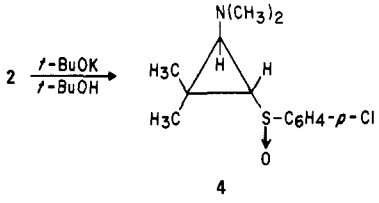
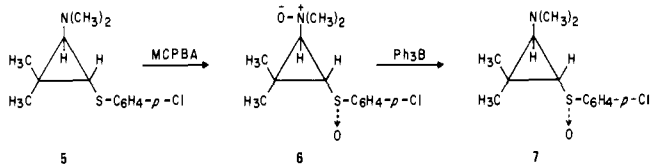


Figure 1. X-ray structure of **2**.



The preparation of the diastereomeric trans sulfoxide **7** was accomplished by way of the amine oxide **6**. Oxidation of *trans*-2-[*p*-chlorophenyl)thio]-*N*,*N*,3,3-tetramethylcyclopropylamine (**5**)[2-4] with 2 equiv of MCPBA in methylene chloride at −60 to −70 °C afforded a 73% yield of (1*RS*,2*RS*)-2-[(*RS*)-(*p*-chlorophenyl)sulfinyl]-*N*,*N*,3,3-tetramethylcyclopropylamine oxide (**6**). Both steric approach control[12] and an attractive interaction between the peracid acid and the amino and/or amine oxide functions would lead preferentially to formation of the sulfoxide of configuration **6**. We have previously described the use of triphenylborane for the conversion of amine oxides to amines.[4] Treatment of **6** with triphenylborane in chloroform afforded an 83% yield of (1*RS*,2*RS*)-2-[(*RS*)-(*p*-chlorophenyl)sulfinyl]-*N*,*N*,3,3-tetramethylcyclopropylamine (**7**). That sulfoxide **7** is diastereomeric with **4** can be seen from their ^{1}H NMR spectra. The chemical shifts for the dimethylamino groups of **7** and **4** are δ 2.25 and 1.88, respectively. These shifts are in accord with the above cited field effects of the sulfinyl group.



Reaction with Acids. In the preparation of **2** it was noticed that a consistent by-product was 2,2-dimethyl-3-[(*p*-chlorophenyl)sulfinyl]propionaldehyde (**9**). We had previously observed that **2** is rapidly hydrolyzed to **9**.[17] As a result, atmospheric water was scrupulously avoided; however, the formation of **9** still occurred. It was observed that the amount of **9** that was formed increased with increased reaction time and temperature. This suggested that the *m*-chlorobenzoic acid that was formed was entering into or catalyzing a reaction which eventually afforded **9**. To evaluate the validity of this proposal, the reaction of **2** with a variety of acids was studied.

Table I. ^{1}H NMR Spectra of **8a–d** in $CDCl_3$

Structure	Chemical shift, δ						
	H^A	H^B	H^C	H^C	H^D	H^D	Aromatic
8a	2.42 (s, 6 H)	5.62 (s, 1 H)	1.25 (s, 3 H)	1.33 (s, 3 H)	2.99 (d, J = 14 Hz, 1 H)	2.72 (d, J = 14 Hz, 1 H)	7.3–7.7 (b, 4 H) 2.04[a] (s, 6 H)
8b	2.52 (s, 6 h)	5.97 (s, 1 H)	1.36 (s, 3 H)	1.45 (s, 3 H)	3.13 (d, J = 13 Hz, 1 H)	2.83 (d, J = 13 Hz, 1 H)	7.2–8.1 (b, 14 H)
8c	2.40 (s, 6 H)	4.87 (s, 1 H)	1.28 (s, 3 H)	1.36 (s, 3 H)	3.07 (d, J = 14 Hz, 1 H)	2.80 (d, J = 14 Hz, 1 H)	6.8–7.6 (b, 14 H)
8d	2.40 (s, 6 H)	4.98 (s, 1 H)	1.29 (s, 3 H)	1.39 (s, 3 H)	3.10 (d, J = 13 Hz, 1 H)	2.78 (d, J = 13 Hz, 1 H)	7.0–7.7 (b, 18 H)

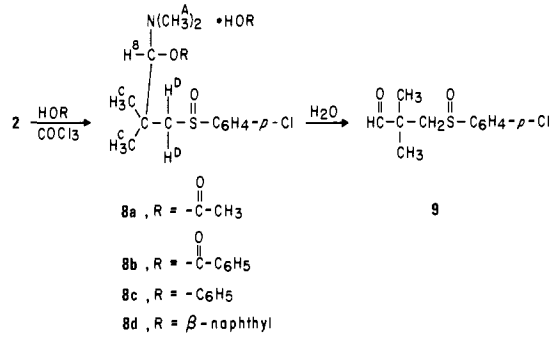
[a] Methyl group of acetic acid and/or acetate group.

Table II. Reaction of **2** with Strong Acids in Chloroform

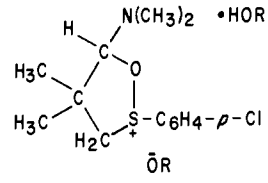
Acid (mol %)	Reaction		Product, rel %[a]		
	Temp, °C	Time	**7**	**4**	**2**
p-Toluenesulfonic acid (20)	61	15 min	87	3	10
Trichloroacetic acid (100)	20–25	20 min	93	5	2
Monochloroacetic acid (100)	20–25	26 h	85	5	10
2,4-Dinitrophenol (200)	20–25	19 h	80	7	13
Hydrogen chloride (100)[b]	20–25	25 min	91	4	5

[a] As determined by relative $-N(CH_3)_2$ absorption intensities in ^{1}H NMR spectra. [b] Hydrochloride salt formed in ether and then dissolved in chloroform.

Treatment of a deuteriochloroform solution of **2** with 2 equiv of acetic acid gave a compound (**8a**), which was stable in solution but on treatment with water afforded an 86% yield of **9**. Structure **8a** was assigned to this compound on the basis of



its ir and ^{1}H NMR spectra and its reaction with water. The ir spectrum of **8a** ($CHCl_3$) showed absorptions at 1720 cm^{-1} (C=O of acetate) and 1095 and 1045 cm^{-1} (S=O). The ^{1}H NMR absorptions and assignments are summarized in Table I. The ^{1}H NMR spectrum and chemical behavior could possibly be accounted for by the cyclic sulfonium salt A.[18] However, the chemical shifts for the methylene protons (δ 2.99 and 2.72) are close to those (δ 2.95) of sulfoxide **9** and are not shifted downfield as would be expected in a cyclic sulfonium salt.[18] This, along with the ir S=O absorption at 1045 cm^{-1}, is strong evidence against structure A.



A

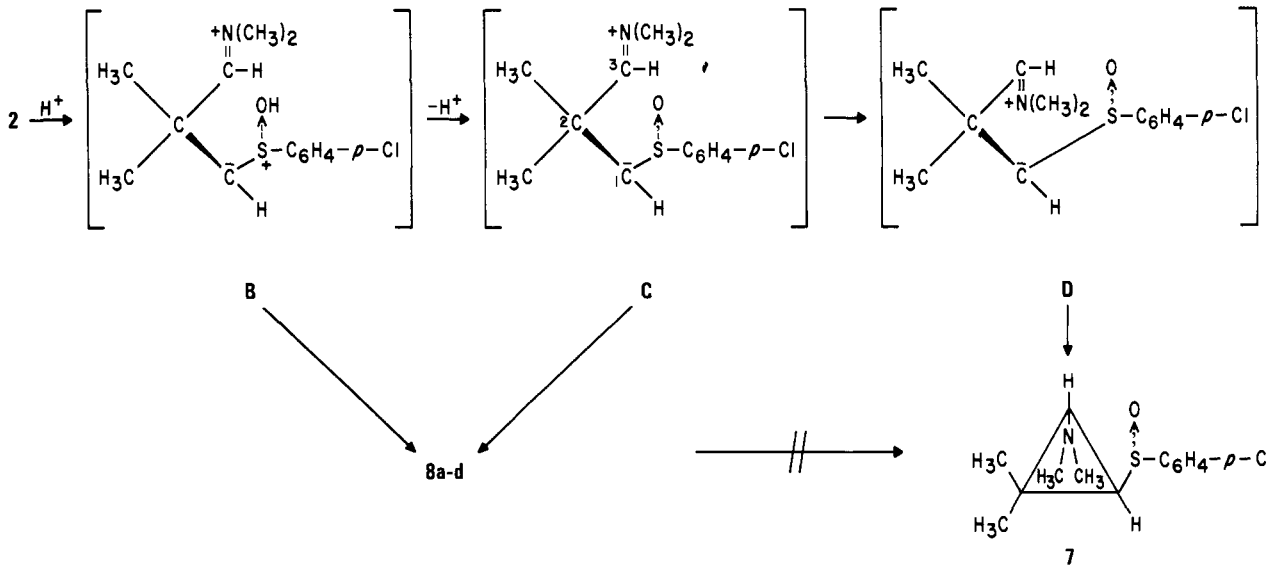
Analogous reactions occurred with the weak acids (K_a $<10^{-4}$) benzoic acid, phenol, and β-naphthol to afford **8b–d**, respectively. The ^{1}H NMR spectra are summarized in Table I. The larger downfield shift of H^B in **8a** and **8b** relative to **8c** and **8d** is consistent with the greater electronegativity of the acetate and benzoate oxygen atoms relative to those of phenolate and β-naphtholate.

It was found that only 1 equiv of weak acid was required; however, the reaction occurred more rapidly with 2 or more equiv. Compound **8a** was also formed when the trans sulfoxides **4** and **7** were treated with acetic acid as described above.

When **2** was treated with the strong acids ($K_a \geq 10^{-4}$) *p*-toluenesulfonic acid, trichloroacetic acid, monochloroacetic acid, 2,4-dinitrophenol, and hydrogen chloride in chloroform (or deuteriochloroform) stereospecific (>90%) isomerization to the trans sulfoxide **7** occurred. The reaction conditions and products are summarized in Table II. The differing chemical behavior of **2** with weak and strong acids can be best rationalized in the following manner. The first step involves acid catalyzed opening of the cyclopropane ring to form intermediate B (Scheme I). Literature precedence is seen in the work of Hartzell and Paige[19] and Kondo and co-workers[20] who have described the acid-catalyzed ring opening of episulfoxides. Loss of the catalytic proton would give rise to the zwitterionic intermediate C. In the case of weak acids the corresponding anion is a good nucleophile and attacks the immium function of B and/or C to afford **8a–d.** The direct formation of **8a–d** by way of a concerted push-pull mechanism[21] cannot be eliminated. According to this concept, the ring opening would occur by simultaneous attack of the nucleophile (push) and rupture of the C(1)–C(3) bond aided by sulfoxide protonation (pull).

With strong acids the corresponding anion is a poor nucleophile and cis-trans isomerization occurs before the immium function can be trapped. The stereospecific formation of the trans diastereomer **7** is most interesting.[22] From a cursory inspection of this conversion it appears as if inversion of configuration about the sulfur atom has occurred; however, this is not the case. The formation of **7** can be best rationalized by preferential rotation about the C(2)–C(3) bond of C to afford D, followed by ring closure to afford the enantiomer of

Scheme I



7 previously shown. Rotation about the C(1)-C(2) bond followed by ring closure would afford diastereomer **4**. It is recognized that if this reaction were carried out with optically pure **2** that it could be determined if loss of configurational integrity at the sulfur atom had occurred. Whether this ring opening and/or closing occurs with inversion or retention of configuration at C(1) is inconsequential to the above results and discussions.[23]

For preparative purposes the conversion of **2** into **7** can be best accomplished by formation of the hydrochloride of **2** in ether with subsequent solution in chloroform. The isomerization occurs smoothly at room temperature to afford an 83% isolated yield of **7** (see Experimental Section).

When **2** was treated with a tenfold excess of hydrogen chloride in methylene chloride–ether at ambient temperature, a clean conversion to 3-chloro-3-[(*p*-chlorophenyl)thio]-2,2-dimethylpropionaldehyde (**10**) occurred. Formation of **10** can be accounted for by the mechanistic sequence shown in Scheme II. The key step in this sequence involves the reaction of hydrogen chloride with a sulfoxide in the presence of a dehydrating agent (immium group) to afford an α-chlorosulfide. Subsequent work has shown that sulfoxides do afford good yields of α-chlorosulfides on treatment with hydrogen chloride in the presence of a dehydrating agent such as an immium salt or molecular sieves.[24]

Additional reactions of aminocyclopropyl sulfoxides will be reported in due time.

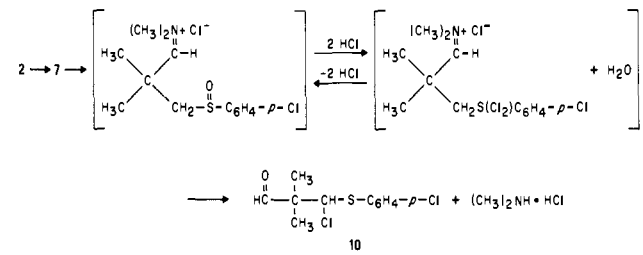
Experimental Section

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Ir spectra were obtained on a Perkin-Elmer Model 421 recording spectrometer, the ^{1}H NMR spectra were recorded on a Varian A-60A spectrometer, and the mass spectra were determined on an Atlas CH-4 spectrometer.

(1*RS*,2*SR*)-2-[(*SR*)-(*p*-Chlorophenyl)sulfinyl]-*N*,*N*,3,3-tetramethylcyclopropylamine (2) and (1*RS*,,2*SR*)-2-[(*RS*)-(*p*-Chlorophenyl)sulfinyl]-*N*,*N*,3,3-tetramethylcyclopropylamine (3). *m*-Chloroperoxybenzoic acid (MCPBA) (85% pure, 12.1 g, 59.4 mmol) in methylene chloride (250 ml) was added dropwise to a stirred, cooled (−60 to −70 °C) solution of **1**[2-4] (15.2 g, 59.4 mmol) in methylene chloride (500 ml). After addition of MCPBA was completed, the reaction mixture was stirred for an additional 0.5 h at −60 to −70 °C and then rapidly poured into a mixture of saturated sodium carbonate (400 ml), water (200 ml), and sodium bisulfite (6.0 g). After vigorous shaking, the layers were separated and the organic layer was dried (Na_2SO_4). The solvent was removed in vacuo to afford 14.8 g (92% yield) of crude product. Analysis of the ^{1}H NMR spectrum showed the ratio of **2**:**3** to be 85:15. Recrystallization from ether afforded 11.3 g (70% yield) of **2**: mp 119–21 °C; ir ($CHCl_3$) 1090 and 1030 cm^{-1} (S=O); ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 3 H), 1.38 (s, 3 H), 1.92 (d, J = 6.5 Hz, 1 H), 2.07 (d, J = 6.5 Hz, 1 H), 2.42 (s, 6 H), 7.45 (q, 4 H); mass spectrum *m/e* 112 (M^+ − 159).

Anal. ($C_{13}H_{18}ClNOS$) C, H, N, Cl, S.

Scheme II



The solvent of the filtrate from the above recrystallization was removed in vacuo, and the residue was subjected to absorption chromatography. The absorbant was Woelm acetyl cellulose which had been soaked in benzene for 20 h, slurry pressure packed into a glass column, and washed thoroughly with *n*-hexane. The column was eluted with 5% acetone in Skelly B.[6] Concentration of the appropriate fractions followed by recrystallization from hexane afforded 0.050 g (0.3% yield) of **3**: mp 83–83.5 °C; ir ($CHCl_3$) 1090 and 1030 cm^{-1} (S=O); ^{1}H NMR ($CDCl_3$) δ 1.20 (s, 3 H), 1.69 (s, 3 H), 1.84 (d, J = 6.5 Hz, 1 H), 2.16 (s, 6 H), 2.20 (d, J = 6.5 Hz, 1 H), 7.62 (q, 4 H); mass spectrum *m/e* 112 (M^+ − 159). Due to the instability of **3** a satisfactory elemental analysis was not obtainable.

(1*RS*,2*RS*)-2-[(*RS*)-(*p*-Chlorophenyl)sulfinyl]-*N*,*N*,3,3-tetramethylcyclopropylamine Oxide (6). *m*-Chloroperoxybenzoic acid (85% pure, 2.87 g, 14.1 mmol) in methylene chloride (100 ml) was added dropwise to a stirred, cooled (−60 to −70 °C) solution of **5** (2.00 g, 7.04 mmol) in methylene chloride (100 ml). After addition was completed, the reaction mixture was stirred for an additional 0.5 h at −60 to −70 °C and then poured directly onto a column of dry grade I Woelm basic alumina (200 g). The column was eluted with 20% methanol in chloroform. Concentration of the appropriate fractions afforded an oil which was triturated with ether to afford an off-white powdery solid. Recrystallization from ether–chloroform afforded 1.30 g (73% yield) of **6**: mp 167–8 °C; ir ($CHCl_3$) 1095 and 1045 cm^{-1} (S=O), 1210–1260 cm^{-1} (N-O); ^{1}H NMR (DMF-d_7) δ 1.42 (s, 3 H), 1.71 (s, 3 H), 3.02 (s, 3 H), 3.38 (s, 3 H), 3.36 (d, J = 4.5 Hz, 1 H), 3.81 (d, J = 4.5 Hz, 1 H), 7.77 (s, 4 H); mass spectrum *m/e* 286, 287, 288 (M^+ − 1), (M^+), (M^+ + 1).

Anal. ($C_{13}H_{18}ClNO_2S$) H, N, S; C: calcd, 54.25; found, 53.68.

(1*RS*,2*RS*)-2-[(*RS*)-(*p*-Chlorophenyl)sulfinyl]-*N*,*N*,3,3-tetramethylcyclopropylamine (7). A solution of **6** (50 mg, 0.17 mmol) and triphenylborane[25] (30 mg, 0.17 mmol) in chloroform (5 ml) was allowed to stand at room temperature for 1 h. The solution was washed with cold 1 N sodium hydroxide and dried (Na_2SO_4). The solvent was

removed in vacuo, and the residue was recrystallized from *n*-hexane to afford 38 mg (83% yield) of **7**: mp 71–72.5 °C; ir ($CHCl_3$) 1090 and 1030 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.31 (s, 3 H), 1.88 (d, J = 4.0 Hz, 1 H), 2.21 (d, J = 4.0 Hz, 1 H), 2.25 (s, 6 H), 7.48 (s, 4 H); mass spectrum *m/e* 112 ($M^+ - 159$).

Anal. ($C_{13}H_{18}ClNOS$) C, H, N, Cl, S.

(1*RS*,2*RS*)-2-[(*SR*)-(*p*-Chlorophenyl)sulfinyl]-*N*,*N*,3,3-tetramethylcyclopropylamine (4). Compound **2** (4.00 g, 14.7 mmol) was dissolved in 1.0 N potassium *tert*-butoxide in *tert*-butyl alcohol and heated at reflux for 18 h under an atmosphere of helium. The solvent was removed in vacuo and the residue was dissolved in ether (300 ml). The solution was washed with water (50 ml) and saturated brine (50 ml) and dried (Na_2SO_4). The solvent was removed in vacuo, and the residue was recrystallized from *n*-hexane to afford 2.10 g (53% yield) of **4**: mp 107–109 °C; ir ($CHCl_3$) 1090 and 1030 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 1.27 (s, 3 H), 1.42 (s, 3 H), 1.73 (d, J = 3.5 Hz, 1 H), 1.88 (s, 6 H), 1.99 (d, J = 3.5 Hz, 1 H), 7.42 (q, 4 H); mass spectrum *m/e* 112 ($M^+ - 159$).

Anal. ($C_{13}H_{18}ClNOS$) C, H, N, Cl.

Reaction of 2 with Weak Acids ($K_a < 10^{-4}$). The reactions of **2** with acetic acid, benzoic acid, phenol, and β-naphthol in $CDCl_3$ were studied. The following reaction of **2** with acetic acid is representative. Compound **2** (100 mg, 0.37 mmol) was dissolved in $CDCl_3$ (1 ml) and acetic acid (44 mg, 0.74 mmol) was added. After standing at ambient temperature for 24 h, a ^1H NMR spectrum showed the formation of **8a** to be complete. An ir spectrum ($CDCl_3$) showed absorptions at 1720 cm^{-1} (C=O) and 1095 and 1045 cm^{-1} (S=O). The sample was poured into water (10 ml), extracted with methylene chloride (2 × 10 ml), and dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was recrystallized from hexane to afford 78 mg (86% yield) of **9**, mp 61–62 °C. The structure of **9** was established by comparison with an authentic sample.[26] The ^1H NMR data for **8a–d** are summarized in Table I.

Reaction of 2 with Strong Acids ($K_a \geq 10^{-4}$). The reactions of **2** with monochloroacetic acid, trichloroacetic acid, *p*-toluenesulfonic acid, hydrogen chloride, and 2,4-dinitrophenol in chloroform were studied. The following reaction of **2** with *p*-toluenesulfonic acid is representative. Compound **2** (1.00 g, 3.68 mmol) in chloroform (20 ml) was treated with *p*-toluenesulfonic acid (0.13 g, 0.74 mmol) and heated at reflux for 15 min. The solution was washed with saturated sodium carbonate solution (10 ml) and dried (Na_2SO_4). The solvent was removed in vacuo to afford 0.89 g (89% yield) of crystalline product. Analysis via ^1H NMR showed it to be a mixture of **7** (87%), **2** (10%), and **4** (3%). The reaction conditions and products obtained are summarized in Table II.

Preparation of 7 from 2. A solution of **2** (1.00 g, 3.68 mmol) in ether (50 ml) was treated with a slight excess of ethereal hydrogen chloride. The ether was immediately removed in vacuo, and the hydrochloride was dissolved in chloroform (20 ml) and allowed to stand at ambient temperature for 25 min. The solution was washed with saturated sodium hydrogen carbonate (2 × 25 ml) and dried (Na_2SO_4). The solvent was removed in vacuo, and the residue was recrystallized from hexane to afford 0.83 g (83% yield) of **7**: mp 71–72.5 °C. The melting point, mixture melting point, ir, ^1H NMR, and mass spectra were identical with those of **7** prepared above.

3-Chloro-3-[(*p*-chlorophenyl)thio]-2,2-dimethylpropionaldehyde (10). A solution of **2** (4.0 g, 14.8 mmol) in methylene chloride (100 ml) was treated with ethereal hydrogen chloride (163 mmol) and allowed to stand at ambient temperature for 2 h. The solvent was removed in vacuo and the semi-solid residue was triturated with ether (3 × 100 ml), and the solid (dimethylamine hydrochloride) was removed by filtration. The solvent of the filtrate was removed in vacuo to afford 3.5 g (90% yield) of noncrystalline **10**: ir (Nujol) 2810 and 2710 cm^{-1} (aldehyde C-H), 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.31 (s, 3 H), 1.34 (s, 3 H), 5.38 (s, 1 H), 7.39 (q, 4 H), 9.53 (s, 1 H); mass spectrum *m/e* 262, 266 (M^+).

Anal. ($C_{11}H_{12}Cl_2OS$) H, S; C: calcd, 50.19; found, 49.65; Cl: calcd, 27.00, found, 26.04.

References and Notes

(1) The preparation of compound **2** was presented at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 8–13, 1973, Abstracts ORGN 124.
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(6) Skelly B is a commercial hexane, bp 60–70 °C, made by Skelly Oil Co., Kansas City, Mo.
(7) Due to the instability of **3** a satisfactory elemental analysis was not obtainable; however, the ir, ^1H NMR, and mass spectra were consistent with structure **3**.
(8) All calculations were done using the CRYM system of programs developed by David J. Duchamp, The Upjohn Company, Kalamazoo, Mich. A paper containing all the details of the x-ray investigation of compound **2** is in press, *Acta Crystallogr.*
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(22) Some of isomer **4** which is formed is the result of epimerization about the sulfur atom after cis–trans isomerization occurs. Studies with pure **4** and **7** showed that 2–4% epimerization about the sulfur atom occurred under these conditions. Prolonged (96 h) heating at 55 °C with *p*-toluenesulfonic acid in deuteriochloroform is required for equilibration between **4** (60%) and **7** (40%). These studies will be presented in a subsequent paper.
(23) We have previously reported (ref 17) that hydrolysis of **2** occurs with inversion of configuration at C(2).
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