carbonyl iodide and H_2 according to eq 2.¹² This reaction, which was first reported by Vallarino¹⁰ and later by Forster,¹² is verified by observation (v). The initial step of eq 2 unquestionably involves protonation by a strong acid. The formation of H₂ may then follow via a hydride/iodide interchange with hydride transfer from Rh(III) to H⁺. Dihydrogen is thus produced by the reduction of protons with concomitant oxidation of Rh(I) to Rh(III). Iodide coordination is necessary for this process.

$$[Rhl_2(CO)_2]^- + 2HI + aI^- \rightarrow [Rhl_b(CO)]^{c^-} + H_2 + CO \quad (2)$$

(a = 0, 1; b = 4, 5; c = 1, 2)

The production of CO_2 takes place by nucleophilic attack of water on a Rh(III)-coordinated carbonyl, eq 3. Activation

$$\begin{array}{cccc} \operatorname{Rh}^{111} \longrightarrow \operatorname{CO} &+ & \operatorname{H}_2 \operatorname{O} & \longrightarrow \left[\begin{array}{c} \operatorname{Rh}^{111} \longrightarrow \operatorname{C} & & \\$$

of the CO ligand to nucleophilic attack is achieved through its coordination to a metal ion in a higher oxidation state which reduces back-donation and increases the residual positive charge on the carbonyl carbon donor atom. This notion receives strong support from numerous sources including (a) the known CO reduction of hydrated RhCl₃,⁹ (b) an ¹⁸O labeling study¹⁷ of the $[RhCl_2(CO)_2]^-$ catalyzed reduction of NO by CO which shows the product CO_2 to contain a labeled oxygen from cocatalyst water, and (c) the ferricyanide oxidation of CO to CO₂ catalyzed by a cobalt carbonyl cyanide species,¹⁸ The Rh(1) anion produced in eq 3 is then able to coordinate a CO ligand, completing the catalytic cycle.

Alternative schemes can be proposed. For example, if X in eq 3 is a hydride and CO₂ production proceeds via a β -elimination from a heteroatom, a Rh(III) dihydride is produced which can reductively eliminate H_2 and regenerate a Rh(1) species. In this scheme, the formation of the Rh(III) carbonyl hydride also involves protonation, and the production of H_2 remains intimately tied to the reactivity of the Rh(I) center. In yet another scheme the catalytic cycle stays entirely in the Rh(III) regime with CO₂ production proceeding via heteroatom β -elimination to produce a Rh(III) hydride, and H₂ production occurring by hydride transfer from Rh(III) to H⁺. Addition of CO to give a Rh(111) carbonyl then completes the cycle.

Observation (iv) unequivocally establishes that CO is the source of the product CO_2 , thus ruling out any possible involvement of acetic acid in this regard. That acetic acid enhances the activity of the catalyst system is shown by observation (iii). The role of acetic acid is as yet undefined, but it may relate to the influence of the ancillary ligands on the reactivity of the rhodium center in each of its oxidation states. While I⁻ activates the Rh(I) center to protonation, it deactivates the Rh(III)-CO moiety to nucleophilic attack by water, thus permitting the isolation of Rh(III) carbonyl iodides, such as [RhI₅(CO)]^{2-.12} Substitution of acetic acid for iodide, however, may facilitate aqueous attack on the coordinated carbonyl and lead to CO_2 formation by eq 3.

It seems certain that optimization of the observed catalysis will be closely related to understanding how the ancillary ligands influence the reactivity of the catalytically active center in its different oxidation states.

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Retention of Stereochemistry in the Extrusion of Sulfur Monoxide from Thiirane Oxides. Synthesis and Thermal Decomposition of cis- and trans-Dideuteriothiirane Oxide

Sir:

The mechanism of the thermal decomposition of thiirane oxides, potentially valuable sources of sulfur monoxide in solution, has been a matter of considerable controversy. Unimolecular decomposition of the parent thiirane oxide¹ ($E_a \approx$ 35 kcal/mol) is expected to result in the "spin-allowed" formation of both singlet ethylene and sulfur monoxide, the latter being an excited state species quite possibly accessible thermodynamically.²⁻⁴ However, attempts to detect singlet sulfur monoxide by physical (microwave, EPR)⁵ or chemical means (trapping with dienes^{4,6} or trienes,⁷ respectively) have provided evidence best accommodated by the assumption of the intermediacy of the corresponding ground state triplet species. Similarly, decomposition of stereochemically labeled thiirane oxides (cis- and trans-diphenyl-,⁸ or dimethylthiirane oxide⁹) resulting in ethylene products in which stereochemical integrity has been lost has been interpreted as a process in which sequential carbon-sulfur bond breaking proceeds via a diradical intermediate.





Figure 1. Deuterium decoupled 100-MHz proton NMR spectra of thiirane oxides 1a (top) and 1b. As the top spectrum indicates there is no significant deuterium isotope effect on the regioselectivity of the sulfoxidation of *cis*-dideuteriothiirane, both stereoisomers being formed in equal amounts.

The following inconsistencies and conflicting details in the reported literature have led to our present contribution to this problem. (1) A recent EPR study has uncovered an unusually efficient heterogeneous deactivation by wall collisions of SO ($^{1}\Delta$) in the gas phase. ¹⁰ This high collisional deactivation efficiency may have precluded the detection of the singlet species in the gas⁵ as well as solution phase.^{4,6,7} (2) The stereochemical results obtained^{4,6} when 2,4-hexadienes were allowed to react



with SO from thiirane oxide to give various isomeric 2,5dimethyl-3-thiolene S-oxides can be explained via the intermediacy of vinylthiiranoxides.¹¹ These might be formed from (possibly stereospecific) reaction of either singlet or triplet SO with one diene double bond. The product determining intermediates would be identical regardless of the precursor. The formation of a dihydrothiepine oxide from a trans-hexatriene7b may be rationalized similarly through the formation of a divinylthiirane oxide, and the conversion of cycloheptatriene to ditropyl in the presence of SO might be a result of SO-redox chemistry.^{3a,7c,24,26} (3) The possible occurrence of a catalyzed thermal isomerization¹² of dialkyl sulfoxides which could lead to stereochemical scrambling in SO-trapping products complicates the analysis of such reactions. (4) Although the decomposition of stilbene episulfoxides seems to choose the biradical pathway with concomitant loss of stereochemical integrity,8 the corresponding 2-butene episulfoxides may elect to decompose via three mechanisms: possibly a concerted cheletropic extrusion, the biradical path, or via sulfenic acid intermediates.⁹ (5) Thiiranes¹³ and thiirane dioxides¹⁴ extrude sulfur with retention of configuration. Why should thiirane oxides be different in their behavior?

We wish to report (a) the synthesis of the simplest stereochemically labeled thiirane oxides, cis- and trans-dideuteriothiirane oxide (1a, b) via the stereospecific formation of the corresponding deuterated epoxides and thiiranes, and (b) the stereochemical results of their decomposition both in the gas and solution phase.

cis- or trans-Dideuterioethylene¹⁵ was stirred with a slight excess of purified¹⁶ m-chloroperbenzoic acid in benzene at room temperature for 3 days (Scheme I). Unreacted ethylene was removed under vacuum and the deuterated epoxide distilled and subsequently reacted with a twofold excess of potassium thiocyanate¹⁷ in a benzene-water mixture for 2 days. The thiiranes were distilled off under vacuum, dried, and oxidized at -20 °C with m-chloroperbenzoic acid in CH₂Cl₂.¹⁸ The product benzoic acid was removed as the ammonium salt, the solvent evaporated, and the thiirane oxides **1a**, **b** distilled to give clear liquids (37% overall yield).¹⁹ The deuterium decoupled NMR spectra are shown in Figure 1. The transisomer **1b** was contaminated with approximately 5% of the cis compound.

Pyrolysis of 1 in the gas (vacuum transfer through a hot tube, 350 °C (0.05 mm)) or solution phase (1,2,4-trichlorobenzene, 150 °C) gave deuterated ethylenes with 95% retention of stereochemistry.²⁰ Pyrolysis of 1 at lower temperatures led to partial recovery of starting material with unchanged stereochemistry. In order to shed some light on the origin of the 5% crossover product, undeuterated thiirane oxide¹ was thermally decomposed in the presence of pure trans-dideuterioethylene (static system). No cis-dideuterioethylene was observed in this experiment.

Our results provide for the first time an unambiguous stereochemical test for the mode of decomposition of simple thiirane oxides. They indicate that these compounds are not unusual in their thermal behavior when compared with their higher and lower oxidized analogues and suggest analogous modes of extrusion of the sulfur-containing species. Our data reopen the question as to the nature of sulfur monoxide formed initially in thiirane oxide decompositions, a question that may ultimately only be answered by spectroscopic means. Although the observed (albeit small) crossover in our experiments tends to point to a biradical mechanism involving production of ground state species, possibly involving a stereochemically rather rigid π -thiacyclopropane oxide "biradical" of the type proposed in thiirane decompositions,^{13,21} a significant contribution of a concerted process cannot be ruled out at present.24

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 (19) 1a: m/e 78 (M⁺, 73%), 62 (52%), 48 (100%); IR v_{C→D} 2260, v_{S==0} 1050 cm⁻¹. 1b: m/e 78 (M⁺, 75%), 62 (61%), 48 (100%); IR v_{C→D} 2280, v_{S==0} 1060 cm⁻¹. For NMR spectra, see the figure. Satisfactory elemental total details of the set of t analyses were obtained.
- (20) The pyrolysis products were collected in an IR–gas cell and compared with standard deuterated ethylene mixtures (98:2, 95:5, 90:10, 85:15). Every mixture was run at six different pressures (200, 100, 50, 25, 12, 6 mm) and the corresponding series of IR spectra compared with the series of spectra depicting pyrolysis product mixtures. Compound 1a gave a 95:5 ratio of cis- to trans-dideuterioethylene; 1b gave an analogous ratio of 10:90. These ratios were reproduced in several duplicate pyrolyses, involving three independently prepared samples.
- (21) It is interesting to note in this connection that the activation energies²² for cleavage of the first carbon-sulfur bond in acyclic dialkyl sulfides (72 kcal/mol), sulfoxides (\sim 57 kcal/mol, this value is a reasonable estimate based on the mean bond dissociation energies in sulfoxides^{22a} and acti-

vation energies for racemization of benzyl sulfoxides, corrected for benzyl-substitution^{22b}), and sulfones (62 kcal/mol) reduce by different amounts (32, 22, 34 kcal/mol, respectively) when going to the corresponding three-membered ring species, ^{1,13,14} and that this kinetic destabilization is close to that encountered in the corresponding hydrocarbon system (cf. central bond in *n*-butane vs. cyclopropane, $\Delta E_a = 18 \text{ kcal/mol})^{23}$ only in the case of sulfoxides.

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Nitrogen Inversion in Piperidine

Sir

Dynamic NMR spectroscopy has not hitherto been applied successfully to the axial-equatorial NH equilibrium in piperidine (I), despite intense interest in the subject.¹⁻⁴ This failure has generally been ascribed to a fast intermolecular exchange of the NH protons in 1.2,4,5 However, conditions where NH protons exchange is slow can be achieved at low temperature (<-10 °C) as shown by the broad NMR line of the NH proton of piperidine (treated with basic alumina) in CHFCl2-CHF2Cl solutions.⁶ Previous workers have been able to obtain NMR spectra of secondary amines under nonexchanging conditions for 4,4-difluoropiperidine,⁷ tetrahydro-1,3-oxazines,⁵ 1-methyl-1,3-diazane,⁵ aziridines,^{8,9} and nortropane.⁴ As is shown in the present work, the barrier to nitrogen inversion in I is quite low, thus requiring both very low temperatures and high magnetic fields for its successful study by dynamic NMR.

Carbon-13 NMR spectra of I at -100 to -172 °C are shown in Figure 1. The β -carbon resonance is quite broad at about -142 °C and gives rise to a doublet in the intensity ratio of 85:15 ($\Delta G^{\circ} = 0.36 \text{ kcal/mol}$) at $-172 \circ \text{C}$.¹⁰ Since entropy differences between the two conformations are likely to be small, ΔG° should be nearly independent of temperature, and population ratios can be calculated to be 80:20 at -142 °C and 65:35 at 25 °C. From a line shape analysis at -142 °C, a first-order rate constant (major form to minor form) of 240 \pm 20 s⁻¹ is calculated. Using the absolute rate theory, we obtain a free energy of activation (ΔG^{\pm}) of 6.1 \pm 0.2 kcal/mol. The dynamic NMR behavior of I was reproducible in many different samples of I and was unchanged when basic alumina was added directly to the solution in the NMR tube. On the other hand, addition of a trace of CF₃COOH completely wiped out the dynamic NMR effect. The ¹³C data clearly show that two conformations are present and these can only be the equatorial (I-E) and the axial (I-A) forms of piperidine (I). However, it is not possible on this evidence alone to determine which is the major conformation.

The free energy barrier for ring inversion in I is known to be 10.4 kcal/mol from ¹H dynamic NMR data,¹¹ so that ring