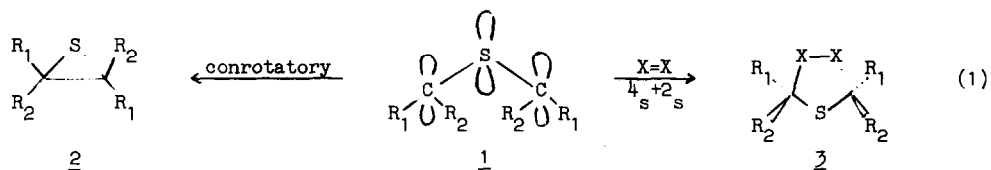


THIOCARBONYL YLIDES.<sup>1</sup> APPLICATION TO THE SYNTHESIS OF  
HINDERED THIIRANES.

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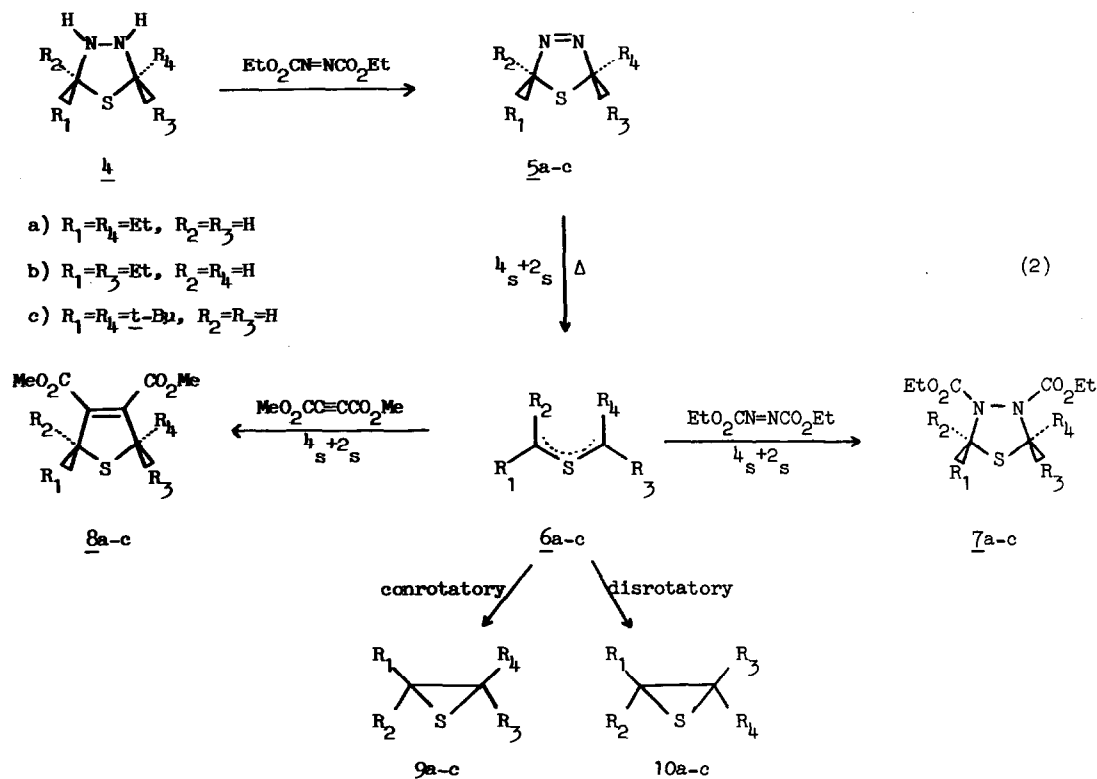
Thiocarbonyl ylides (1) are the fundamental examples of "tetravalent sulfur" compounds.<sup>2</sup> Their chief reactions are ring-closure to give thiiranes (2) and formation of cyclo-adducts (3) with suitable dipolarophiles (eq 1).<sup>1,3</sup>



For the geometric model 1,<sup>4a,b</sup> simple theory predicts ring-closure to be conrotatory and configuration to be maintained during cycloaddition ( $4_s+2_s$ ).<sup>5</sup> Such behavior has been demonstrated for azomethine ylides<sup>6</sup> and strongly implied for carbonyl ylides<sup>7</sup> (sulfur replaced by nitrogen and oxygen, respectively). We now demonstrate the validity of these a priori considerations for thiocarbonyl ylides even in the face of an impressively unfavorable thermodynamic situation.

Condensation of propionaldehyde, hydrazine, and  $H_2S$  gives a mixture of two thia-diazolidines;<sup>8</sup> trans-configuration is tentatively assigned to the more stable 4a (eq 2), mp 75.4-76.9°, isolated by tedious recrystallization from pet. ether. The other isomer (4b), presumably cis, decomposes spontaneously at room temperature and can only be handled as a mixture (ca 20%) with 4a. Addition of  $H_2S$  to the azine of pivalaldehyde in ether under pressure gives 4c as a highly unstable white solid; nmr ( $CDCl_3$ ,  $-20^\circ$ )  $\delta$  1.01 (s, 18,  $C(CH_3)_3$ ),  $\delta$  3.41 (s, 2, N-H),  $\delta$  4.43 (s, 2, 2,5-H), tentatively considered to be trans. Dehydrogenation of 4a-c with diethyl azodicarboxylate<sup>9</sup> at  $-10^\circ$  gives the thiocarbonyl ylide precursors 5a-c in quantitative yield. Trans and cis stereochemistry, respectively, for 5a and 5b (isolated by working at  $<10^\circ$ ) are based on the difference in chemical

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shifts ( $\text{CCl}_4$ ) for the 2,5-protons,  $\delta$  5.9-6.25 (multiplet) and  $\delta$  3.8-4.2 (broadened quartet), respectively, which is clearly in the expected order.<sup>10</sup> Unambiguous assignment can be made for 5c, mp 62-63° (decomp); nmr ( $\text{CCl}_4$ )  $\delta$  0.97 (s, 18,  $\text{C}(\text{CH}_3)_3$ ),  $\delta$  5.62 (s, 2, 2,5-protons) which reacts with *m*-chloroperbenzoic acid (MCPBA) in  $\text{CHCl}_3$  to give a sulfoxide, mp 99-105° (decomp), ir (KBr) 1060  $\text{cm}^{-1}$  (SO), in which the 2,5-protons are nonequivalent ( $\delta$  4.05 and  $\delta$  5.68) and couple,  $J=1.4$  Hz, consistent only with trans-t-butyl groups. Moreover, the similarity of chemical shifts for the 2,5-protons in 5c and 5a is completely consistent with the relative stereochemical assignments.

Pyrolysis of trans-isomer 5a ( $k_{55}=9.61 \times 10^{-4} \text{ sec}^{-1}$ ,  $\Delta E^\ddagger=27.5 \text{ kcal/mole}$ ,  $\Delta S^\ddagger=11.4 \text{ e.u.}$  between 40-55°) gives in 100% yield<sup>11</sup> cis and trans-2,3-diethylthiiranes (9a and 10a) in 93:7 ratio (glpc). These two thiiranes were synthesized by an independent route for comparison.<sup>12</sup> The minor (disrotatory) product 10a may arise partially from undetected isomer contamination in 4a (nmr control with +5% accuracy). For cis-isomer 5b, a selectivity of 100 + 5% conrotatory ring-closure to trans-thiirane 9b is calculated. Trans-2,5-di-t-butyl thiadiazoline (5c) decomposes smoothly ( $k_{90}=2.52 \times 10^{-4} \text{ sec}^{-1}$ ,  $\Delta E_a^\ddagger=30.7 \text{ kcal/mole}$ ,  $\Delta S^\ddagger=7.1 \text{ e.u.}$  between 85-100°) giving in 100% yield a

thiirane, uv (max) 2650 Å,  $\epsilon=105$ ;  $^{13}\text{C}$  nmr ( $\text{CCl}_4$ )  $\delta$  1.12 (s, 18,  $\text{C}(\underline{\text{CH}_3})_3$ ) and  $\delta$  2.73 (s, 2, 2,3-H), and M.W. 172 (mass spectral). At  $120^\circ$ , this thiirane converts slowly ( $k_{\text{isom}} < 10^{-5} \text{ sec}^{-1}$ ) to an isomer, nmr ( $\text{CCl}_4$ )  $\delta$  0.92 (s, 18,  $\text{C}(\underline{\text{CH}_3})_3$ ),  $\delta$  2.51 (s, 2, 2,3-H). Isomerization may also be effected photochemically. The thiirane formed initially, when treated carefully with phenyllithium in ether,  $^{12}$  gives in quantitative yield cis-2,3-di-t-butylethylene. Its isomer yields trans-2,3-di-t-butylethylene.  $^{14}$  In view of the known stereospecificity of such desulfurizations,  $^{12}$  the thiiranes must have the same relative configurations as the alkenes and therefore are 9c and 10c, respectively.

We conclude that thiocarbonyl ylides 6a-c are formed from 5a-c with retention of configuration ( $^4_s + 2_s$ ) and undergo conrotatory ring-closure with nearly complete stereospecificity. The overall conversion of a readily available trans-precursor (4c) to hindered cis-2,3-di-t-butylthiirane (9c) represents a particularly heartening victory of orbital symmetry requirements over thermodynamics.

As expected, thiocarbonyl ylides retain configuration during cycloaddition ( $^4_s + 2_s$ ). With a one-fold excess of diethyl azodicarboxylate, 5a gives in 92% yield cycloadduct 7a, nmr ( $\text{CCl}_4$ )  $\delta$  0.97 (t, 6,  $\underline{J}=7.2 \text{ Hz}$ ,  $\underline{\text{CH}_3}$ ),  $\delta$  1.28 (t, 6,  $\underline{J}=7.5 \text{ Hz}$ ,  $\underline{\text{CH}_3}$ ),  $\delta$  1.40-2.00 (complex multiplet, 4,  $\underline{\text{CH}_2\text{CH}}$ ),  $\delta$  4.20 (q, 4,  $\underline{J}=7.5 \text{ Hz}$ ,  $\underline{\text{OCH}_2}$ ), and  $\delta$  5.50 (t, 2,  $\underline{J}=5.2 \text{ Hz}$ , t-C-H). With  $\text{NaIO}_4$  in methanol 7a gives a sulfoxide, ir (neat) 1060, 1075  $\text{cm}^{-1}$  ( $\text{S=O}$ ) in which the 2,5-protons absorb at  $\delta$  5.0 (broad) and  $\delta$  4.80 (t,  $\underline{J}=7.0 \text{ Hz}$ ) and the ester methylenes at  $\delta$  4.22 and  $\delta$  4.18 (q,  $\underline{J}=7.0 \text{ Hz}$ )  $^{15}$  consistent with a trans-configuration and hence retention of configuration during cycloaddition. Further oxidation of this sulfoxide with MCPBA gives a single sulfone, mp  $75-76^\circ$ , ir (KBr) 1100, 1330  $\text{cm}^{-1}$  ( $\text{SO}_2$ ) in which the 2,5-protons and ester methylene groups are again identical.  $^{15}$  With a one-fold excess of dimethyl acetylenedicarboxylate, 5a yields 2,5-dihydrothiophene 8a in 78% yield; a 74:26 mixture of 5a:5b gives 8a and 8b (separated by glpc) in a ratio of 78:22. The nmr spectra of 8a and 8b accord fully with stereochemical assignments.  $^{15}$  With 5c, cycloadducts 7c and 8c are obtained in yields of 100% and 67%, respectively. Trans-configuration for 7c was demonstrated by its oxidation with MCPBA to a sulfoxide, mp  $57-59^\circ$  in which the methylene groups are nonequivalent ( $\text{CCl}_4$ ,  $\delta$  4.19 and  $\delta$  4.27,  $\underline{J}=7.0 \text{ Hz}$ ) as well as the ester methyl groups ( $\delta$  1.28 and  $\delta$  1.33,  $\underline{J}=7.0 \text{ Hz}$ ); the 2,5-protons absorb at  $\delta$  4.78. Further oxidation with MCPBA produces a sulfone, mp  $64-66^\circ$ , in which the methylene and methyl groups are again equivalent ( $\text{CCl}_4$ ,  $\delta$  4.26 and  $\delta$  1.32,  $\underline{J}=7.1 \text{ Hz}$ ); the 2,5-protons absorb at  $\delta$  4.50.

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