

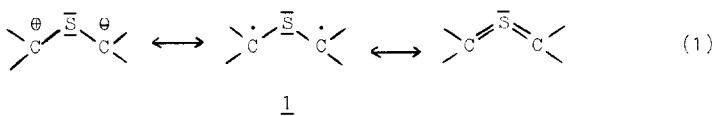
THIOCARBONYL YLIDES. AN APPROACH TO "TETRAVALENT SULFUR" COMPOUNDS.

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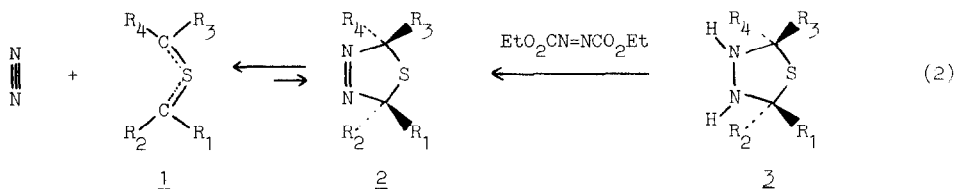
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We wish to describe a rational approach to the generation of thiocarbonyl ylides, (1), a new class of reactive intermediates. Thiocarbonyl ylides, as depicted in eq. 1, may be described in terms of 1,5-dipolar<sup>2</sup>, biradical, or "tetraivalent sulfur"<sup>3-5</sup> resonance structures.<sup>6</sup> The previously described azomethine<sup>7</sup> and carbonyl ylides<sup>8</sup> are related formally to 1 by replacement of sulfur by nitrogen and oxygen, respectively.



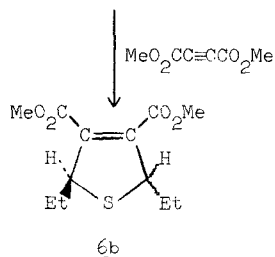
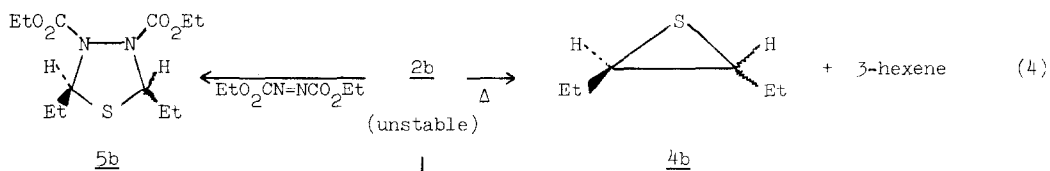
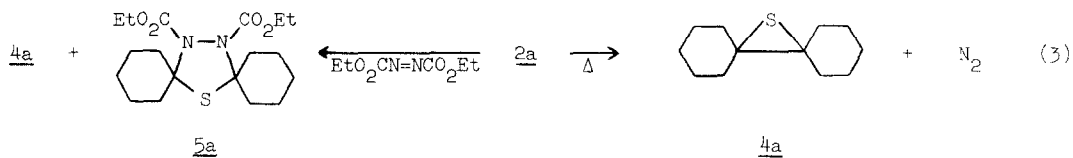
Two orbital symmetry allowed<sup>9</sup> paths for the generation of 1, viewing it as isoelectronic with the allyl anion<sup>10</sup>, were considered. Most obvious was the conrotary electrocyclic ring-opening of an episulfide, a type of reaction which has been effected with appropriately substituted azirines<sup>7</sup> and epoxides.<sup>8</sup> An alternative and, for us, more successful attack on the problem makes use of the thermally induced loss of nitrogen from 1,3,4-thiadiazolines (2) which are, of course, the expected  $4_s + 2_s$  cycloadducts of 1 with nitrogen (eq. 2).<sup>9</sup>

The pivotal compounds 2, cardinal to the latter approach, were obtained from the previously reported 1,3,4-thiadiazolidines<sup>11</sup> 3 which were dehydrogenated using diethylazodicarboxylate.<sup>12</sup> This dehydrogenation proceeds smoothly with 3a at room temperature in ether solution to give stable 2a, in 54% yield, mp 81-82° (without decomposition); ir (KBr) 1579  $\text{cm}^{-1}$  (N=N); uv max (96% EtOH) 2890 Å ( $\epsilon$  342) and 3220 Å ( $\epsilon$  238).<sup>13,14</sup>



- a)  $R_1, R_2 = R_3, R_4 = (\text{CH}_2)_5$   
 b)  $R_1 = R_3 (R_4) = \text{Et}$   
 $R_2 = R_4 (R_3) = \text{H}$

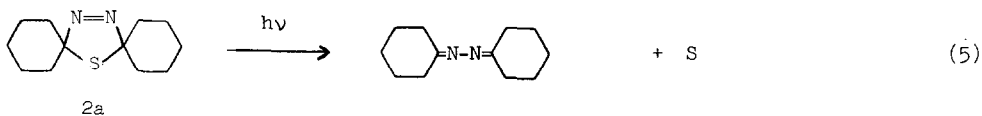
Either in the melt at  $100^\circ$  or in hydrocarbon solution at  $90^\circ$ , 2a loses nitrogen smoothly (eq. 3) to give in 99% yield the thirane 4a, mp  $75-77^\circ$ ; mol. wt. (osmet. in  $\text{C}_6\text{H}_6$ ) 198.2; uv max (96% EtOH)  $2590 \text{ \AA}$  ( $\epsilon = 50$ ).<sup>15</sup> Reaction with *n*-butyllithium<sup>16</sup> in ether converted 4a to cyclohexylidenecyclohexane in 77% yield. Attempts to intercept the suspected intermediate 1a with either *trans*-stilbene or dimethyl acetylenedicarboxylate met with failure. However, when 2a was allowed to decompose in the presence of an equimolar quantity of diethylazodicarboxylate a mixture was isolated consisting of 4a (33% isolated) and 5a (42% isolated), mp  $65-67.5^\circ$ , ir (KBr)  $1710 \text{ cm}^{-1}$  ( $\text{NC}=\text{O}$ ); nmr ( $\text{CCl}_4$ )  $\delta$  4.10 (q, 4,  $J = 7.0 \text{ Hz}$ ,  $\text{OCH}_2$ ),  $\delta$  1.25 (t, 6,  $J = 7.0 \text{ Hz}$ ,  $\text{CH}_3$ ), and  $\delta$  1.36-2.11 (broad multiplet, 20,  $(\text{CH}_2)_5$ ).<sup>14</sup> Thirane 4a fails to react with diethylazodicarboxylate under similar conditions.



Analogous reactions were carried out with the known cis and trans-3b.<sup>17</sup> Here, however, an enormous difference was found in the thermal stability of 2b as compared to 2a. When equimolar amounts of 3b and diethylazodicarboxylate in ether solution are held at  $-10^{\circ}$  for 5 hr, diethylhydrazinodicarboxylate is formed in 73% yield along with an unstable compound [uv max ( $C_5H_{12}$ ) 3180 Å and 2820 Å] which is most likely 2b.<sup>18</sup> Above  $10^{\circ}$  this unstable compound loses nitrogen and yields cis and trans-2,3-diethylthiirane (4b) and some cis and trans-3-hexene (36% combined yield after distillation) as well as some cycloaddition product 5b (eq. 4).<sup>19</sup> The latter compound, ir (neat)  $1710\text{ cm}^{-1}$ , nmr ( $CCl_4$ )  $\delta$  5.48 (overlapping triplets, 2,  $J = 7.2\text{ Hz}$ ,  $\underline{t-C-H}$ ),  $\delta$  4.23 (overlapping quartets, 4,  $J = 7.5\text{ Hz}$ ,  $OCH_2$ ),  $\delta$  1.40-2.00 (complex multiplet, 4,  $CH_2CH$ ),  $\delta$  1.28 (t, 6,  $J = 7.5\text{ Hz}$ ,  $CH_3$ ), and  $\delta$  0.97 (overlapping triplets, 6,  $J = 7.2\text{ Hz}$ ,  $CH_3$ ) is obtained in 67% yield if an extra equivalent of diethylazodicarboxylate is added to the reaction mixture prior to warming to room temperature. If the unstable 2b is warmed to room temperature in the presence of one equivalent of dimethylacetylene dicarboxylate, a 20% yield of 2,5-dihydrothiophene 6b (with expected spectra) is obtained.

These observations are congruous with our supposition that thiocarbonyl ylides should be generated during thermal decomposition of thiadiazolines 2. As expected, these intermediates cyclize readily to the thiiranes but also add to appropriately substituted  $2\pi$  systems at a competitive rate. In this respect, their behavior agrees fully with that of azomethine and carbonyl ylides. We are now investigating the stereochemistry of the ring-closure and cycloaddition reactions of 2b.

Rather to our surprise, 2a, upon irradiation, lost sulfur cleanly to give cyclohexanone azine as the only demonstrable organic product (eq. 5).



This reaction pertains even at  $-170^{\circ}$  in a methylcyclohexane matrix. This dichotomy of thermal and photochemical behavior may arise from the absence of an orbital symmetry allowed path for the loss of nitrogen from 2a (assuming excitation to be centered in the azo chromophore) whereas a cheletropic<sup>9</sup> elimination of sulfur is an allowed process. This reaction finds some precedent in the photochemically induced elimination of sulfur dioxide from butadiene sulfones.<sup>20</sup>

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