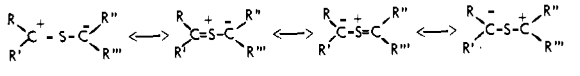
Simple Generation of Thiocarbonyl Ylides

Sir:

Thiocarbonyl ylides are species represented by **1**.[1] They can be generated by the thermal extrusion of nitrogen from thiadiazolines (**2**) yielding thiiranes (**3**) as final products (eq 1).[2,3] Unfortunately, preparation of the thiadiazoline precursors is not trivial.[2,3] We report a new method for the generation of thiocarbonyl ylides which is simple and promises to be very general.



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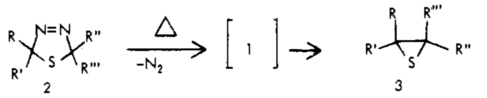
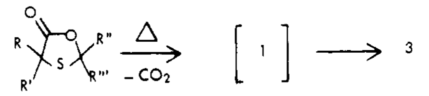


(1)

Our approach to these reactive intermediates is outlined in eq 2. Analogous loss of nitrogen is well established (eq 1)[2,3] and loss of carbon dioxide by a 1,3 cycloreversion is precedented in Δ^2- and Δ^3-oxazolinones,[4] but never before has carbon dioxide elimination been used successfully for the formation of an allylic ylide like **1**. In particular, 2,4-diphenyl-1,3-oxathiolan-5-one[5,6] undergoes loss of carbon dioxide at 600 °C to give a quantitative yield of thiirane (eq 3).[7] The reaction also procedes well with only one phenyl substituent in the molecule, but a slightly higher temperature is required (eq 4).[8,9]



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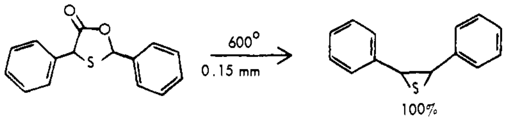

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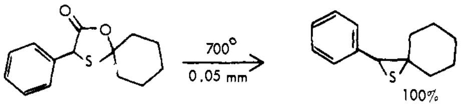
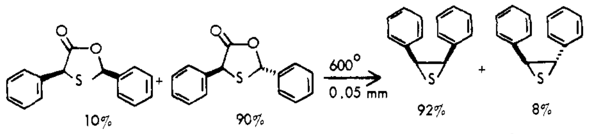


(4)

If the loss of carbon dioxide illustrated in eq 3 and 4 is concerted, the conversion of a 1,3-oxathiolan-5-one into a thiirane should be stereospecific. Furthermore, the overall process should procede with inversion of configuration based on orbital symmetry considerations.[10,11] Indeed, the initial reaction of eq 3 gave encouraging results since the original mixture of starting 1,3-oxathiolan-5-ones was 62% cis and the resulting thiirane mixture was 65% trans. In addition, another mixture of these 2,4-diphenyl-1,3-oxathiolan-5-ones containing 40% cis isomer yielded 37% trans product upon pyrolysis. This seems to rule out thermal isomerization of the thiiranes; however, in order to remove any possible ambiguity, fractional sublimation was used to obtain the nearly pure cis and trans isomers of 1,2-diphenyl-1,3-oxathiolan-5-one and these were pyrolyzed separately (eq 5 and 6). These results show that the conversion is almost 100% stereospecific and this supports the hypothesis of a *concerted loss of carbon dioxide.*



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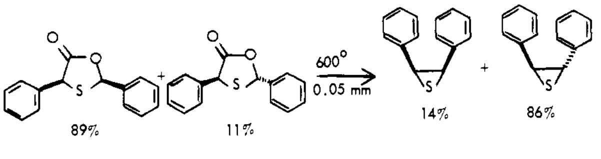

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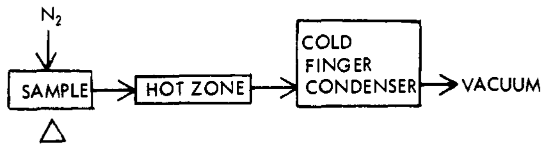

Figure 1. Flash vacuum pyrolysis unit.

We have used flash vacuum pyrolysis to carry out all of the thermal reactions. This technique is characterized by high temperatures, low pressures, and short contact times.[12] In particular, the compounds were slowly swept with a stream of nitrogen into a hot quartz tube with a cold finger condenser at the exit (see Figure 1). This should allow the isolation of even thermally labile products on preparative scales.[12]

We are currently studying the scope of the reaction and trapping of the thiocarbonyl ylides as well as extension to oxygen and nitrogen analogues. Complete details of the present work and the results of other efforts in this area are forthcoming.

References and Notes

(1) (a) Huisgen, R. *Proc. Chem. Soc.* **1961**, 357. (b) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565.

(2) Buter, J.; Wassenwaar, S.; Kellogg, R. M. *J. Org. Chem.* **1972**, *37*, 4045.

(3) Kaufmann, G. M.; Smith, J. A.; Van der Stouw, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1965**, *87*, 935.

(4) Steglich, W.; Gruber, P.; Heinlinger, H.; Kniedie, F. *Chem. Ber.* **1971**, *104*, 3816.

(5) Prepared from α-phenylmercaptoacetic acid and benzaldehyde according to the general procedure of Miller, E. H.; Hechenbleikner, I.; Homberg, O. A. French Patent 1 386 914; *Chem. Abstr.* **1965**, *63*, 605c.

(6) All new compounds have satisfactory combustion analyses and IR and NMR spectra.

(7) The crude product was pure by NMR and TLC but was recrystallized for an analytical sample, mp 34–37 °C, 83% yield.

(8) Pyrolysis at 600 °C as in the diphenyl system (eq 3) gives only a 65% conversion. It is tempting to correlate necessary pyrolysis temperature with apparent stability of the ylide, but is rather speculative with only two systems.

(9) The pure, crude thiirane was distilled to obtain a boiling point: bp 74–75 °C (0.001 mm), 91% yield.

(10) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim/Bergstr., Germany, 1970.

(11) This is a consequence of disrotatory ring opening with loss of carbon dioxide followed by conrotatory ring closure of the ylide.

(12) For example, see the excellent review: Seybold, G., *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 365.

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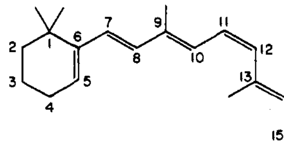
Polyene Chain Conformations of 13-Demethylretinals

Sir:

Considerable recent attention has been focussed upon the conformation of the polyene chain portion of 11-*cis*-retinal (I), the visual pigment chromophore. A number of experimental and theoretical studies[1,2] have contributed to the mounting body of evidence that the conformation about the 12–13 single bond, while distorted *s*-cis in the crystal state, is labile in solution, so that a mixture of conformers of 11-*cis*-retinal exists in solution. It has been proposed that the conformation when bound to the protein is 12-*s*-trans and that the wavelength of



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