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THE REACTIONS OF THIOCARBONYL YLIDES WITH ORGANIC ACIDS

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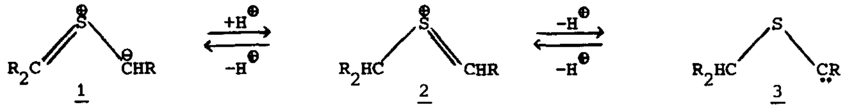
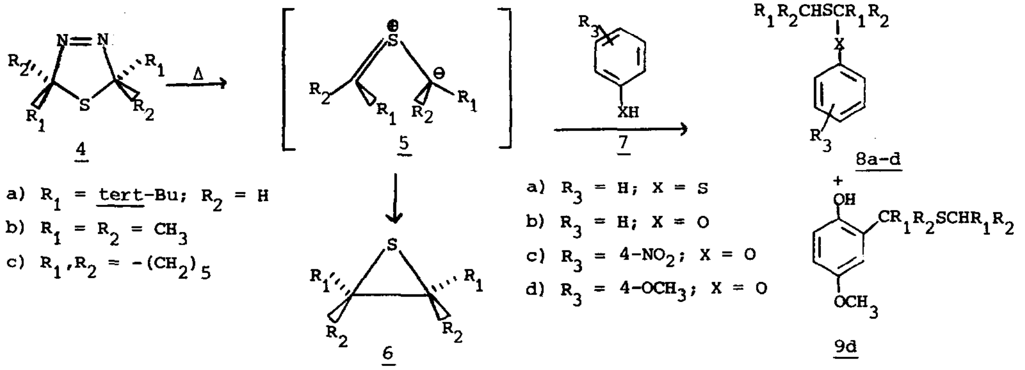
The known reactions of thiocarbonyl ylides (1, R = H and alkyl) reveal their propensity to engage either in cycloadditions with 1,3-dipolarophiles or to undergo valence isomerization to thiiranes.[1] We wish here to emphasize another facet of thiocarbonyl ylide chemistry. The aliphatically substituted derivatives are good bases. That this might be so becomes apparent on realizing that thiocarbonyl ylides can be viewed as the conjugate bases of the cations (2). The carbenes (3) are better known, however, in this capacity (eq 1). Deprotonation of 2 (R = H, the thiomethoxymethyl cation)[2] apparently fails[3] but more acidic derivatives of 2 such as dithiomethoxymethyl cations[4] and 1,3-dithiolium salts[5] readily afford carbenes (3) on treatment with strong bases. The challenge of accomplishing deprotonation of derivatives of 2 to give thiocarbonyl ylides has rarely been attacked or even considered although some precedent for this type of reaction, albeit with rather special systems, is available.[6,7]



(1)

Salient experimental results obtained with the thiocarbonyl ylides 5a-c are shown in eq 2. In a typical experiment 4 (3.75 mmoles) dissolved in methylcyclohexane (20 ml) was added over 30 min



(2)

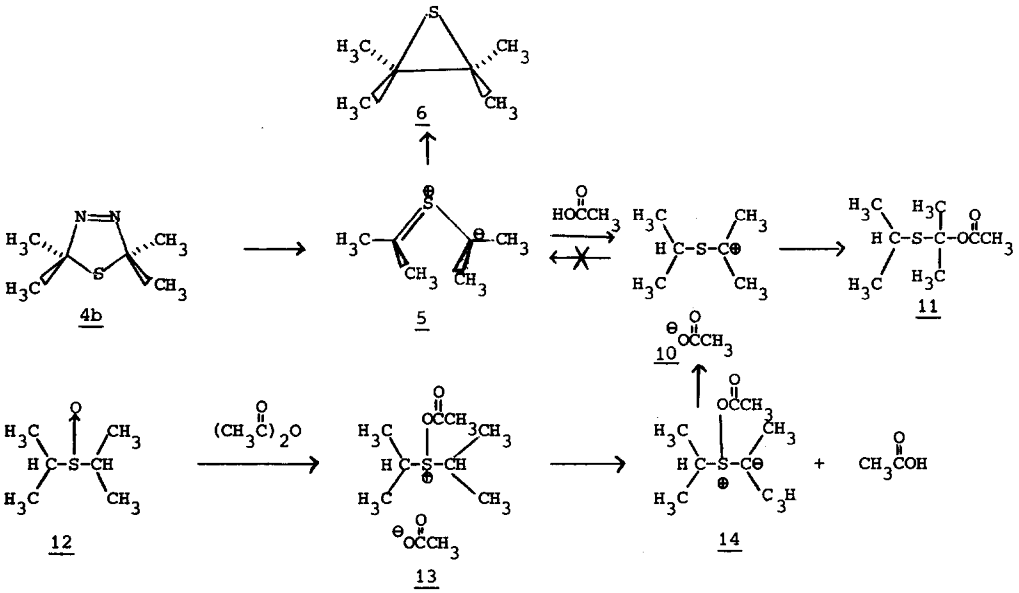
to a refluxing solution of phenol or thiophenol (8 mmole) in the same solvent. The thiocarbonyl ylides 5 are known to be generated under these conditions.[1a] With 7a-c as trapping agents yields of 8 directly after reaction were quantitative as determined by pmr spectroscopy on the crude reaction mixtures. No thiirane 6 could be detected; this is the exclusive product in the absence of trapping agent.[1a] The adducts 8 from 4b,c are sensitive to moisture being transformed to thioketals $R_1R_2C(SCHR_1R_2)_2$.[8] The highest isolated yield of pure product 8 (after chromatography over silica gel and distillation) was from 4a with 7b (67%). Compounds 9 were also formed in the reaction of 4a,b with 7d and were isolated by preparative glcp in ca 15% yield; the balance of the product was 8. Substitution in 9 ortho to the hydroxyl group is suggested but rigorous degradation experiments have not been carried out.

These observations are consistent with initial protonation of 5 (eq 3) followed by coupling of the resultant ions to form 8 (and 9 when electron rich phenols are used). Heuristic aspects

$$\underset{(X\,=\,O,S)}{\underline{5} + HXAr} \longrightarrow R_1R_2HCS\overset{\oplus}{C}R_1R_2,ArX^{\ominus} \longrightarrow \underline{8} + \underline{9} \qquad (3)$$

of eq 3 must be emphasized. We fully realize that particularly in the formation of 9 more complex mechanisms involving, for example, ylides of oxysulfonium salts might be involved.[9,10] Protonation of the thiocarbonyl ylide must, however, be a nearly unavoidable preface to reaction.[11,12]

The reactions of 4 with acetic acid were also examined in the light of ideas concerning postulated mechanisms for the Pummerer reaction of sulfoxides with acetic anhydride.[13] This is



(4)

illustrated for 4b in eq 4. The thiocarbonyl ylide 5 generated *in situ* from 4b with excess acetic acid affords exclusively 11, which undergoes pyrolytic elimination of acetic acid on extended heating. This reaction presumably goes through 10, which is an intermediate that is often invoked in the Pummerer reaction, as illustrated for diisopropyl sulfoxide 12.[14] The α-acetoxy sulfide 11 is formed also in high yield from rearrangement of 12.[13] On substituting 4b for 12 under the usual Pummerer conditions (acetic anhydride in benzene as solvent)[13] and including one equivalent of acetic acid about a 2:1 mixture of 11 and 6 is formed. It is unlikely, however, that the thiocarbonyl ylide 5 is an intermediate in the Pummerer rearrangement of 12 since attempts to circumvent the formation of 11 by either trapping 5 by cycloaddition or by promoting the formation of 5 from 10 by removing acetic acid formed during reaction had no detectable effect on the yield of 11.

The most economical explanation of the results of eq 4 is to assume that the thiocarbonyl ylide 5 is sufficiently basic to be rapidly protonated by acetic acid. This protonation is not reversible with this system. However, since basicity is subject to regulation by proper choice of substituents, the possibility offers itself of reversing the protonation equilibrium and of using the Pummerer or related reactions to generate properly substituted thiocarbonyl ylides. This is being investigated.

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3. R.A. Olofson and D.W. Hansen, Jr., *Tetrahedron*, **27**, 4209 (1971) and accompanying articles.
4. R.A. Olofson, S.W. Walinsky, J.P. Marino, and J.L. Jernow, *J. Amer. Chem. Soc.*, **90**, 6554 (1968).
5. See, for example: (a) H. Prinzbach, H. Berger, and A. Luttringhaus, *Angew. Chem.*, **10**, 453 (1965); (b) D.L. Coffen, J.Q. Chambers, D.R. Williams, P.E. Garrett, and N.D. Canfield, *J. Amer. Chem. Soc.*, **93**, 2258 (1971).
6. M. Takaku, S. Mitamura, and H. Nozaki, *Tetrahedron Lett.*, 3651 (1968).
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8. The reactions of 4a,b with 7a-d have been completely examined; with 4c only the reactions with 7a,b were performed. In the addition products 8 and 9, the terms a,b,c, and d refer to the substitution pattern in 7. The sensitivity of the initial addition products 8 to moisture prevented the obtainment of completely satisfactory analytical data in a number of cases.

Acceptable analyses were found with *8a*, *8c*, *8d* and *9d* (R_1 = *tert*-Bu; R_2 = H). Spectral data for all products were in accord with expectation.

9. See, for example: (a). R.A. Olofson and J-P. Marino, *Tetrahedron*, **27**, 4195 (1971).
10. (a) M.G. Burdon and J.G. Moffatt, *J. Amer. Chem. Soc.*, **89**, 4725 (1967) and preceding papers; (c) P.G. Gassman and D.R. Amick, *Tetrahedron Lett.*, 889 (1974).
11. Radical inhibitors have no effect on these reactions. Various attempts to trap radicals were also unsuccessful. We believe that on energetic grounds a concerted reaction involving a sigma bond (OH or SH) is also unlikely.
12. Protonation of 1,3-dipolar species is not an especially well recognized reaction. One of the better examples is found with nitrile oxides: Ch. Gutterman and P. Grünanger, *The Nitrile Oxides*, Springer Verlag Berlin (1971), p. 147.
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