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CHARACTERIZATION OF THIOCARBONYL YLIDES IN THE REACTION OF TRIPLET CARBENES WITH THIOKETONES [1]

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Abstract: The reactions of fluorenylidene and diphenyl carbene with di-tert-butylthioketone and adamantanethione lead to the rapid formation of strongly absorbing, long-lived ylides.

The formation and characterization of carbonyl ylides formed in the reaction of fluorenylidene with ketones has been discussed in earlier reports from this laboratory.[2,3] We now wish to report the extension of this photochemical reaction to include thiocarbonyl ylides. We have obtained the spectra of ylides formed in the reactions of carbenes with thioketones, and, as well, carried out the first kinetic measurements for these reactions and for the decay of the ylides. Further, our results show conclusively that the reaction can occur directly from triplet carbene rather than from the singlet state in equilibrium with the triplet.

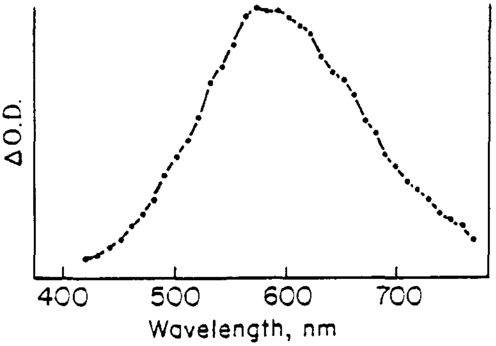
Thiocarbonyl ylides have been the subject of interest in recent years due to their possible role as intermediates in a variety of reactions including, for example, the production of thiiranes,[4-8] as well as five membered ring sulphur heterocycles.[9,10] Ylide production has been achieved by a variety of pathways, including 1,3-dipolar addition of diazocompounds to thioketones to produce Δ^3-1,3,4-thiodiazolines followed by elimination of nitrogen.[7] Other pathways include addition of thioketones to oxiranes[11] attack of carbenes on sulphides[6] and photorearrangement of aryl vinyl sulphides.[9,10] In particular, this last process has been examined by flash photolysis and has been the subject of some controversy.[9,10]

We have investigated the thiocarbonyl ylides formed in the photoreactions of diazofluorene and diphenyldiazomethane with di-tert- butylthioketone and adamantanethione.[12] Laser photolysis of 1×10^{-3}M Freon-113 solutions of the diazocompounds (337.1 nm, ~8 ns, <10 mJ/pulse)[13] led to the corresponding carbenes which were readily scavenged by the thioketones. Concurrent formation of new intermediates was indicated by the appearance of absorption bands with λ_{max} between 500 and 700 nm (Figure 1). Table 1 summarizes the data for these species. The pseudo first order rate constant for the growth of these transients was a linear function of the thioketone concentration. This is shown in Figure 2 for the fluorenylidene-adamantanethione system.

Table 1. Kinetic and spectroscopic parameters for the reaction of triplet carbenes with thioketones in Freon-113 at 300K.

Carbene	Thioketone	λ_{max} (nm)	$k_{formation}$[a] ($M^{-1}s^{-1}$)	τ_{decay}[b] (μs)
Fluorenylidene	di-tert-butylthioketone	700	$(1.1\pm0.1)\times10^{9}$	>100
Fluorenylidene	adamantanethione	580	$(6.4\pm1.1)\times10^{9}$	18.5
Diphenylcarbene	di-tert-butylthioketone	580	$(9.1\pm0.7)\times10^{7}$	44
Diphenylcarbene	adamantanethione	500	$(1.3\pm0.1)\times10^{9}$	26

[a] Errors as $\pm2\sigma$. [b] Lifetime, not half-life.



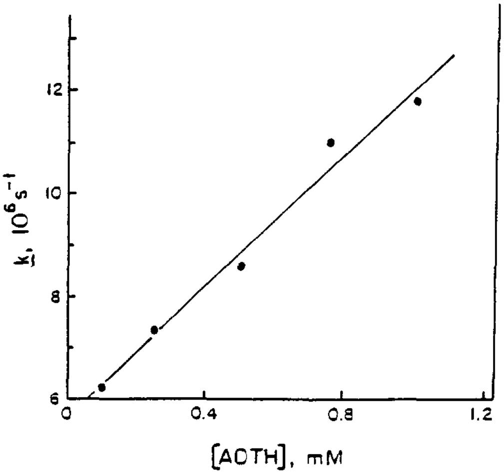
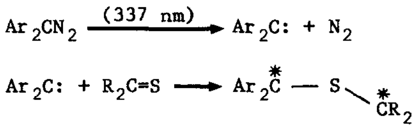


Figure 1 (left): Transient absorption spectrum of the fluorenylidene-adamantanethione ylide. **Figure 2** (right): Dependence of the pseudo first order rate constant for the growth of the same ylide as in Figure 1 on adamantanethione concentration ([ADTH]).

The slope of Figure 2 represents the bimolecular rate constant for carbene scavenging by thioketone. The new intermediates are assigned to the corresponding thiocarbonyl ylides formed in Scheme I.[14]

Scheme I



$$Ar_2CN_2 \xrightarrow{(337\ nm)} Ar_2C: + N_2$$

$$Ar_2C: + R_2C{=}S \longrightarrow Ar_2\overset{*}{C} - S - \overset{*}{C}R_2$$

The validity of this Scheme, which involves direct carbene attack on the thioketone, is supported by the concentration dependence observed (Figure 2), which would not be expected if ylide formation involved other pathways, such as photochemical nitrogen elimination from thiodiazoline formed prior to irradiation. The values of λ_{max} observed for the ylides were similar to those found for isomer carbonyl ylides and with other thiocarbonyl ylides formed in the photolysis of 2-naphthylvinylsulphides.[9,11]

To further support Scheme I, the reaction mixture was saturated with oxygen. Under these conditions the ylide signal was reduced (although the decay kinetics were not appreciably altered) while at the same time the characteristic absorption band due to fluorenone-oxide was observed (λ_{max}=450 nm).[15] This evidence indicates competition for fluorenylidene by oxygen and thioketone. Similarly, when methanol was added to the reaction mixture, the ylide signal was either reduced or was absent completely.

Ylides are generally expected to have ground state singlets. It is frequently assumed that their formation from carbenes involves attack by singlet carbene in thermal equilibrium with ground state triplet carbene.[16] When this is the case it is difficult to differentiate between a true reaction of the triplet carbene and one that involves singlet carbene in equilibrium with the triplet; for example, the diphenylcarbene-methanol system has been the subject of some controversy.[17] Our results for thioketones show conclusively that for these examples, the formation of ylides can proceed directly from the triplet carbene, not from the singlet in equilibrium with the triplet.[18] That is, the singlet carbene cannot be present in sufficient concentrations to account for the near diffusion controlled rate of ylide formation observed for some of the reactions. Conceivably the reactions may involve "radical-like" triplet carbene attack on the thioketone followed by rapid intersystem crossing to the singlet ground state ylide.[19] The differences in reactivity for each system (see Table 1) probably reflect the difference in steric hindrance in the two thioketones as well as the well documented higher reactivity of fluorenylidene relative to diphenylcarbene.[20]

References and Notes

1) Issued as NRCC- 24871.
2) P.C. Wong, D. Griller and J.C. Scaiano, J. Am. Chem. Soc., 104, 6631 (1982).
3) Carbonyl ylides produced by reactions of carbenes or by oxirane ring opening have also been observed in flash photolysis studies and in matrix isolation studies. E.g. see: G.W. Griffin, Angew. Chem. Int. Ed. Engl., 10, 537 (1971); A.M. Trozzolo, T.M. Leslie, A.S. Sarpotdar, R.D. Small and G.J. Ferraudi, Pure Appl. Chem., 51, 261 (1979); C.V. Kumar, S.K. Chattopadhyay and P.K. Das, J. Phys. Chem., 88, 5639 (1984).
4) W.J. Linn and E. Ciganek, J. Org. Chem., 34, 2146 (1969).
5) R.M. Kellogg, Tetrahedron, 32, 2165 (1976).
6) W. Ando, Acc. Chem. Res., 10, 179 (1977).

7) T.B. Cameron and H.W. Pinnick, J. Am. Chem. Soc., 101, 4755 (1979).

8) K. Oka, A. Dobashi and S. Hara, Tetrahedron Lett., 21, 3579 (1980).

9) T.J. Wolff, J. Am. Chem. Soc., 100, 6157 (1978).

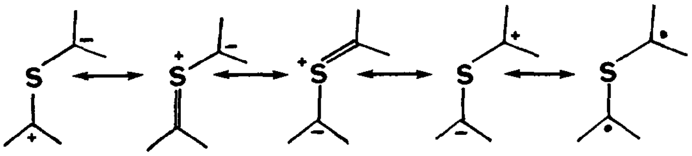
10) W.G. Herstroeter and A.G. Schultz, J. Am. Chem. Soc., 106, 5553 (1984).

11) W.J. Middleton, J. Org. Chem., 31, 3731 (1966).

12) Thioketones were prepared and purified following procedures in the literature: J.W. Greidanus, Can. J. Chem., 48, 3530 (1970); D.H.R. Barton, F.S. Guziec Jr. and J. Shahak, J. Chem. Soc. Perkin Trans. 1, 1794 (1974).

13) The experimental setup has been described previously: J.C. Scaiano, J. Am. Chem. Soc., 102, 7747 (1980).

14) The following are possible resonance structures for the thiocarbonyl ylides



15) H.L. Casal, M. Tanner, N.H. Werstiuk and J.C. Scaiano, J. Am. Chem. Soc., (in press).

16) Except for carbonyl-oxides where direct attack of triplet carbene on ground state oxygen is spin allowed.

17) D. Griller, A.S. Nazran and J.C. Scaiano, J. Am. Chem. Soc., 106, 198 (1984); G.L. Closs and B.E. Rabinow, J. Am. Chem. Soc., 98, 8190 (1976); D. Bethell, G. Stevens and P. Tickle, Chem. Commun., 792 (1970); K.B. Eisenthal, N.J. Turro, M. Aikawa, J.A. Butcher, Jr., C. DuPuy, G. Hefferon, W. Hetherington, G.M. Korenowski and M.J. McAuliffe, J. Am. Chem. Soc., 102, 6563 (1980).

18) At very high thioketone concentration a direct reaction with singlet carbene, before equilibration would be possible and, indeed, likely.

19) Thioketones are excellent traps for a variety of carbon, organometallic and phosphorus-centred radicals. E.g. see: J.R. Bolton, K.S. Chen, A.H. Lawrence and P. de Mayo, J. Am. Chem. Soc., 97, 1832 (1976); J.C. Scaiano and K.U. Ingold, J. Am. Chem. Soc., 98, 4727 (1976); W.G. McGimpsey, M.C. Depew and J.K.S. Wan, Phosphorus and Sulphur, 21, 135 (1984).

20) D. Griller, A.S. Nazran and J.C. Scaiano, Acc. Chem. Res., 17, 283 (1984).

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