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A NOVEL ROUTE TO THIOKETENES BY FLASH VACUUM THERMOLYSIS OF SILYLATED KETENE DITHIOACETALS, SYNTHESIS OF PROPADIENETHIONE.

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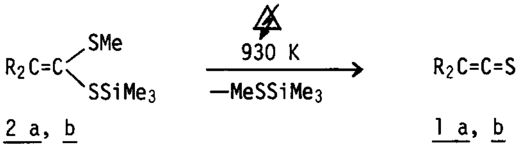
Flash vacuum thermolysis (fvt) of silylated ketene dithioacetals 2 leads to reactive thioketenes 1. This method, added to a retrodienic reaction, allowed access to propadienethione 3.

Thioketenes 1, when devoid of bulky substituents [1], are very reactive species which have been observed only at low temperatures, and characterized by in situ trapping reactions [2]. Few methods are available for their synthesis [2, 3]. The most usual are : thermolysis of their dimers (desaurins) [3], thermolysis or photolysis of 1,2,3-thiadiazoles [4, 5], and, in the case of thioketene itself (1, R= H) thermolysis of dithioacetic acid [5].

Some years ago, the gas phase thermolysis of silylated ketene monothioacetals was investigated [6] as a potential way to thioketenes. However, as in the case of ketene acetals [7], these reactions led to ketenes. We report herein that monosilylated ketene dithioacetals 2 are efficient precursors of thioketenes.



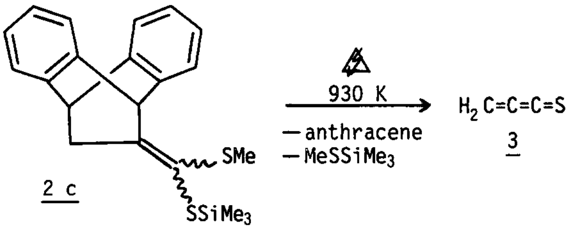
$$R_2C{=}C\begin{matrix}SMe\\SSiMe_3\end{matrix}\ \xrightarrow[-MeSSiMe_3]{930\ K}\ R_2C{=}C{=}S$$

2 a, b 1 a, b

a : R = Me

b : R_2 = $-(CH_2)_4-$

Compounds 2 a, b [8] were choosen as representative examples and submitted to fvt experiments. The ir spectrum of their thermolysis products (fvt temperature : 930 K [9]) recorded under vacuum at 77 K, showed the presence of $MeSSiMe_3$ [10], and 1 a or 1 b (ν C=C=S, 1 a : 1794 cm^{-1} [11], 1 b : 1783 cm^{-1} [12]) as the only detectable products [13]. In addition, trapping of 1 a with gaseous dimethylamine injected immediately at the oven exit gave N,N-dimethyl isopropylthiocarboxamide in 65 % yield. In the case of 1 b the same reaction conditions gave N,N-dimethyl cyclopentylthiocarboxamide in 25 % yield.



As an extension of this work, we also thermolysed the ketene dithioacetal 2 c prepared as above [8] from the corresponding dithioester [14].

In this case, loss of MeSSiMe$_3$ associated with a retrodienic reaction [15] gave anthracene in nearly quantitative yield and, as the only detectable volatile products, MeSSiMe$_3$ and propadienethione 3. The latter was characterized by its low temperature (77 K) ir spectrum [ν C=C=C=S 2105 (s) and 2170 cm^{-1} (m), in good agreement with the values reported for propadienone [16] and propadieneselone [17]] [18]. Compounds 1 a, b and 3 are very reactive species which rapidly polymerize above 120 K [19].

References and notes

[1] For the synthesis of stable thioketenes see, inter alia : E. Schaumann, and W. Walter ; Chem. Ber., 107, 3562 (1974) ; E.U. Elam, F.H. Rash, J.T. Dougherty, V.W. Goodlett and K.C. Brannock ; J. Org. Chem., 33, 2738 (1968) ; R. Mayer, and H. Kröber ; Z. Chem., 15, 91 (1975) ; and ref [2] .

[2] F. Duus, Comprehensive Organic Chemistry, D. Barton and W.D. Ollis Ed., Pergamon Press, Oxford, Vol. 3, 403 (1979) ; A. Ohno, Organic Compounds of Sulphur, Selenium, and Tellurium ; The Royal Society of Chemistry Ed., London, Vol. 6, 158 (1981). See also preceeding volumes in the same series, and D. Borrmann, Houben-Weyl Methoden der organischen Chemie, Georg Thieme Verlag, Stuttgart, Vol. 7/4, 312 (1968).

[3] G. Seybold, and C. Heibl ; Chem. Ber., 110, 1225 (1977).

[4] A. Krantz, and J. Laureni ; J. Am. Chem. Soc., 96, 6768 (1974) ; G. Seybold, and C. Heibl ; Angew. Chem. Int. Ed. Engl., 14, 248 (1975).

[5] H. Bock, B. Solouki, G. Bert, and P. Rosmus ; J. Am. Chem. Soc., 99, 1663 (1977).

[6] L. Carlsen, H. Egsgaard, E. Schaumann, H. Mrotzek, and W.R. Klein ; J. Chem. Soc. Perkin II, 1557 (1980).

[7] C. Ainsworth, F. Chen, and Y.N. Kuo ; J. Organomet. Chem, 46, 59 (1972) ; C. Ainsworth, and Y.N. Kuo ; ibid., 46, 73 (1972).

[8] Prepared according to R.S. Sukhai, and L. Brandsma ; Synthesis, 455 (1979).

[9] A short path oven was used (l= 10 cm), P= 10^{-5} Torr. For more technical details see : Y.M. Malécot, J.L. Ripoll, and A. Thuillier ; J. Chem. Research, S 86, M 0959 (1983).

[10] K.A. Hooton, and A.L. Allred ; Inorg. Chem., 4, 671 (1965).

[11] In good agreement with the previously reported value of 1789 cm^{-1} : G. Seybold ; Tetrahedron Lett., 555 (1974).

[12] Until now 1 b was known only as its adduct with diethyleneglycol : U. Timm, H. Bühl, and H. Meier ; J. Heterocyclic Chem., 15, 697 (1978).

[13] The uv - visible spectra of the thermolysis products were also recorded at 77 K. An absorption was observed in the 600 nm region (1 a : 597, 1 b : 608 nm) which could be assigned to the $n \longrightarrow \pi^*$ thioketene absorption [2]. However, formation of reddish polymers absorbing in the same region did not allow us to observe the expected disappearance of these bands upon warming.

[14] P. Gosselin, S. Masson, and A. Thuillier ; Tetrahedron Lett. 21, 2421 (1980).

[15] For a review, see : M.C. Lasne, and J.L. Ripoll ; Synthesis, 121 (1985).

[16] R.F.C. Brown, F.W. Eastwood, and G.L. Mc Mullen ; J. Am. Chem. Soc., 98, 7421 (1976) ; Aust. J. Chem., 30, 179 (1977).

[17] W.W. Sander, and O.L. Chapman ; J. Org. Chem., 50, 543 (1985).

[18] In the low temperature uv - visible spectrum of the thermolysis product of 2 c, a transient strong band at 365 nm could be attributed to the $\pi \longrightarrow \pi^*$ absorption of 3 ; no band observed near 600 nm. An attempt at trapping 3 by HNMe$_2$ did not permit us to identify N,N-dimethyl thioacrylamide in the complex reaction mixture obtained.

[19] Full experimental details and further applications will be published later.

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