Intramolecular 1,3-Dipolar Cycloadditions of Thiocarbonyl *S*-Sulfides (Thiosulfines) with Non-activated Alkenes

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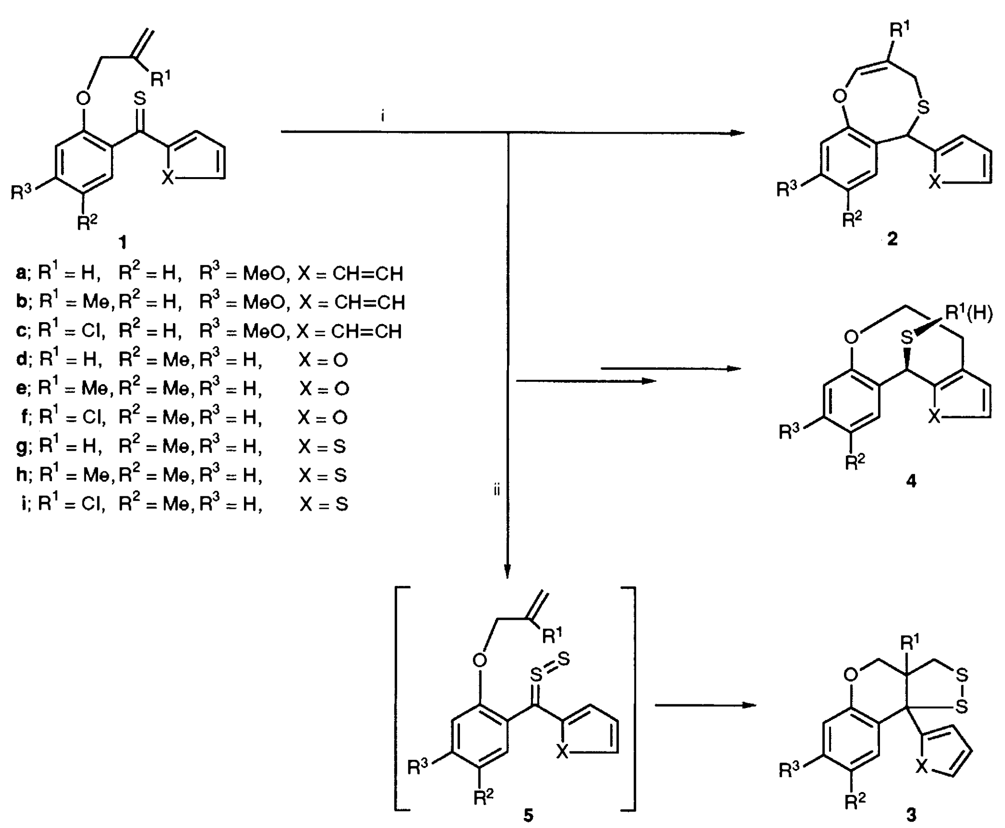
Novel examples are described that involve unequivocal evidence for the existence of thiocarbonyl *S*-sulfides *via* intramolecular [3 + 2]-trapping by non-activated alkenes.

Despite a number of reports since 1921,[1] thiocarbonyl *S*-sulfides (thiosulfines) compounds are still postulated as intermediary species.[2-4] The most noteworthy reports describe (*i*) intermolecular interception of thiosulfines *via* 1,3-dipolar cycloaddition giving, *e.g.* dithioles or trithiolanes,[2] (*ii*) thiosulfines $\rightleftharpoons$ dithiiranes equilibration followed by rearrangement to dithiocarboxylic acid esters[3] and (*iii*) their transformation to thiocarbonyl or related compounds.[2-4]

On the other hand, we have described in recent reports that thiobenzophenones connecting an allyl group by a chain undergo thermal intramolecular type III ene reactions to afford eight- and ten-membered-cyclic sulfides and that the reactions largely depend on the nature and position of the substituent(s) and chain length.[5] In continuing studies on intramolecular cycloadditions,[6] we have found that the thiosulfines formed by sulfurization of the thioketones, could



Scheme 1 *Reagent and conditions*: i, at 140 °C in xylene; ii, 'S' (S_8) at 140 °C in xylene

be intramolecularly trapped. This appears to be the first reported straightforward evidence for the existence of thiosulfines by intramolecular [3 + 2]cycloaddition with non-activated alkenes.†

When the thiobenzophenones **1a–c** and heteroaromatic thioketones **1d–i** were heated under elementary sulfur-free conditions at 140 °C in xylene, the intramolecular ene products **2a–c** were obtained exclusively in the former cases,[5] and in the latter **2d–i**‡ and **3d–i**‡ were formed comparably (Scheme 1, Table 1). With **1d, g** bearing an unsubstituted alkene (R^1 = H), compounds **4d, g**‡ were obtained as the minor products which were rearomatized products of the initially formed intramolecular hetero-Diels–Alder adducts by way of a 1,3-H shift.

Table 1 Intramolecular cycloadditions of thioketones **1** and thioketone *S*-sulfides **5**

	In the absence of S_8				In the presence of S_8			
		Product yield (%)				Product yield (%)		
Entry	Time/ h	**2**	**3**[b]	**4**	Time/ h	**2**	**3**	**4**
a	1	83[a]	—	—	1.5	19	49	—
b	1.5	83[a]	—	—	1.5	47	21	—
c	24	78[a]	—	—	2	21	31	—
d	3	40	17	6	0.3	11	60	8
e	51	37	25	—	1	23	55	—
f	24	11	23	—	1.5	6	64	—
g	34	41	18	10	0.7	12	73	Trace
h	120	23	44	—	2	30	56	—
i	61	12	48	—	1	6	65	—

[a] Reported in ref. 5. [b] Based on a half equimolar amount of **1**. (We assumed that the second-sulfur donor originated from the thioketone itself, *e.g.* [2 + 2] dimers.[2])

In the presence of S_8, the thermal reaction also produced mainly **2** and **3** but the distribution of the yields changed significantly. The high efficiency for the thiosulfines **5** generation using S_8 and for the subsequent intramolecular trapping is unambiguous from the comparisons of the data in Table 1, *viz.* in the presence of S_8, the considerably reduced reaction time and yield of **2** with an increase in the yield of **3** in each case, compared with those in the absence. Remarkable are the cases of the thiobenzophenones **1a–c** and of the heteroaromatic thioketones **1d–i** for the distributions (**2**/**3**) and for the reaction time, the latter being relatively stable and reluctant to the ene reaction under the conditions leading to **2d–i**.

Thus, molecular sulfur S_8 could be conveniently activated by simply heating at 140 °C in xylene to generate an active sulfur 'S' which was captured by **1** to form the thioketone

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† Recently Ishii and Nakayama *et al.* reported 1,2,4-trithiolane production in sulfurization of a certain diketone which might involve intramolecular cycloaddition of the thiosulfine with a thiocarbonyl.[7]

‡ **2d**: ^1H NMR ($CDCl_3$, *J* values in Hz) δ 2.20 (3H, s), 2.61 (1H, dd, *J* 14.0 and 9.0), 2.94 (1H, ddd, *J* 14.0, 9.0 and 1.3), 4.59 (1H, ddd, *J* 9.0, 9.0 and 7.5), 5.69 (1H, s), 6.29 (1H, dd, *J* 3.4 and 1.8), 6.37 (1H, dd, *J* 7.5 and 1.3), 6.47 (1H, dd, *J* 3.4 and 1.0), 6.88 (2H, d, *J* 1.0), 7.00 (1H, br s) and 7.32 (1H, dd, *J* 1.8 and 1.0); ^{13}C NMR δ 20.86 (q), 24.01 (t), 38.89 (d), 100.84 (d) −151.72 (s); MS *m/z* 258 (19%, M^+), 225 (64), 211 (100); M 258.0712 $C_{15}H_{14}O_2S$ requires M 258.0715.

3d: ^1H NMR δ 2.24 (3H), 3.05–3.59 (3H, m), 4.02 (1H, ddd, *J* 11.8, 3.4 and 1.0), 4.20 (1H, ddd, *J* 11.8, 5.7 and 1.0), 6.28 (1H, dd, *J* 3.4 and 2.0), 6.39 (1H, dd, *J* 3.4 and 1.0), 6.72 (1H, d, *J* 8.3), 6.95 (1H, dd, *J* 8.3 and 3.3), 7.12 (1H, d, *J* 3.3) and 7.34 (1H, dd, *J* 2.0 and 1.0); ^{13}C NMR δ 20.57 (q), 40.01 (t), 48.20 (d), 64.38 (s), 65.41 (t), 110.29 (d) −154.21 (s); MS *m/z* 290 (16%, M^+), 225 (100), 211 (10); M 290.0427 $C_{15}H_{14}O_2S_2$ requires M 290.0436.

4d: ^1H NMR δ 2.28 (3H, s), 2.84–3.40 (3H, m), 4.06 (1H, ddd, *J* 12.5, 1.5 and 1.5), 4.60 (1H, s), 4.62 (1H, dd, *J* 12.5 and 3.0), 6.22 (1H, d, *J* 1.8), 6.72–7.16 (3H, m) and 7.13 (1H, d, 1.8); ^{13}C NMR δ 20.62 (q), 29.10 (t), 39.33 (d), 39.87 (d), 79.39 (t), 110.29 (d) −156.45 (s); MS *m/z* 258 (100%, M^+) and 225 (10).

S-sulfide **5**.§ Taking advantage of the intramolecularity, the labile C=S=S function, thus formed, was trapped effectively by the internal dipolarophile to produce **3**.

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§ Formation of **5** *via* 1,2,4,5-tetrathiane is unlikely: see ref. 2(*a*), p. 90.