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# GENERATION OF THIOKETENES VIA CYCLOREVERSION OF 1,3-DITHIOLANE-DERIVED SULFUR YLIDES

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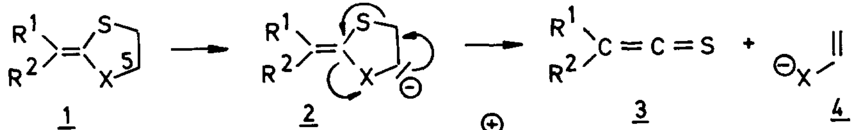
Summary - On treatment with base, 1-aryl-2-alkylidene-1,3-dithiolanium salts 6 give clean cycloreversion providing thioketenes 3 and vinyl sulfides 7.

Recently, thioketenes 3 have emerged as synthetically useful species allowing ready access to α-thiolactones[1], ß-thiolactams[2], and five-membered heterocycles[3]. However, a major limitation in the exploitation of thioketene chemistry has been the limited choice of methods to generate the reactive species. Sterically hindered derivatives are accessible via thionation of acyl chlorides[4] and allylic thioketenes via the thia-Cope rearrangement of alkynyl(allyl)sulfides[5]. For other examples, flash-thermolysis of 1,2,3-thiadiazoles has been employed[6]. As a more convenient and general approach, the (3+2) cycloreversion of 2-alkylidene-1,3-dithiolane 1,1-dioxide carbanions 2a has been suggested[7]. For the corresponding sulfur ylides 2b, an even smoother cycloreversion is anticipated, since the second fragment would be an uncharged and, under the reaction conditions, chemically inert vinyl sulfide 4b. However, selective carbanion formation in the 5-position of 1b would require, in the α-position, a less acidic or preferably hydrogen-free sulfur substituent $R^3$. Since S-arylation of sulfoxides is known[8], we investigated whether 1,3-dithiolane 1-oxides 1c could be transformed into sulfonium salts and, via deprotonation, provide convenient access to thioketenes 3.



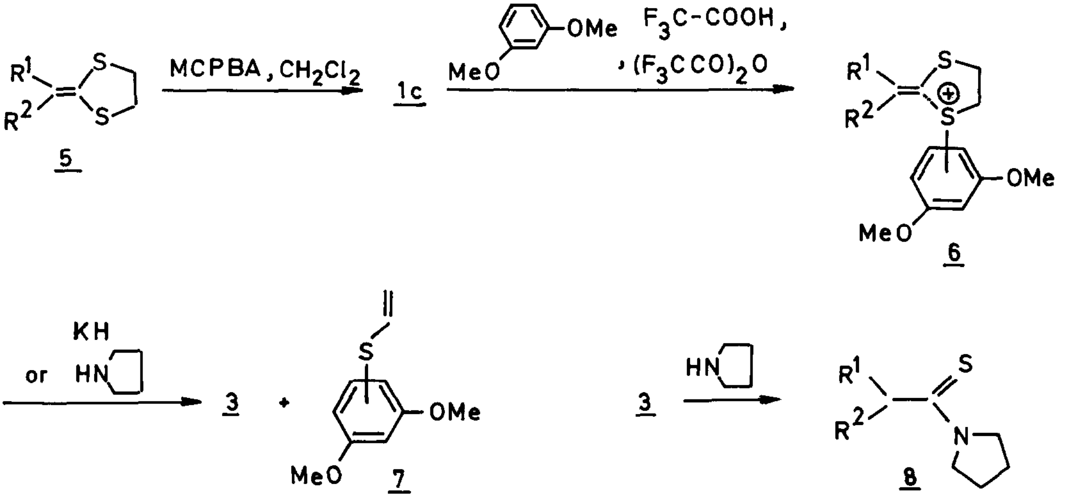
1,2,4a: X = $SO_2$ ; b: X = $\overset{\oplus}{S}-R^3$ ; 1c: X = SO

Oxidation of 2-alkylidene-1,3-dithiolanes 5 with one equivalent of m-chloroperbenzoic acid to give S-monoxides 1c is uneventful (Table). S-Arylation is achieved by reaction with m-dimethoxybenzene under acidic conditions providing sulfonium salts 6 as a mixture presumably of the 2- and 4-aryl derivatives. The crude salts can be transformed into S-ylides 2b ($R^3=C_6H_3(OMe)_2$) using potassium hydride or the amine which is also intended to serve as a trapping-agent for thioketenes 3. The cycloreversion is a smooth and clean process as

Table. Formation of S-oxides 5, vinyl sulfides 7, and thioamides 8 from 1,3-dithiolanes 5[a)].

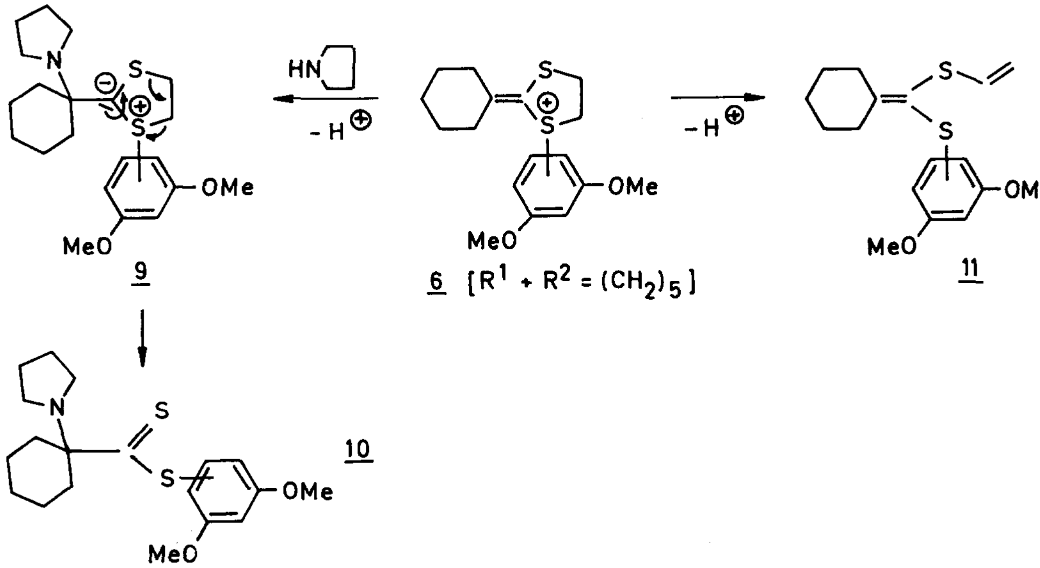
| Entry | 1c $R^1$ | $R^2$ | Yield[b)] [%] | m.p. [°C] | Method[c)] | 7 Yield [%] | 8 $R^1$ | $R^2$ | Yield [%] | m.p. [°C] |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | $O_2N$ | H | 94 | 95 | A | 63 | $O_2N$ | H | 53 | 81 |
| 2 | Ph-$SO_2$ | H | 53 | 146 | A | 57 | Ph-$SO_2$ | H | 53 | 159 |
| 3 | | | | | B | 39 | | | 38 | |
| 4 | $(CH_2)_5$ | | 100 | 82-83 | A | 27 | $(CH_2)_5$ | | 26 | 106 |
| 5 | | | | | B | 27 | | | 15 | |
| 6 | tBu | NC- | 78 | 98-100[d)] | A | 95 | tBu | NC- | 91 | 112 |
| 7 | Ph | NC- | 95 | 119-121[d)] | B | 100 | Ph | NC- | 82 | 87 |
| 8 | | | | | A | 80 | Ph | $H_2N$-CO[c)] | 61 | 181 |
| 9 | Ph | $H_5C_2$-CO | 63 | 90/120[e)] | A | 99 | Ph | H | 60 | 73[f)] |
| 10 | Cl | Cl | 61[g)] | 70 | A | 100 | | | - | -[h)] |

[a)] All new compounds gave satisfactory IR, NMR, and analytical data. - [b)] Yield based on converted 5. - [c)] See text. - [d)] Ref. 9. - [e)] Two diastereomers. - [f)] Ref. 10. - [g)] Yield for oxidation (MCPBA) and dehydrochlorination (basic alumina, tBuOMe) of 2-(trichloromethyl)-1,3-dithiolane. - [h)] The product could not be obtained in a pure form.



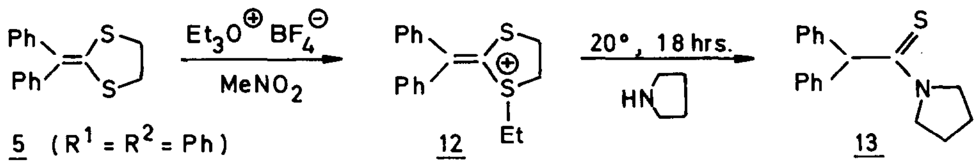
demonstrated by usually high yields of vinyl sulfides 7 (Table). Thioketenes are formed at the same time and can be trapped by the added pyrrolidine. Taking into account the second functional group, at least some of the isolated thioamides 8 would not be accessible using conventional methods.

A special feature is observed for the case of 1c ($R^1$ = Ph, $R^2$ = CN). If trifluoroacetic anhydride is omitted in the preparation of sulfonium salt 6, the liberated water adds to the cyano group under the reaction conditions generating a carboxamido group (cf. Table, entry 8). In some instances, side or subsequent reactions interfere. Thus, pyrrolidine may add to the more polarized C=C bond of vinylsulfonium salt 6 ($R^1$+$R^2$ = $(CH_2)_5$; entry 4) to give S-ylide 9 which fragments to furnish dithiocarboxylate 10 (12-23 %; m. p.95 °C) in analogy to similar S-ylides[11]. Moreover, deprotonation in the 4-position competes with formation of 2b to afford the Hofmann elimination product 11 (54-56 %; m. p. 55 °C).



The ß-oxo thioamide formed from propionyl(phenyl)thioketene undergoes acid cleavage under the reaction conditions to give phenylthioacetyl pyrrolidine (entry 9). Dichlorothioketene leads to dichlorothioacetyl pyrrolidine only as an intermediate as the chlorine substituents are exchanged by excess amine to give an N,N-acetal which could not be obtained in a pure form (entry 10); using sodium ethoxide as a base in the generation of 3 ($R^1$ = $R^2$ = Cl) gives an oligomer of the thioketene (39 %).

S-Oxide 1c ($R^1$ = $R^2$ =Ph) does not give the desired S-arylation. As an alternative, the S-ethyl salt 12 can be prepared and gives 5-deprotonation on treatment with pyrrolidine. The resulting diphenylthioketene 3 ($R^1$ = $R^2$ = Ph) is trapped as thioamide 13 (78%, based on 5; m. p. 164 °C).



General procedure for preparation of sulfonium salts 6. Under $N_2$, sulfoxide 1c (1 mmol) and 1,3-dimethoxybenzene (0.126 ml; 1 mmol) are dissolved in $F_3C$-COOH (2ml) at 0°C. The clear solution is cooled until crystallization begins ( -30°C) and, with stirring, trifluoroacetic anhydride (0.282 ml, 2 mmol; 1 mmol for entries 1, 9) is added. The mixture is allowed to warm to room temperature overnight, concentrated in vacuo, and the residual oil again evaporated with a few ml of chloroform to remove the last traces of $F_3C$-COOH.

*Generation and trapping of thioketenes 3*. *Method A*. Under nitrogen, the crude salt *6* is dissolved in dry THF (1 ml) and added dropwise to pyrrolidine ( 3ml; dried by filtration through molecular sieves 3/4 Å) at 0°C. After 1 hr, the mixture is concentrated at a rotary evaporator and products *7*, *8*, *13* are isolated by column chromatography (silica gel).

*Method B*. At -78°C, a solution of crude salt *6* in dry THF (5 ml) is added dropwise to a stirred suspension of KH (44 mg; 1.1 mmol) in THF (1 ml). After hydrogen-evolution has subsided (15-30 min), pyrrolidine (3 ml) is added and the reaction mixture quickly warmed to 20°C by placing it in a water-bath. For workup see method A.

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