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KETENE THIOACETALS FROM α-CHLOROMERCAPTALS

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Abstract: Excellent yields of ketene thioacetals are obtained from 2-(1-chloroalkyl)-1,3-dithiolanes or 2-(1-chloroalkyl)-1,3-dithianes.

Ketene thioacetals are intermediates of increasing interest in synthesis and a variety of methods for their preparation has been developed.[1] Generally, these compounds are obtained by connective methods, like Peterson or Horner-Emmons olefination of aldehydes or ketones.[1] Non-connective procedures have also been developed like those starting from esters[1] or dithioesters.[2] Among these strategies, however, those exploiting the possibility of sulphur to increase the adjacent proton acidity,[3] thus favouring a β-elimination, have been neglected; as far as we know, only preparations with potassium tert-butylate from α–alkylmercapto[4] or α–alkoxy-[5] or α–chloro-[6] acetaldehyde mercaptals are reported using a tedious procedure.

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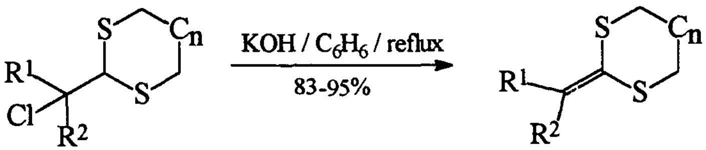
Recently, we developed an easy and efficient procedure from α-chloroacetals to the corresponding α-chloromercaptals.[7] Also owing to their stability, these thioderivatives may be useful synthons, and an immediate application is their dehydrochlorination to ketene thioacetals. However, on using the reported method[6] on 2-(1-chloroalkyl)-1,3-dithiolanes, unsatisfactory conversion yields (<60%) were observed even under forcing conditions, by heating the mixture at reflux for 8 h with 2.6 eq. of potassium *tert*-butylate.

We report now a simple, versatile and very high yields procedure for the preparation of ketene thioacetals from a number of 2-(1-chloroalkyl)-1,3-dithiolanes and 2-(1-chloroalkyl)-1,3-dithianes with KOH in boiling benzene[8] (Table).



On replacing KOH by equivalent amounts of NaOH, dehydrohalogenations are slow and poor conversions are observed. Since C-2 deprotonated 1,3-dithiolanes are unstable, giving rise to an easy elimination of ethylene,[9] and dithiocarboxylic acid adducts are not observed as side products, HCl elimination reasonably occurs through a concerted mechanism, without formation of any free negative charge.

Starting from 2-(1-chloroalkyl)-1,3-oxathiolanes the method fails, likely owing to the lower acidity of the C3 proton,[10] and unreacted substrates are recovered.

Table. Synthesis of Ketene Thioacetals.

R^1	R^2	n	TIME (h)	YIELD (%)	B.p./°C (mmHg)	Lit. data
n-C_4H_9	H	0	2	94	94-7 (0.6)	
n-C_4H_9	H	1	2	92	146-51 (2)	140 (0.5)[a]
-C_5H_{10}-		0	6	94	84-8 (0.05)	
-C_5H_{10}-		1	1	95	M.p. 98-100	M.p. 94[b]
H	H	0	1	93	55-60 (0.05)	55 (9)[c]
H	H	1	1	91	78-83 (0.1)	100 (20)[d]
$PhCH_2$	H	0	2	83	134-9 (0.05)	
$PhCH_2$	H	1	1	85	157-62 (0.01)	
CH_3	CH_3	0	1	88	94-8 (1)	80-1 (4)[c]
CH_3	CH_3	1	1	92	147-51 (16)	56 (0.5)[d]

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Experimental

^{1}HNMR spectra have been recorded on Bruker FP80 and Varian XL200 spectrometers. Mass spectra have been obtained on a HP 5989A MS Engine. Reagents and solvents were standard grade commercial products, and were used without further purification. α-Chloromercaptals were prepared by αchloroaldehydes dimethyl acetals transdithioacetalisation with ethanedithiol or 1,3-propanedithiol according to our reported method.[7]

General procedure for α-Chloromercaptals dehydrochlorination. In a double necked round bottom flask (25 ml) fitted with a condenser, the 2-(1-chloroalkyl)-1,3-dithiolane or -1,3-dithiane (1.0 mmole) was dissolved in benzene (2 ml). To the stirred solution finely grounded KOH (6.0 mmoles) was added; the mixture was heated at reflux and the reaction monitored by TLC, using ethyl ether/n-hexane (0.5:9.5) as eluant. When conversion was complete, the reaction mixture was filtered on a mixed bed of celite and Na_2SO_4. A rather clean product was obtained after solvent evaporation at reduced pressure. Further purification was effected by preparative TLC, using ethyl ether/n-hexane (1:9) as eluant, or by bulb to bulb distillation in an air bath thermostat.[11]

2-(3-Phenyl-propyliden)-1,3-dithiolane

^1H NMR ($CDCl_3$) : 3.44 (4H, m, -S(CH_2)S-); 3.55 (2H, d, Ph-CH_2-C=); 5.68 (1H, t, Ph-C-CH=); 7.21 (5H, m, -C_6H_5).

m/z: 208 (M^+, 100); 147 (56).

2-(3-Phenyl-propyliden)-1,3-dithiane

^1H NMR ($CDCl_3$): 2.16 (2H, m, -S-C-CH_2-C-S-); 2.89 (4H, m, 2 x S-CH_2-); 3.57 (2H, d, Ph-CH_2-C=); 6.11(1H, t, Ph-C- CH=); 7.23 (5H, m, -C_6H_5).

m/z: 222 (M^+, 100); 147 (95).

2-Pentyliden-1,3-dithiolane

^1H NMR ($CDCl_3$): 0.94 (3H, t, CH_3-C); 1.35 (4H, m, C-(CH_2)-C); 2.09 (2H, q, CH_2-C=); 3.31 (4H, m, -S(CH_2)$_2$S-); 5.52 (1H, t, -CH=S).

m/z: 174 (M^+, 5); 131 (100).

2-Cyclohexyliden-1,3-dithiolane

^{1}H NMR ($CDCl_3$): 1.52 (6H, m, 3 x CH_2); 2.20 (4H, m, 2 x CH_2-C=); 3.33 (4H, s, -$S(CH_2)_2S$-).

m/z: 186 (M^+, 100); 158 (56).

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11) Since the boiling points have been determined by this procedure, the reported values are uncorrected.

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