A Simple and Convenient Method for the Cleavage of Dithioacetals to the Correspondig Carbonyl Compounds

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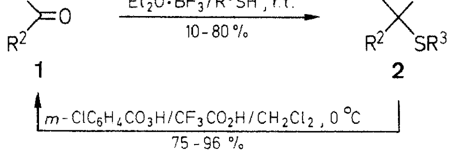
Carbonyl compounds were regenerated in high yields when corresponding diphenyl and diethyl dithioacetals were treated with a mixture of *m*-chloroperoxybenzoic acid/trifluoroacetic acid in dichloromethane.

The synthetic usefulness of the umpolung reactivity of carbonyl compounds through their thioacetals is well documented.[1] The conversion of dithioacetals **2** to their corresponding carbonyl compounds **1** can be performed under a variety of reaction conditions.[2] The number of these methods shows that these reactions are not general. Among such methods, the oxidative ones are in general a two steps sequence.[3,4] The application of these oxidative methods to polyfunctional molecules is limited due to the drastic conditions required, and to the difficulty to obtain reproducible yields.

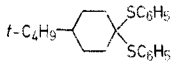
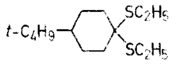
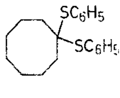
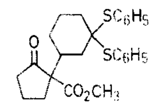
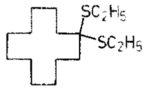
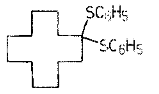
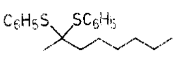
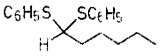
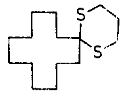
Here we report a convenient and mild method for the regeneration of carbonyl compounds from their diphenyl and diethyl dithioacetal derivatives, which are synthesized by one of the standard methods.[1]



The deprotection step is carried out by treating compound **2** with a mixture of trifluoroacetic acid (2 equivalents) and *m*-chloroperoxybenzoic acid (1.5 equivalents) at 0 °C in dichloromethane. The reaction was complete in an hour (Table). Under these conditions, the cyclic trimethylene dithioacetal derivative **2i** did not undergo cleavage to give the parent ketone.

In summary, the one-pot cleavage of diphenyl and diethyl dithioacetals is selective, very simple to carry out, very fast, and gives high and reproducible yields of the parent carbonyl compound.

Table. Cleavage of Dithioacetals **2** to Carbonyl Compounds **1**

Dithioacetal **2**		Yield (%)	m.p. (°C)	Molecular Formula[a] or Lit. m.p. (°C)	MS m/e (M^+)	IR ($CDCl_3$) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C-NMR ($CDCl_3$/TMS)	Carbonyl Compound **1**[c] from Dithioacetal **2** by Deprotection, Yield (%)
2a		75	76	82–82.5[5]	356	1500, 1450, 1240, 1020	0.9 (s, 9H); 1.25–2.0 (m, 9H); 7.0–8.0 (m, 10H)	65, 47, 37, 32, 27, 23	95
2b		80	oil[b]	$C_{14}H_{28}S_2$ (260.5)	260	1500, 1450, 1240, 1020	0.9 (s, 9H); 1.25 (t, 6H, J = 7); 1.5–2.25 (m, 10H); 2.5 (2q, 2H each, J = 7)	61, 48, 38, 32, 31, 27, 23, 22, 22, 15, 14	96
2c		10	78	$C_{20}H_{24}S_2$ (328.5)	328	1500, 1450, 1240, 1020	1.25–2.0 (m, 14H); 7.0–8.0 (m, 10H)	63	87
2d		55	145	$C_{25}H_{28}O_3S_2$ (440.6)	440	1750, 1725, 1450, 1240, 910	1.0–3.0 (m, 15H); 3.55 (m, 3H); 7.0–8.0 (m, 10H)	213, 170, 65, 64, 53, 39	90[d]
2e		70	oil[b]	$C_{16}H_{32}S_2$ (288.6)	288	1500, 1450, 1020	1.25 (t, 6H, J = 7); 1.25–2.0 (m, 22H); 2.55 (q, 4H, J = 7)	65, 33, 26, 23, 22, 14	95
2f		75	66	67–68[6]	384	1500, 1450, 1240, 1020	1.25–2.0 (m, 22H); 7.0–8.0 (m, 10H)	70, 34, 27, 26, 23, 20	98
2g		65	oil[b]	$C_{20}H_{26}S_2$ (330.6)	330	1500, 1450, 1240, 1020	1.0–2.0 (m, 13H); 1.5 (s, 3H); 7.0–8.0 (m, 10H)	64, 41, 32, 29, 28, 25, 22, 14	75
2h		50	oil[b]	oil[7]	302	1500, 1450, 1240, 1020	0.75–2.5 (m, 9H); 4.50 (t, 1H, J = 7); 7.0–8.0 (m, 10H)	58, 35, 31, 26, 22, 14	92
2i		80	81	81–82[6]	270	1470, 1445, 1345, 1275	1.3–1.35 (m, 18H); 2.0 (m, 6H); 2.80 (m, 4H)	61, 27, 28, 46	0

[a] Satisfactory microanalyses were obtained: C ±0.25, H ±0.21.

[b] Viscous liquid purified by silica gel chromatography.

[c] All carbonyl compounds except **2d** are known and gave satisfactory IR and NMR data.

[d] m.p. 80–82 °C.
$C_{13}H_{18}O_4$ calc. C 65.54 H 7.60
(238.3) found 65.50 7.65
IR($CHCl_3$): ν = 1750, 1725, 1710, 1250 cm^{-1}.
^{1}H-NMR($CDCl_3$): δ = 1.25 – 3.0 (m, 15H); 3.75 (s, 3H).
^{13}C-NMR($CDCl_3$, 15 MHz): δ = 213, 209, 170.

All starting materials were distilled before use. CH_2Cl_2 was distilled over CaH_2. The products were purified by distillation or by column chromatography on silica gel. Melting points are uncorrected and determined on a Büchi apparatus. Mass spectra were recorded on a Jeol Spectrometer and IR spectra recorded on a Philips SP 2000 Spectrometer. ^{1}H-NMR spectra were recorded on a Bruker SP 80 and ^{13}C-NMR spectra on a Bruker WP 60 apparatus.

Diphenyl and diethyl dithioacetals **2** were prepared according to literature,[1] by reacting the carbonyl compounds with the corresponding thiol in presence of Et_2OBF_3 at room temperature (Table).

Cleavage of Dithioacetals 2 to Carbonyl Compounds 1; General Procedure:

To a stirred solution of dithioacetal **2** (10 mmol) in CH_2Cl_2 (50 mL) at 0 °C is added dropwise a mixture of *m*-chloroperoxybenzoic acid (2.58 g, 15 mmol) and CF_3CO_2H (1.5 mL, 20 mmol) in CH_2Cl_2 (20 mL). The mixture is stirred at room temperature until completion of the reaction (30 min to 1 h) as monitored by TLC. The mixture is quenched with a 3N solution of NaOH (20 mL), the organic layer is separated, washed with a 3 M solution of Na_2SO_3 (10 mL) and dried ($MgSO_4$). Evaporation of solvent gives the crude material which is purified by distillation or by column chromatography on silica gel (eluent: hexane/EtOAc, 90 : 10).

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