# Electrochemical Removal of 1,3-Dithian Protecting Groups

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*Summary* Anodic cleavage provides an efficient and convenient method for the regeneration in neutral media of a variety of aldehydes and ketones from the dithian derivatives.

GOOD general methods for the removal of dithian protecting groups are scarce. Usual methods involve metal-ion induced hydrolysis in which for several cases the metal-ion is believed to act as an oxidant.[1] In at least one successful method,[2] the inorganic species $Ce(NH_4)_2(NO_3)_6$ probably functions as a one-electron oxidant, and certainly anodic oxidation[3] of some *gem*-disulphides gives cleavage of carbon–sulphur bonds with concomitant production in aqueous solution of carbonyl compounds. These results indicate that anodic cleavage of dithians might constitute a useful preparative method and, together with the recent publication[4] of another oxidative method (with $Ph_2Se_2O_3$) for the removal of dithians and dithiolans, prompt us to report on the development of a generally applicable and efficient electrochemical method for dithian cleavage.

For dithian derivatives of the carbonyl compounds listed in the Table single sweep cyclic voltammetry [Pt bead, MeCN–$H_2O$ (10% v/v), $NaClO_4$ (0·1 M), 0·4 V $s^{-1}$] gave sharp but irreversible oxidation peaks; for 2-phenyl-1,3-dithian irreversible oxidation persisted even at 40 V $s^{-1}$ in dry MeCN–$LiClO_4$ (0·1 M). Peak potentials were in the range 1·5—1·9 V (*vs.* Ag–AgI). Rapid chemical reaction after initial electron transfer is indicated which confirms earlier results.[3]

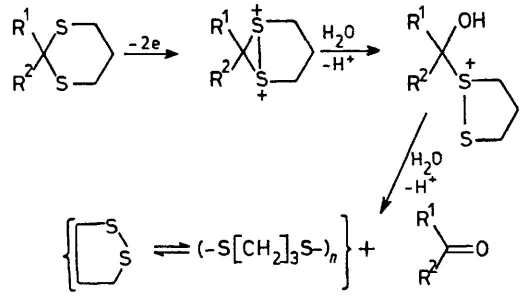
Preparative scale electrolyses were performed at controlled potential [1·5 V (*vs.* Ag–AgI)] and at controlled current (0·03 A $cm^{-2}$). Conventional H-cells were used with a platinum gauze anode; 0·2—7·0 g of dithian were electrolysed and electrolysis to 2 F $mol^{-1}$ took 2—6 h. Work-up was simple; the electrolyte was diluted with water and the carbonyl compound was extracted into methylene chloride. Details of reaction conditions and the results are summarised in the Table.

TABLE. Anodic removal of dithians

| Carbonyl compound | Electrolyte | Yield (%) |
|---|---|---|
| PhCHO | MeCN–$H_2O$ (10% v/v), $NaClO_4$ (0·1M) | 58[a] |
| PhCHO | MeCN–$Bu_4NClO_4$ (0·25M) | 60[a] |
| PhCHO | $CH_2Cl_2$–$Bu_4NClO_4$ (0·25M) | 60[a] |
| PhCHO[b] | MeCN–$H_2O$ (10% v/v), $NaClO_4$ (0·25M) | 77 |
| PhCHO[b] | HOAc–$H_2O$ (5% v/v), NaOAc (0·5M) | 35 |
| 4-$O_2N.C_6H_4$.CHO | MeCN–$H_2O$ (10% v/v), $NaClO_4$ (0·25M) | 45[c] |
| PhCOMe | MeCN–$H_2O$ (10% v/v), $NaClO_4$ (0·25M) | 66[a] |
| 4-$O_2N.C_6H_4$-.COMe | MeCN–$H_2O$ (10% v/v), $NaClO_4$ (0·25M) | 66 |
| 5-α-Cholestan-3-one[d] | MeCN–THF (1 : 1)–$H_2O$ (10% v/v), $LiClO_4$ (0·1M) | 51 |
| 5-α-Cholest-4-en-3-one[d] | MeCN–THF (1 : 1)–$H_2O$ (10% v/v), $LiClO_4$ (0·1M) | 52 |

[a] Isolated as the dinitrophenylhydrazone derivative; yields of the free carbonyl compound would be *ca.* 10% higher. [b] Electrolysis at constant current. [c] Starting material (dithian) recovered in 10% yield. [d] Periodic pulsing to 0 V used to maintain current. (THF=tetrahydrofuran).

Isolated yields of recovered carbonyl compounds are generally good and compare well with those obtained using chemical methods. No attempt has, as yet, been made to optimise yields. Dithiolans are not cleaved efficiently under these conditions. 2-Phenyl-1,3-dithiolan, at *ca.* 0·03 A $cm^{-2}$ in aqueous acetonitrile, gave only 5% benzaldehyde.



SCHEME

The probable mechanism, summarised in the Scheme, is similar to that proposed by Simonet *et al.*[3,5] for *gem*-disulphides. It accounts for: (i) the required potentials being similar to those for oxidation at sulphur in comparable conditions[6] [*cf.* $(PhCH_2)_2S$, $E_p$ 1·48 V (Ag–$Ag^+$)]; (ii) the consumption of 2 F $mol^{-1}$; (iii) the specificity to dithians, and (iv) the formation of significant amounts of 1,2-dithiolan and a solid with the reported[7] properties of $(-S[CH_2]_3S-)_n$.

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