Anodic Oxidation of Vinyl Sulphides. A Convenient Synthesis of α-Thiolated Aldehydes

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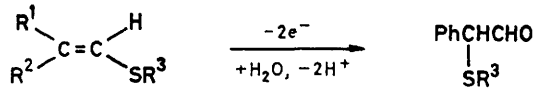
Summary Anodic oxidation of vinyl sulphides in aqueous acetonitrile gives α-thiolated aldehydes in good yields.

α-THIOLATED aldehydes are valuable building blocks in organic synthesis, and many synthetic methods for these compounds have been developed.[1] All the methods, however, involve several steps or else require the use of reactive sulphenylating reagents under delicate conditions. We now report a new convenient electrochemical synthesis of α-thiolated aldehydes (**2**)† from vinyl sulphides (**1**).‡



(**1**) (**2**)

a; R^1 = H, R^2 = Ph, R^3 = *p*-Bu^{t}C$_6$H$_4$
b; R^1 = Ph, R^2 = H, R^3 = *p*-MeC$_6$H$_4$
c; R^1 = H, R^2 = Ph, R^3 = *p*-MeC$_6$H$_4$
d; R^1 = Ph, R^2 = H, R^3 = Ph
e; R^1 = H, R^2 = Ph, R^3 = Bu^n
f; R^1 = Ph, R^2 = H, R^3 = *p*-ClC$_6$H$_4$

On single-sweep cyclic voltammetry in acetonitrile containing 2% water and 0·2 M sodium perchlorate at 25 °C, the first anodic peak of the compounds (**1**) was irreversible. Peak potentials were as follows (platinum disc electrode, sweep rate 100 mV s^{-1}): (**1a**), 1·15; (**1b**), 1·10; (**1c**), 1·22; (**1d**), 1·12; (**1e**), 1·15; and (**1f**), 1·27 V *vs.* S.C.E. (standard calomel electrode). Controlled-potential electrolysis of the compounds (**1**) was carried out in the same solvent–electrolyte system as used in the cyclic voltammetry experiments at 1·20 or 1·30 V *vs.* S.C.E. at a platinum plate electrode in a divided cell. A coulometric *n*-value of *ca.* 2 F mol^{-1} was obtained in every case (Table).

TABLE. Results of controlled-potential electrolysis of the vinyl sulphides (**1**).

Substrate[a] conc./mM	Applied potential[b]	Coulometric *n*-value/F mol^{-1}	Products and yields/%[c]
(**1a**)(12·0)	1·20	2·00	(**2a**)(62)
(**1b**)(14·6)	1·20	1·95	(**2b**)(93)
(**1c**)(18·7)	1·20	2·00	(**2b**)(93)
(**1d**)(18·9)	1·20	2·00	(**2d**)(88)
(**1e**)(20·0)	1·20	2·00	(**2e**)(50)
(**1f**)(12·4)	1·30	1·96	(**2f**)(89)

[a] Electrolyses were performed with 25 ml of aqueous acetonitrile at 25 °C. [b] V *vs.* S.C.E. [c] Yields were determined by g.l.c.

The electrolysed solution was concentrated *in vacuo*§ and extracted with chloroform. α-Thiolated aldehydes (**2**) were obtained in good yields by appropriate treatment of the chloroform layer. This is a promising method for the synthesis of the α-thiolated aldehydes of type (**2**) because of the mild reaction conditions, simple manipulation, and the good yields.

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† All products were satisfactorily characterized by ^{1}H n.m.r., i.r., and mass spectroscopy and elemental analyses.

‡ The compounds were prepared according to literature methods.[2] Compound (**1a**) was prepared according to the method used for (**1b**), m.p. 89·5 °C.

§ The use of $NaClO_4$ has proved safe during concentration but an Et_4NBF_4 supporting electrolyte may also be used to avoid any possibility of explosion.

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