

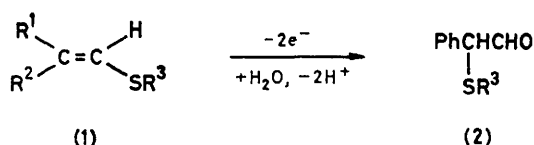
Anodic Oxidation of Vinyl Sulphides. A Convenient Synthesis of α -Thiolated Aldehydes

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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).[‡]



- a**; R¹ = H, R² = Ph, R³ = *p*-Bu^tC₆H₄
b; R¹ = Ph, R² = H, R³ = *p*-MeC₆H₄
c; R¹ = H, R² = Ph, R³ = *p*-MeC₆H₄
d; R¹ = Ph, R² = H, R³ = Ph
e; R¹ = H, R² = Ph, R³ = Buⁿ
f; R¹ = Ph, R² = H, R³ = *p*-ClC₆H₄

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 <i>n</i> -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 ¹H 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 NaClO₄ has proved safe during concentration but an Et₄NBF₄ supporting electrolyte may also be used to avoid any possibility of explosion.

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