Anodic Acetamidosulphenylation of Alkenes†

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Summary Anodic oxidation of disulphides in acetonitrile in the presence of an alkene gives acetamidosulphides.

TROST *et al.*[1] have recently described the oxidation of disulphides by lead(IV) in trifluoroacetic acid to give intermediates capable of reaction with alkenes. The result is an effective route from an alkene to a vicinal hydroxysulphide.

We now report the anodic oxidation of disulphides in acetonitrile, which permits the transformation of an alkene to a vicinal acetamidosulphide.

Little is known concerning the electrochemistry of disulphides beyond a report[2] on cyclic voltammetry suggesting irreversible anodic oxidation of simple diaryl disulphides. We find that in acetonitrile a single irreversible oxidation wave ($E_{p/2}$ + 1·34 V *vs.* Ag/0·01 M Ag$^+$ reference electrode; sweep rate 0·1 V/s) is obtained for diphenyl disulphide. Similarly dimethyl disulphide shows an irreversible wave at $E_{p/2}$ + 1·11 V. On the reverse cathodic sweep no reduction wave is observed for diphenyl disulphide but dimethyl disulphide gives a reduction wave

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† No reprints available.

at + 0·35 V. The height of this reduction wave is progressively diminished by addition of an alkene (*e.g.* cyclohexene). Even at high sweep speeds (100 V/s) there is no evidence of stable cation radical formation but these results suggest the interception of an anodically generated intermediate by the alkene (see Scheme). This is consistent with earlier cyclic voltammetry results[2] in acetonitrile and the view[1] that, in trifluoroacetic acid, addition to alkenes proceeds with intermediacy of an electrophilic species RS^+.

$$\mathrm{RSSR} \xrightarrow{\text{Anode}} \mathrm{RSSR}^{\cdot+}$$

$$\mathrm{RSSR}^{\cdot+} \xrightarrow{\text{MeCN}} \mathrm{RS{-}N{=}C^{+}Me}$$

$$\mathrm{RS{-}N{=}C^{+}Me} \xrightarrow{\text{Alkene}} \text{Products}$$

SCHEME

Alkene	Disulphide[a]	Products[b]	Yield/%[c]
Cyclopentene	PhSSPh	*trans*-2-Acetamido-1-phenylthiocyclopentane	56
Cyclohexene	PhSSPh	*trans*-2-Acetamido-1-phenylthiocyclohexane	50
Cyclohexene	MeSSMe	*trans*-2-Acetamido-1-methylthiocyclohexane	58
Hex-1-ene	PhSSPh	2-Acetamido-1-phenylthiohexane	57
Hex-1-ene	MeSSMe	2-Acetamido-1-methylthiohexane	30[d]
Oct-1-ene	PhSSPh	2-Acetamido-1-phenylthio-octane	84
Oct-1-ene	MeSSMe	2-Acetamido-1-methylthio-octane	52
Oct-2-ene	PhSSPh	2-Acetamido-3-phenylthio-octane	34[e]
		3-Acetamido-2-phenylthio-octane	50[e]
Oct-2-ene	MeSSMe	2-Acetamido-3-methylthio-octane	52[e]
		3-Acetamido-2-methylthio-octane	43[e]

[a] PhSSPh was electrolysed at +1·40 V *vs.* Ag/0·01 M Ag^+ reference electrode, MeSSMe was electrolysed at +1·20 V *vs.* Ag/0·01 M Ag^+ electrode. [b] Products identified by i.r., n.m.r., and m.s. analysis. [c] Yields of isolated products unless otherwise stated. [d] Yield determined by g.l.c. analysis. [e] Isomer ratio determined by g.l.c.

Preparative electrolyses in acetonitrile using a three-compartment cell are reported in the Table. Using a platinum foil anode and Bu_4NBF_4 as supporting electrolyte, 2 C equiv./mol of disulphide were passed and the anolyte was quenched with water. Products were isolated by extraction and yields are reported for the crystalline materials. The following points are particularly noteworthy. (i) Vicinal addition to alkenes giving adducts having nitrogen and sulphur functionalities is possible using electrochemical methods. Such additions, in contrast to hydroxysulphenylation, have not been achieved using inorganic oxidants. Whereas introduction of oxygen functionality is possible using either electrochemical methods or inorganic oxidants, use of acetonitrile to introduce nitrogen functionality effectively requires electrochemical methods. (ii) Addition to cyclic olefins proceeds stereoselectively to give the *trans*-acetamidosulphide. (iii) Addition to terminal olefins is highly regioselective. Under typical conditions the terminal sulphide is the sole isolated product. (iv) Mixtures of regioisomers are obtained by addition to the non-terminal alkene, oct-2-ene.

The method offers an easy procedure for the preparation of compounds having vicinal substitution of nitrogen and sulphur. The difficulty of achieving such substitution is highlighted by the multi-step synthesis required for production of penicillamine. Extension of the above method to substituted olefins and to the generation of electrophilic species of elements other than sulphur is continuing.

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[1] B. M. Trost, M. Ochiai, and P. G. McDougal, *J. Amer. Chem. Soc.*, 1978, **100**, 7103.
[2] G. Bontempelli, F. Magno, and G. A. Mazzachin, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1973, **42**, 57.