Anodic Acetamidosulphenylation of Alkenes *via* Anodic Oxidation of Disulphides

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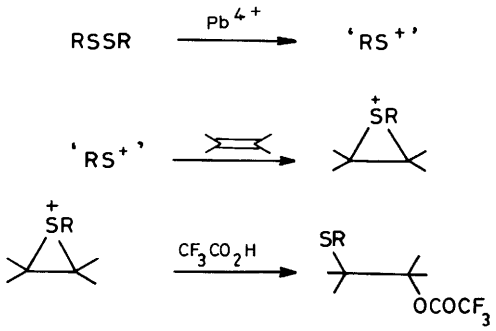
Anodic oxidation, at platinum and carbon electrodes, of dimethyl, diphenyl, dibenzyl, and heterocyclic disulphides in acetonitrile in the presence of alkenes affords products of acetamidosulphenylation. With cyclic alkenes a high selectivity for *trans*-addition is observed. With terminal alkenes the terminal sulphides are formed with high regioselectivity. The mechanism of addition is discussed in the light of product and electroanalytical studies.

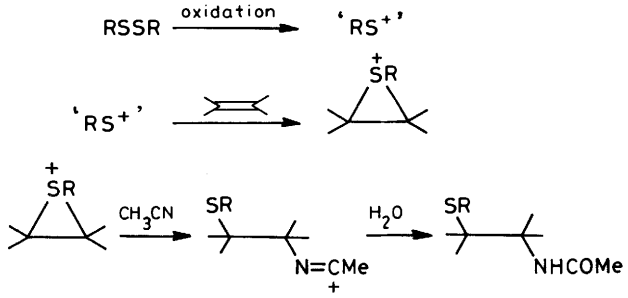
The lead(IV) oxidation of diaryl disulphides leads to efficient methods[1] of hydroxysulphenylation of alkenes. In spite of the potential importance of vicinally substituted aminosulphides there is a paucity of methods of azasulphenylation of alkenes. At the outset of our studies[2] our attention was directed to a possible electrochemical oxidation of disulphides in acetonitrile to give, directly, products of acetamidosulphenylation from alkenes. We report in this paper electrochemical procedures giving, directly, vicinally substituted amidosulphides from alkenes. In the following papers[3,4] we describe non-electrochemical methods which extend the scope of metal-ion oxidations of a range of organic disulphides permitting elaboration of alkenes to give both amidosulphides and other vicinally substituted products.

Although the detail of the mechanism of lead(IV) oxidation of disulphides[1] in trifluoroacetic acid leading to products of hydroxysulphenylation from alkenes has not been fully clarified an electrophilic attack on the alkene possibly gives an episulphonium ion (Scheme 1). In trifluoroacetic acid the episulphonium ion would give, as initially isolated products, the vicinally substituted trifluoroacetoxysulphides. A similar scheme (Scheme 2) proceeding by metal-ion oxidation of a disulphide leading in acetonitrile to an acetamidosulphide has not been achieved. This failure can be attributed to the general difficulty of oxidizing organic substrates by inorganic oxidants, and in particular lead(IV) salts in acetonitrile. There is precedent for avoiding this problem in acetonitrile by replacing the inorganic oxidant with an electrochemical method of oxidation. Thus metal-ion oxidation of saturated hydrocarbons by lead(IV) salts in trifluoroacetic acid[5] can proceed efficiently to give ester products but the method of choice for conversion of saturated hydrocarbons into amides[6] is electrochemical oxidation in acetonitrile.

The feasibility of such an electrochemical acetamidosulphenylation is supported by a number of earlier studies. The anodic oxidation of diphenyl disulphide has been studied[7] and both product and electroanalytical studies establish initial formation of 'PhS$^+$' or the solvated complex in acetonitrile. In recent, more detailed studies using *in situ* modulated specular reflectance spectroscopy[8] we have confirmed this conclusion and extended the method to other disulphides, thus indicating the typical anodic behaviour of organic disulphides. The later stages in Scheme 2 have good precedent. Studies[9] indicate that sulphenyl halides in the presence of silver salts, *e.g.* $AgBF_4$ and $AgSbF_6$, add to alkenes in acetonitrile. The products of acetamidosulphenylation are formed *via* episulphonium ions. In further important synthetic studies[10] describing the formation of vicinally substituted products by reaction of dimethyl(methylthio)sulphonium tetrafluoroborate with nitrogen nucleophiles in the presence of alkenes the intermediacy of episulphonium ion intermediates is probable. Episulphonium



Scheme 1.



Scheme 2.

ions are likely intermediates in related reactions,[11] for example, the formation of vicinally substituted trifluoroacetoxysulphides by reaction of alkenes with thiol sulphinates and trifluoroacetic anhydride, or in reaction of alkenes with the *p*-nitrosulphenium ion in trifluoroacetic acid, and similarly in the addition of chloramine T–organic disulphide reagents[12] to alkenes in acetonitrile to give vicinally substituted products. Therefore good precedent exists for each of the steps in the proposed Scheme 2.

Initial experiments were made with diphenyl disulphide using a divided cell with both a platinum anode and cathode. Electrolyses were conducted in acetonitrile using tetra-n-butylammonium tetrafluoroborate as electrolyte. In a typical experiment in the presence of excess of cyclohexene in the anolyte, oxidation at 1.3 V was effected with passage of 2 equivalents of charge (relative to disulphide) and then products were isolated following chromatography. Later experiments with ranges of different disulphides and of alkenes were conducted under similar conditions but the use of graphite or Papyex (carbon paper) as anode material was sometimes advantageous. Results are summarized in the Table.

Table. Anodic addition of disulphides to alkenes in acetonitrile

Disulphide	Alkene	Electrode	Anode Potential[a] (V)	Product	Yield[b] (%)
Diphenyl	Cyclohexene	Pt	1.3	(1)	87
Diphenyl	Cyclohexene	Papyex	1.3	(1)	151
Diphenyl	Oct-1-ene	Pt	1.4	(6)	84
Diphenyl	*trans*-Oct-2-ene	Pt	1.4	(11) and (12)	90[c]
Diphenyl	Ethene	Pt	1.3	(15)	129
Dimethyl	Cyclohexene	Pt	1.2	(2)	58
Dimethyl	Oct-1-ene	Pt	1.2	(8)	52
Dimethyl	*trans*-Oct-2-ene	Pt	1.2	(13 and (14)	91[d]
Dibenzyl	Cyclohexene	Pt	1.3	(3)	112
Dibenzyl	Cyclohexene	Papyex	1.4	(3)	101
Dibenzyl	Ethene	Pt or Papyex	1.4	(16)	0
Dibenzyl	Oct-1-ene	Pt	1.3	(9)	17
Dibenzyl	Oct-1-ene	Papyex	1.4	(9)	16
2,2′-Dipyridyl	Cyclohexene	Pt	1.4	(4)	77
2,2′-Dipyridyl	Cyclohexene	Graphite	1.4	(4)	32
2,2′-Dipyridyl	Cyclohexene	Papyex	1.4	(4)	112
2,2′-Dipyridyl	Oct-1-ene	Pt	1.4	(10)	33
2,2′-Dipyridyl	Oct-1-ene	Papyex	1.4	(10)	61

[a] For conditions see Experimental section. [b] Yield with respect to 1 mol. equiv. of disulphide. [c] Two isomers obtained (ratio 3:2). [d] Two isomers obtained (ratio 1:1).

The major problems in structure assignment concerned the discrimination between possible stereoisomers in the addition to cyclohexene and between possible regioisomers in the addition to the aliphatic alkenes. Addition of diphenyl disulphide to cyclohexene gives the *trans*-acetamidosulphide (**1**). Signals in the ^{1}H n.m.r. spectrum of compound (**1**) at δ 3.00 and 3.80 are associated with the methine protons. The latter signal is coupled to the amide proton which is observed at δ 6.45. The *trans*-stereochemistry is clearly defined by observation of couplings of 10, 10, and 4 Hz for the methine proton at δ 3.00. This *trans*-assignment based on the ^{1}H n.m.r. spectrum is independently confirmed by comparison of the physical data of compound (**1**) obtained by the above electrochemical route with that of the known[13] acetamidosulphide (**1**) obtained *via* addition of thiophenol to the aziridine (**5**).

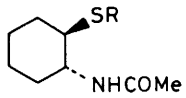
In an analogous manner dimethyl disulphide, dibenzyl disulphide, and 2,2′-dipyridyl disulphide added to cyclohexene to give the amides (**2**), (**3**), and (**4**) respectively. In each case the *trans* stereochemical assignment is based on observation of a 10 Hz coupling between the axial methine protons.

Addition of diphenyl disulphide to oct-1-ene might lead to the Markownikoff product (**6**) or to the regioisomer (**7**). Formation of compound (**6**) is established by observation of the coupling of the amide proton with the methine proton situated at δ 4.17, and is consistent with other features of the ^{1}H n.m.r. spectrum, and with the mass spectrum of compound (**6**).

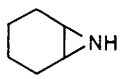
In an analogous manner dimethyl disulphide, dibenzyl disulphide, and 2,2′-dipyridyl disulphide added to oct-1-ene to give the amides (**8**), (**9**), and (**10**) respectively. In each case formation of the terminal sulphide is based on observation of the coupling between the methine proton and the amide proton.

Anodic addition of diphenyl disulphide or of dimethyl disulphide to *trans*-oct-2-ene gave mixtures of isomers. In both cases two isomers were formed in approximately the same amounts. As a result of this lack of selectivity the products were not fully characterized. However, g.c.–m.s. suggested the formation of pairs of regioisomers. With the assumptions that (i) additions were to *trans*-oct-2-ene (implying that addition to *cis*-oct-2-ene *via* an acid-catalysed equilibrium of *trans*-oct-2-ene was unimportant) and that (ii) these additions were by a *trans* attack, structures of products could be assigned. Diphenyl disulphide gives compound (**11**) and (**12**) and dimethyl disulphide gives compounds (**13**) and (**14**).

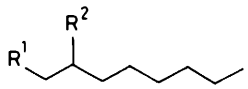
Although the acetamidosulphide (**15**) formed by anodic addition of diphenyl disulphide to ethene could be identified unambiguously by spectroscopy, further support for the structure was obtained. Acid-catalysed reaction of 2-methyloxazoline with thiophenol afforded the acetamidosulphide (**15**) directly.



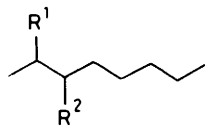
(**1**) R = Ph
(**2**) R = Me
(**3**) R = CH_2Ph
(**4**) R = 2-C_5H_4N



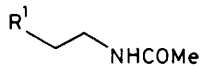
(**5**)



(**6**) R^1 = SPh , R^2 = NHCOMe
(**7**) R^1 = NHCOMe , R^2 = SPh
(**8**) R^1 = SMe , R^2 = NHCOMe
(**9**) R^1 = SCH_2Ph , R^2 = NHCOMe
(**10**) R^1 = 2-C_5H_4N, R^2 = NHCOMe



(**11**) R^1 = SPh , R^2 = NHCOMe
(**12**) R^1 = NHCOMe , R^2 = SPh
(**13**) R^1 = SMe , R^2 = NHCOMe
(**14**) R^1 = NHCOMe , R^2 = SMe



(**15**) R^1 = SPh
(**16**) R^1 = SCH_2Ph

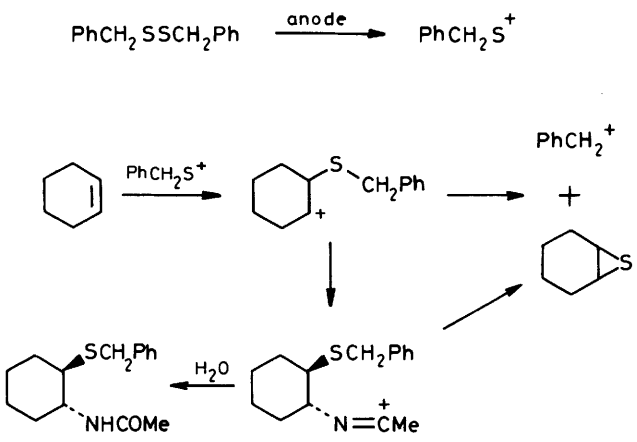
The observed stereo- and regio-selectivity of the above additions are consistent with earlier studies. In previous examples of electrophilic additions to alkenes formation of an episulphonium ion[9] leads, by subsequent attack of acetonitrile, to *trans*-substituted products. The factor controlling this formation of a *trans* product is the preference for back-side attack by the solvent acetonitrile on the episulphonium ion. It is interesting to note that where this control is absent [for example[14] in protioacetamidation of alkenes (the Ritter reaction)] electrophilic additions to alkenes in acetonitrile can occur *via cis*-addition. Our observed *trans*-addition suggests the intermediacy of an episulphonium ion.

The opening of an episulphonium ion by back-side attack of acetonitrile can, in general, give pairs of regioisomers. With terminal alkenes, acetonitrile behaving as a small nucleophile might be expected to attack at the more hindered site leading to a terminal sulphide by an over-all Markownikoff addition. In contrast a bulky nucleophile might attack the episulphonium ion derived from a terminal alkene at the less hindered terminal site to give a non-terminal sulphide. Examples[12] of preferential attack by the incoming nucleophile at the terminal site are known. However, under very polar conditions, preferential or exclusive attack by a small nucleophile at the non-terminal site is well known.[9] Under the conditions of electrolysis with high concentrations of electrolyte the observed regiospecificity is determined by the quenching with water of the nitrilium ions present in the anolyte. Exclusive formation of the terminal sulphide indicates either a kinetic preference for formation of the non-terminal nitrilium ion by attack by acetonitrile at the more hindered site, which has good precedent, or possibly that in equilibration of the two possible nitrilium ions *via* the episulphonium ion the non-terminal nitrilium ion is thermodynamically favoured. Such isomerization[15] of two nitrilium ions *via* carbenium ion intermediates again has a precedent. Although we are unable at this stage to distinguish clearly between the possible origins of the observed regiospecificity we favour a kinetic preference for formation of the non-terminal nitrilium ion.

The observed specificity parallels that generally observed in opening of epoxides[16] and episulphides[17] under acid conditions, and of episelenonium ions,[18] in acetonitrile. In each of these cases attack of the incoming nucleophile at the more substituted site of derivatives of terminal alkenes gives the major or exclusive product.

From the results presented in the Table and in the Experimental section, three major points need further discussion: (i) the relative behaviour of the different disulphides, (ii) the influence of the nature of the anode material, and (iii) the consequence of the presence of traces of water or of added acid to the course of the electrolysis.

Diphenyl disulphide undergoes efficient oxidative addition even to the poorly nucleophilic ethene. However, dibenzyl disulphide not only gives a markedly lower yield of an acetamidosulphide on addition to oct-1-ene but fails to add to ethene to give the expected product (**16**). Even in the oxidative addition of dibenzyl disulphide to cyclohexene the yield of isolated products depends critically upon the precise conditions of electrolysis. In 'dry' acetonitrile without deliberate addition of water no acetamidosulphide (**3**) could be isolated. Instead benzylacetamide was recovered. Satisfactory yields of compound (**3**) were obtained when traces of water and trifluoroacetic acid were added to the anolyte. Similarly the yield of the acetamidosulphide (**15**) obtained by addition of diphenyl disulphide to ethene was markedly influenced by addition of small quantities of trifluoroacetic acid (see Experimental section for yields). As the yield of compound (**15**) is also enhanced by addition of small quantities of sulphuric acid this effect is attributed to the increased acidity of the reaction



Scheme 3.

medium. The explanation of this acidity effect and the role of added water are less clear. Support for the view that water traps the initially formed nitrilium ion to give directly an acetamidosulphide in the course of electrolysis comes from the behaviour of dibenzyl disulphide. The possibility of a competitive fragmentation to give an episulphide and the benzyl cation is shown in Scheme 3. We observe formation of benzylacetamide but are unable to isolate either the episulphide or products derived from it. A similar fragmentation would not be expected, and is not observed, with the other disulphides.

With 2,2′-dipyridyl disulphide extensive electrode fouling is observed on platinum. The use of Papyex electrodes (a sheet form of crystallized graphite manufactured by Le Carbone Ltd) reduced such fouling and permitted higher cell currents to be maintained and the isolation of products in higher yields. The convenience, relatively low cost, and high surface area of Papyex suggest it may have considerable potential as an electrode material in organic electrochemistry.

The results in the Table establish that electrochemical acetamidosulphenylation of alkenes is applicable to aliphatic and to aromatic disulphides. The resulting structural unit $-S-\overset{|}{C}-\overset{|}{C}-N<$ occurs in cimetidine and related anti-ulcer drugs.[19] The potential for synthesis of such varied structures is indicated by the ability to add dibenzyl disulphide to alkenes, which by removal of the protecting groups constitutes a formal synthesis of vicinal aminothiols from alkenes. The rather complicated dependence of yields on added acid and added water suggests that the yields reported in the Table can be improved by further studies.

Experimental

Cyclic voltammetry of disulphides and of alkenes was carried out in cells that have been described previously.[6] For preparative electrolyses a three-compartment cell with a fine frit (No. 4) dividing the anolyte and catholyte compartments was used. The apparatus was carefully dried before use. The working electrode was platinum gauze (area 2 cm^2), which occasionally required flaming, graphite (area *ca.* 3 cm^2) which required rubbing with emery paper to give an effective clean surface, or Papyex (Le Carbone Ltd). Platinum gauze (area 2 cm^2) was used for the counter electrode and the reference electrode [a silver wire in a solution of silver tetrafluoroborate in acetonitrile (0.01M)] was separated from the working electrode by a carefully positioned Luggin capillary. All electrolyses were conducted in acetonitrile (Fisons h.p.l.c. far-U.V. grade) using carefully dried Bu_4NBF_4 (0.1M solution) as support electrolyte. The cell was driven by a

Hi-Tek instruments potentiostat type DT 2101. Background currents in the working range (+1.0 to +1.5 V) were low (<400 μA) in the absence of added disulphides. Preparative t.l.c. (p.l.c.) was carried out on plates (20 × 20 cm) of silica gel (Merck Kieselgel type 60) using ether as eluant unless otherwise stated. Gas liquid chromatography (g.l.c.) was carried out on a Celite column (2 m) with OV 1 (5%) as stationary phase at 160 °C for products from dimethyl disulphide and 200 °C for products of diphenyl disulphide. Yields unless otherwise stated are based upon the disulphide consumed and are with respect to (w.r.t.) 1 mol. equiv. General experimental details are described elsewhere.[3]

Typical Procedure for Anodic Acetamidosulphenylation.—trans-1-*Acetamido*-2-*phenylthiocyclohexane* (**1**). Diphenyl disulphide (100 mg) and cyclohexene (1 ml) were dissolved in acetonitrile (15 ml) containing added electrolyte. Following electrolysis using a platinum anode with passage of 2 coulomb equiv. of charge per mole of disulphide after 18 h, the anolyte was poured into water and extracted with ether (3 × 20 ml). The combined extracts were washed with water, dried over magnesium sulphate, and filtered. Removal of solvent under reduced pressure afforded a yellow oil. Purification by p.l.c. afforded a white solid, which was further purified by recrystallization (dichloromethane–pentane) to give *trans*-1-acetamido-2-phenylthiocyclohexane (**1**) (100 mg, 87% w.r.t. diphenyl disulphide), m.p. 134—135 °C (lit.,[13] 135—137 °C) (Found: M^+, 249.1223. Calc. for $C_{14}H_{19}NOS$: M, 249.1220); m/z 249 (M^+, 2%) and 190 ($M - CH_3CONH_2$, 100); $\nu_{max.}$($CHCl_3$) 3 420, 3 000, 2 930, 1 660, 1 500, 1 430, 1 230, and 1 190 cm^{-1}; δ_H 1.0—2.5 (11 H, complex), 3.00 (1 H, dt, J 10, 10, and 4 Hz), 3.80 (1 H, m), 6.45 (1 H, br), and 7.25—7.5 (5 H, complex); δ_C 23.3 (CH_3), 24.5 (CH_2), 25.6 (CH_2), 32.9 (CH_2), 33.4 (CH_2), 51.4 (CH), 52.4 (CH), 127.1, 128.9, 132.8, and 134.2 (aromatic carbons), and 169.75 p.p.m. (CO).

In a further experiment diphenyl disulphide (148 mg) and cyclohexene (1 ml) were dissolved in acetonitrile (15 ml) containing added electrolyte. Oxidation at 1.3 V at a Papyex anode (area 6 cm^2) for 2.5 h with passage of 139 coulombs, followed by work-up by the above procedure, afforded a crude product. Column chromatography (eluant ether) gave *trans*-1-acetamido-2-phenylthiocyclohexane (**1**) (255 mg, 151% w.r.t. diphenyl disulphide).

trans-1-*Acetamido*-2-*methylthiocyclohexane* (**2**). Dimethyl disulphide (96 mg) and cyclohexene (405 mg) were electrolysed at 1.2 V at a platinum anode in acetonitrile (15 ml) containing added electrolyte with passage of 2 coulomb equiv. of charge per mole of disulphide. Work-up by the above procedure and p.l.c. afforded, as a pale oil, *trans*-1-acetamido-2-methylthiocyclohexane (**2**) (105 mg, 58% w.r.t. dimethyl disulphide), m/z 187 (M^+, 4%) and 128 ($M - CH_3CONH_2$, 100); $\nu_{max.}$(film) 3 280 and 1 650 cm^{-1}; δ_H 1.1—2.6 (14 H, complex), 3.22 (1 H, dt, J 10, 10, and 4 Hz), 3.70 (1 H, m), and 6.53 (1 H, br).

trans-1-*Acetamido*-2-*benzylthiocyclohexane* (**3**). Dibenzyl disulphide (1 g) and cyclohexene (5 ml) were electrolysed at 1.3 V at a platinum anode in acetonitrile (15 ml) containing added electrolyte and water (1 ml), with passage of 1 115 coulombs during 18 h. Work-up by the above procedure and column chromatography (eluant ether) afforded a crude product. Recrystallization (dichloromethane–pentane) gave trans-1-*acetamido*-2-*benzylthiocyclohexane* (**3**) (422 mg, 39.5% w.r.t. dibenzyl disulphide), m.p. 108—110 °C (Found: M^+, 263.1242. $C_{15}H_{21}NOS$ requires M, 263.1252); m/z 263 (M^+, 1%), 204 ($M - CH_3CONH_2$, 99), and 91 (100); $\nu_{max.}$($CHCl_3$) 3 420, 3 000, 2 930, 1 660, 1 510, 1 450, 1 230, and 1 200 cm^{-1}; δ_H 1.0—2.3 (11 H, complex), 2.40 (1 H, dt, J 10, 10, and 4 Hz), 3.74 (3 H, complex), 5.65 (1 H, br), and 7.2—7.4 (5 H, complex); δ_C 23.2 (CH_3), 24.3 (CH_2), 25.6 (CH_2), 33.1 (CH_2), 34.2 (CH_2), 48.5 (CH), 51.4 (CH), 126.8, 128.4, 128.8, and 138.6 (aromatic carbons), and 169.6 p.p.m. (CO). In a similar experiment oxidation of dibenzyl disulphide (100 mg) at 1.4 V at a platinum anode in the absence of added water but in the presence of cyclohexene (1 ml) and trifluoroacetic acid (0.1 ml) gave, after 4 h, the amide (**3**) (120 mg, 112% w.r.t. dibenzyl disulphide).

In a further experiment dibenzyl disulphide (137 mg) and cyclohexene (1 ml) were dissolved in acetonitrile containing added electrolyte. Oxidation at 1.4 V at a Papyex anode (area 6 cm^2) for 2 h with passage of 116 coulombs, followed by work-up by the above procedure, afforded a crude product. Column chromatography (eluant ether) gave *trans*-1-acetamido-2-benzylthiocyclohexane (**3**) (147 mg, 100.5% w.r.t. dibenzyl disulphide).

trans-1-*Acetamido*-2-(2-*pyridylthio*)*cyclohexane* (**4**). 2,2′-Dipyridyl disulphide (Aldrithiol-2) (562 mg) and cyclohexene (5 ml) were electrolysed at 1.4 V at a platinum gauze anode (area 50 cm^2) in acetonitrile (50 ml) containing added electrolyte with passage of 491 coulombs during 6 h. Work-up by the above procedure and column chromatography (alumina, eluant ether) afforded, as a pale yellow oil, trans-1-*acetamido*-2-(2-*pyridylthio*)*cyclohexane* (**4**) (490 mg, 77% w.r.t. Aldrithiol-2) (Found: M^+, 250.1138. $C_{13}H_{18}N_2OS$ requires M, 250.1138); m/z 250 (M^+, 19%), 191 ($M - CH_3CONH_2$, 65), and 162 (100); $\nu_{max.}$(film) 3 260, 2 960, 1 650, 1 580, 1 540, 1 460, and 1 420 cm^{-1}; δ_H 1.0—2.2 (11 H, complex), 2.35 (1 H, dt, J 10, 10, and 4 Hz), 3.68 (1 H, m), and 7.2—8.5 (4 H, complex). Similarly 2,2′-dipyridyl disulphide (125 mg) and cyclohexene (1 ml) were electrolysed at a graphite anode at 1.4 V and, after passage of 109 coulombs during 1.5 h, work-up and p.l.c. (alumina, eluant ether) afforded *trans*-1-acetamido-2-(2-pyridylthio)cyclohexane (**4**) (45 mg, 32% w.r.t. Aldrithiol-2).

In a further experiment 2,2′-dipyridyl disulphide (112 mg) and cyclohexene (1 ml) were electrolysed at a Papyex anode at 1.4 V and, after passage of 99 coulombs during 1.5 h, work-up and column chromatography (alumina, eluant ether) afforded *trans*-1-acetamido-2-(2-pyridylthio)cyclohexane (**4**) (42 mg, 34% w.r.t. Aldrithiol-2). Similarly 2,2′-dipyridyl disulphide (138 mg) and cyclohexene (1 ml) were electrolysed at a Papyex anode at 1.4 V and, after passage of 182 coulombs during 2.5 h, the above procedure afforded *trans*-1-acetamido-2-(2-pyridylthio)cyclohexane (**4**) (176 mg, 112% w.r.t. Aldrithiol-2). Similarly 2,2′-dipyridyl disulphide (111 mg) and cyclohexene (1 ml) were electrolysed at a Papyex anode at 1.4 V and, after passage of 195 coulombs during 5 h, the above procedure afforded *trans*-1-acetamido-2-(2-pyridylthio)cyclohexane (**4**) (126 mg, 100% w.r.t. Aldrithiol-2).

2-*Acetamido*-1-*phenylthio-octane* (**6**). Diphenyl disulphide (250 mg) and oct-1-ene (430 mg) were electrolysed at 1.4 V at a platinum anode in acetonitrile (15 ml) containing added electrolyte with passage of 2 coulomb equiv. of charge per mole of disulphide. Work-up by the above procedure and p.l.c. afforded a white solid. Recrystallization from dichloromethane–pentane gave 2-*acetamido*-1-*phenylthio-octane* (**6**) (230 mg, 84% w.r.t. diphenyl disulphide), m.p. 60—61 °C (Found: C, 68.4; H, 9.1; N, 5.0. $C_{16}H_{25}NOS$ requires C, 68.8; H, 9.0; N, 5.0%); m/z 279 (M^+, 3%), 220 (66), 156 (16), 123 (15), and 114 (100); $\nu_{max.}$($CHCl_3$) 3 280 and 1 640 cm^{-1}; δ_H 0.89 (3 H, t), 1.1—1.5 (10 H, complex), 1.93 (3 H, s), 3.12 (2 H, d, J 5 Hz), 4.17 (1 H, dt, J 7, 5, and 5 Hz), 6.33 (1 H, br, NH), and 7.2—7.5 (5 H, complex); δ_C 14.1 (CH_3), 22.6 (CH_2), 23.1 (CH_2), 26.0 (CH_2), 29.1 (CH_2), 31.7 (CH_2), 33.4 (CH_2), 38.5 (CH_2), 49.1 (CH), 126.1, 129.0, 129.3, and 136.6 (aromatic carbons), and 170.0 p.p.m. (CO).

2-*Acetamido*-1-*methylthio-octane* (**8**). Dimethyl disulphide (96 mg) and oct-1-ene (358 mg) were electrolysed at 1.2 V at a platinum anode in acetonitrile (15 ml) containing added electrolyte with passage of 2 coulomb equiv. of charge per mole of disulphide. Work-up by the above procedure and p.l.c.

afforded, as a pale oil, 2-acetamido-1-methylthio-octane (**8**) (106 mg, 52% w.r.t. dimethyl disulphide), *m/z* 189 (M^+, 5%), 130 ($M - CH_3CONH_2$, 37), and 86 (100); $\nu_{max.}$(film) 3 290 and 1 645 cm^{-1}; δ_H 0.8—2.2 (15 H, complex), 2.64 (2 H, d, *J* 6 Hz), 4.10 (1 H, m), and 5.85 (1 H, br).

2-Acetamido-1-benzylthio-octane (**9**). Dibenzyl disulphide (123 mg) and oct-1-ene (1 ml) were electrolysed at 1.3 V at a platinum anode in acetonitrile (15 ml) containing added electrolyte and water (0.1 ml) with passage of 123 coulombs during 2 h. Work-up by the above procedure and p.l.c. afforded a crude product. Recrystallization (dichloromethane–pentane) gave *2-acetamido-1-benzylthio-octane* (**9**) (25 mg, 17% w.r.t. dibenzyl disulphide), m.p. 60.5—61.5 °C (Found: C, 69.7; H, 9.5; N, 4.9. $C_{17}H_{27}NOS$ requires C, 69.6; H, 9.3; N, 4.8%); *m/z* 233 ($M - CH_3CONH_2$, 13%) and 91 (100); $\nu_{max.}$($CHCl_3$) 3 280, 2 940, 2 920, 2 840, 1 650, 1 540, 1 450, 1 370, 1 280, 1 230, and 1 020 cm^{-1}; δ_H 0.88 (3 H, t), 1.0—1.7 (10 H, complex), 1.94 (3 H, s), 2.54 (2 H, d, *J* 7 Hz), 3.74 (2 H, s), 4.10 (1 H, m), 6.53 (1 H, br), and 7.2—7.4 (5 H, complex); δ_C 14.1 (CH_3), 22.6 (CH_3), 29.1 (CH_2), 31.7 (CH_2), 33.9 (CH_2), 35.0 (CH_2), 36.6 (CH_2), 42.8 (CH_2), 45.4 (CH_2), 48.4 (CH), 128.5, 129.0, 138.5, and 138.7 (aromatic carbons), and 170.0 p.p.m. (CO).

Similarly dibenzyl disulphide (123 mg) and oct-1-ene (1 ml) were electrolysed at a Papyex electrode at 1.3 V and, after passage of 128 coulombs during 3 h, work-up and column chromatography (eluant ether) afforded 2-acetamido-1-benzylthio-octane (**9**) (23 mg, 16% w.r.t. dibenzyl disulphide).

2-Acetamido-1-(2-pyridylthio)octane (**10**). 2,2′-Dipyridyl disulphide (Aldrithiol-2) (104 mg) and oct-1-ene (1 ml) were electrolysed at 1.4 V at a platinum anode in acetonitrile (15 ml) containing added electrolyte during 18 h. Work-up by the above procedure and p.l.c. (alumina, eluant ether) afforded, as a pale yellow oil, 2-acetamido-1-(2-pyridylthio)octane (**10**) (44 mg, 33% w.r.t. Aldrithiol-2) (Found: M^+, 280.1617. $C_{15}H_{24}N_2OS$ requires *M*, 280.1616); *m/z* 280 (M^+, 2%), 221 ($M - CH_3CONH_2$, 8), and 125 (100); $\nu_{max.}$(film) 3 270, 2 940, 2 910, 2 840, 1 720, 1 650, 1 580, 1 550, 1 450, 1 415, 1 370, and 1 270 cm^{-1}; δ_H 0.8—2.2 (16 H, complex), 3.42 (2 H, d, *J* 8 Hz), 4.2 (1 H, m), and 7.2—8.5 (4 H, complex).

Similarly 2,2′-dipyridyl disulphide (124 mg) and oct-1-ene (1 ml) were electrolysed at a Papyex anode at 1.4 V and, after passage of 98 coulombs during 2 h, work-up and column chromatography (alumina, eluant ether) afforded 2-acetamido-1-(2-pyridylthio)octane (**10**) (78 mg, 51% w.r.t. Aldrithiol-2). Similarly 2,2′-dipyridyl disulphide (106 mg) and oct-1-ene (1 ml) were electrolysed at a Papyex anode at 1.4 V and, after passage of 177 coulombs during 6 h, work-up and column chromatography afforded 2-acetamido-1-(2-pyridylthio)octane (**10**) (82 mg, 61% w.r.t. Aldrithiol-2).

Anodic addition of diphenyl disulphide to trans-*2-octene*. Diphenyl disulphide (300 mg) and *trans*-oct-2-ene (1.44 g) were electrolysed at 1.4 V at a platinum anode in acetonitrile (15 ml) containing added electrolyte with passage of 2 coulomb equiv. of charge per mole of disulphide. Work-up by the above procedure and p.l.c. afforded an oil (321 mg), $\nu_{max.}$(film) 3 300 and 1 650 cm^{-1}; δ_H 0.8—2.1 (17 H, complex), 3.24 (0.4 H, m), 3.50 (0.6 H, m), 4.2 (1 H, br), 5.9 (1 H, br), and 7.2—7.6 (5 H, complex). Analysis (g.l.c.) of the oil showed two peaks (ratio 40:60). Analysis by g.l.c.–m.s. suggested the minor component, having the lower retention time, to be 2-acetamido-3-phenylthio-octane (**12**), *m/z* 279 (M^+, 3%), 220 ($M - CH_3CONH_2$, 50), 193 ($M - CH_3CHNHCOCH_3$, 16), 86 ($CH_3CHNHCOCH_3$, 37), and 44 (100), and the major component, having the higher retention time, to be 3-acetamido-2-phenylthio-octane (**11**), *m/z* 279 (M^+, 2%), 220 ($M - CH_3CONH_2$, 31), 142 ($M - CH_3CHSPh$, 22), 137 (CH_3CHSPh, 8), and 100 (100).

Anodic addition of dimethyldisulphide to trans-*oct-2-ene*. Dimethyl disulphide (96 mg) and *trans*-oct-2-ene (360 mg) were electrolysed in acetonitrile at 1.2 V at a platinum anode in acetonitrile (15 ml) containing added electrolyte with passage of 1.5 coulomb equiv. of charge per mole of disulphide. Work-up by the above procedure and p.l.c. afforded an oil (186 mg), $\nu_{max.}$(film) 3 290 and 1 650 cm^{-1}; δ_H 0.7—2.15 (20 H, complex).

Analysis (g.l.c.) of the oil showed two peaks (ratio 55:45). Analysis by g.l.c.–m.s. suggested the major component, having the lower retention time, to be 3-acetamido-2-methylthio-octane (**13**), *m/z* 217 (M^+, 1%), 158 ($M - CH_3CONH_2$, 32), 142 ($M - CH_3CHSMe$, 23), and 100 (100), and the minor component, having the higher retention time, to be 2-acetamido-3-methylthio-octane (**14**), *m/z* 217 (M^+, 1%), 158 ($M - CH_3CONH_2$, 82), 131 ($M - CH_3CHNHCOCH_3$, 37), 86 ($CH_3CHNHCOCH_3$, 88), and 44 (100).

1-Acetamido-2-phenylthioethane (**15**). Diphenyl disulphide (1 g) was electrolysed at 1.3 V at a platinum anode (area 50 cm^2) in acetonitrile (50 ml) containing added electrolyte and trifluoroacetic acid (2.1 g). During a period of 4 h, 892 coulombs were passed and ethene was bubbled continuously through the anode compartment. Work-up by the above procedure and column chromatography (eluant ether) afforded a white solid. Recrystallization from dichloromethane–pentane gave 1-acetamido-2-phenylthioethane (**15**) (780 mg, 87% w.r.t. diphenyl disulphide), m.p. 88—89 °C (Found: C, 61.6; H, 6.7; N, 7.2; S, 16.7. $C_{10}H_{13}NOS$ requires C, 61.5; H, 6.7; N, 7.2; S, 16.4%); *m/z* 195 (M^+, 11%) and 136 ($M - CH_3CONH_2$, 100); $\nu_{max.}$($CHCl_3$) 3 300, 3 120, 2 980, 2 940, 2 880, 1 640, 1 570, and 1 450; δ_H 1.90 (3 H, s), 3.00 (2 H, t, *J* 7 Hz), 3.40 (2 H, m), 6.9 (1 H, br), and 7.3—7.5 (5 H, complex); δ_C 30.0 (CH_3), 33.1 (CH_2), 38.9 (CH_2), 126.3, 129.1, 129.4, and 135.4 (aromatic carbons), and 170.7 p.p.m. (CO).

In a series of small-scale experiments the influence of added acids upon the yield of 1-acetamido-2-phenylthioethane was investigated. Diphenyl disulphide (100 mg) was electrolysed at 1.3 V at a platinum anode in acetonitrile containing added electrolyte and trifluoroacetic acid. Ethene was bubbled through the anode compartment and after work-up the amide (**15**) was isolated by column chromatography and shown to be pure (one spot by t.l.c.). At the following molar ratios of diphenyl disulphide to trifluoroacetic acid the yield of (**15**) w.r.t. diphenyl disulphide was: 1:0, 22%; 1:1, 23%; 1:2, 46%; 1:3, 70%; 1:4, 130%; 1:5, 59%; 1:6, 42%. Duplicate experiments confirmed these results. When diphenyl disulphide (100 mg) was oxidized in acetonitrile in the presence of added sodium trifluoroacetate (190 mg) no amide (**15**) was isolated. Addition of either acetic or sulphuric acid instead of trifluoroacetic acid was less effective than addition of trifluoroacetic acid but some enhancement in the yield of the amide (**15**) was observed: 44% for acetic acid at a ratio acetic acid:diphenyl disulphide 3:1, and 50% for sulphuric acid at a ratio sulphuric acid:diphenyl disulphide 3:1.

Alternative preparation of 1-acetamido-2-phenylthioethane (**15**). Thiophenol (12 g) and 2-methyloxazoline (1,3-dihydro-2-methyloxazate (9 g) were heated under reflux in acetonitrile (60 ml) containing toluene-*p*-sulphonic acid (1 g) for 4 h. The cold reaction mixture was poured into 5M aqueous sodium hydroxide solution (150 ml) and extraction with dichloromethane (3 × 150 ml) and work-up afforded a crude solid product. Recrystallization (dichloromethane–pentane) gave 1-acetamido-2-phenylthioethane (**15**) (18.2 g, 85%), m.p. 88—89 °C, identical (t.l.c., mixed m.p.) with a sample of compound (**15**) obtained by anodic addition to ethene (see above).

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