Additions to Alkenes *via* Metal Ion-Promoted Oxidation of Dialkyl and Diaryl Disulphides

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Reactions of alkenes with di-n-propyl, diphenyl, and dibenzyl disulphide in the presence of lead(IV) salts in trifluoroacetic acid–dichloromethane are described. The products, vicinal trifluoroacetoxysulphides, are obtained in higher yields with manganese(III) salts as the oxidant. Alternative reaction conditions with use of iron(III) salts or in the absence of added metal salts are also described. Trifluoroacetoxysulphides derived from diphenyl disulphide react with acetonitrile under Ritter conditions to give acetamidosulphides but trifluoroacetoxysulphides derived from dibenzyl disulphide only give the vicinal acetamidosulphides in poor yield as a result of an alternative reaction pathway affording benzylacetamide. Conversions of acetamidosulphides into aminosulphides and into acetamidothiols are described.

The oxidation of an organic disulphide by a lead(IV) salt has been reported[1] by Trost *et al.* as a satisfactory general method of vicinal addition to alkenes to give products of hydroxysulphenylation. In the preceding paper[2] we describe a related electrochemical oxidation of organic disulphides, permitting the acetamidosulphenylation of alkenes by reaction in acetonitrile. In this and the following paper[3] we extend the scope of non-electrochemical oxidations of organic disulphides in the presence of alkenes. In this paper we report further examples of useful additions under Trost conditions using lead(IV) as an oxidant in dichloromethane–trifluoroacetic acid, the use of other metal ions as oxidants, and the surprising observation that additions proceed in high yield even in the absence of metal-ion oxidants. We further report the useful synthetic elaboration of the initially formed vicinal trifluoroacetoxysulphides to give a variety of vicinally substituted products. In the following paper[3] we report the additions of amino-substituted disulphides to alkenes which fail under Trost conditions.

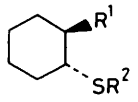
The previous study of hydroxysulphenylation[1] was based on the use of diphenyl disulphide or methoxy-substituted diphenyl disulphides. In view of the successful precedent[2] of anodic addition of a range of other disulphides such as dimethyl disulphide and dibenzyl disulphide to alkenes we initially studied a wider range of organic disulphides by the Trost procedure.[1] Results of some additions using lead(IV) salts to give some vicinal trifluoroacetoxysulphides are given in Table 1. In each of these reactions more than one stereo- or regio-isomer might be expected. In accord with previous results[1] we find that oxidative addition of diphenyl disulphide to cyclohexene gives a single isomer (**1**) by *trans*-addition. The *trans* stereochemistry in compound (**1**) was assigned by observation of the coupling constant associated with the two methine protons. Similarly in additions giving the *trans*-adducts (**2**), (**3**), and (**24**), only the *trans*-adducts were observed. In formation of the trifluoroacetoxysulphides from styrene and oct-1-ene only those adducts corresponding to Markownikoff addition are observed. These structures are assigned on the basis of the relative chemical shifts of the methylene and methine protons proximate to the heteroatoms in the adducts. Confirmation of formation of a single regioisomer in the case of compound (**8**) was obtained by hydrolysis to give the single hydroxysulphide (**12**) which was characterised spectroscopically. Our results closely accord with the stereochemical and regiochemical outcome of analogous examples reported by Trost,[1] but in addition to hept-1-ene an anti-Markownikoff product was observed as a minor adduct.

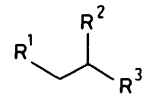
By comparison with earlier studies[1] these results and others reported establish the possibility of oxidative addition of a wider range of disulphides to alkenes. In particular the

Table 1. Additions to alkenes by metal ion-promoted oxidation of organic disulphides

Alkene	Disulphide	Product	Yield[a] of vicinal trifluoroacetoxysulphide (%) Pb^{4+}[b]	Mn^{3+}[b]	No added salt[c]
Cyclohexene	Diphenyl	(**1**)	74[d]	99	129
Oct-ene	Diphenyl	(**8**)	37	49	34
Styrene	Diphenyl	(**9**)	100	97	87
Cyclopentene	Diphenyl	(**24**)	63	80	—
Cyclohexene	Di-n-propyl	(**2**)	97	91	107
Cyclohexene	Dibenzyl	(**3**)	—	82	120
Oct-1-ene	Dibenzyl	(**10**)	17	59	46
Styrene	Dibenzyl	(**11**)	51	—	78

[a] Yields relative to moles of disulphide. [b] Reactions at 0 °C for 30 min; for procedure see preparation of compound (**1**). [c] Reaction at room temperature for several days; for procedure see preparation of compound (**9**). [d] See reference 1.





(**1**) R^1 = $OCOCF_3$, R^2 = Ph
(**2**) R^1 = $OCOCF_3$, R^2 = Pr^n
(**3**) R^1 = $OCOCF_3$, R^2 = CH_2Ph
(**4**) R^1 = NHAc, R^2 = Pr^n
(**5**) R^1 = NHAc, R^2 = CH_2Ph
(**6**) R^1 = NHAc, R^2 = Ph
(**7**) R^1 = NHAc, R^2 = H
(**8**) R^1 = SPh, R^2 = $OCOCF_3$, R^3 = $C_6H_{13}{}^n$
(**9**) R^1 = SPh, R^2 = $OCOCF_3$, R^3 = Ph
(**10**) R^1 = SCH_2Ph, R^2 = $OCOCF_3$, R^3 = $C_6H_{13}{}^n$
(**11**) R^1 = SCH_2Ph, R^2 = $OCOCF_3$, R^3 = Ph
(**12**) R^1 = SPh, R^2 = OH, R^3 = $C_6H_{13}{}^n$
(**13**) R^1 = SPh, R^2 = NHAc, R^3 = $C_6H_{13}{}^n$
(**14**) R^1 = SCH_2Ph, R^2 = NHAc, R^3 = $C_6H_{13}{}^n$
(**15**) R^1 = SCH_2Ph, R^2 = NHAc, R^3 = Ph
(**16**) R^1 = SPh, R^2 = NHAc, R^3 = Ph
(**17**) R^1 = SPh, R^2 = NHAc, R^3 = $CH_2CH_2CH{=}CH$
(**18**) R^1 = SPh, R^2 = NHAc, R^3 = H
(**19**) R^1 = SPh, R^2 = NH_2, R^3 = H
(**20**) R^1 = SCH_2Ph, R^2 = NH_2, R^3 = H
(**21**) R^1 = SH, R^2 = NHAc, R^3 = Ph
(**22**) R^1 = SH, R^2 = NHAc, R^3 = $C_6H_{13}{}^n$
(**23**) R^1 = SH, R^2 = NHAc, R^3 = H

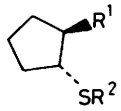
opportunity to add dibenzyl disulphide offers the advantage of subsequent conversion into thiols as reported below. In contrast to the successful electrochemical addition of 2,2′-dipyridyl disulphide (Aldrithiol-2) to alkenes, attempted lead(IV)-promoted addition failed. Similarly lead(IV)-promoted reaction of alkenes with 2,2′-diaminodiphenyl disulphide failed. These failures prompted a search for alternative procedures using different metal salts. Results with copper(II) salts are reported in the following paper[3] and those with manganese(III) acetate in Table 1.

Under the same conditions as described by Trost,[1] but employing a molar equivalent of manganese(III) acetate rather than a molar equivalent of lead(IV) acetate, oxidative additions proceeded in comparable, and in the case of dibenzyl disulphide improved, yields relative to those with lead(IV) acetate. As a procedure for synthesis of vicinally substituted trifluoroacetoxysulphides from alkenes we find no disadvantage relative to the earlier described procedures[1] using lead(IV) salts. Reactions of diphenyl disulphide with cyclohexene to give the trifluoroacetoxy sulphide (**1**) were also examined using copper(II), iron(III), and mercury(II) salts as promoters. Although the adduct (**1**) is obtained, reactions with either copper(II) or iron(III) are markedly slower than the reactions with either lead(IV) or manganese(III). Thus the use of molar quantities of copper(II) and iron(III) salts has no marked advantage relative to the use of manganese(III) salts for the additions described in this paper. For example after 30 min at 0 °C the following yields of trifluoroacetoxysulphide (**1**) (relative to diphenyl disulphide) are obtained: copper(II), 43%; iron(III) 35%; lead(IV) 74%; and manganese(III) 99%. However, by longer reaction times with copper(II) and iron(III) salts at 0 °C higher yields can be obtained. The possibility that these oxidative additions could be made catalytic in metal ion using oxygen as the ultimate oxidant was investigated alongside a series of blank experiments involving possible reaction of disulphides with alkenes in dichloromethane–trifluoroacetic acid in the absence of any added metal salts. The results of using catalytic quantities of metal salts are reported in the following paper,[3] but surprisingly for the disulphides described in this paper oxidative addition to alkenes requires no added metal salts. Typically, diphenyl disulphide and cyclohexene after 2 days at room temperature in dichloromethane–trifluoroacetic acid under air give the trifluoroacetoxysulphide (**1**) in 129% yield (with respect to diphenyl disulphide, assuming as with other yields reported in this paper that the disulphide has only one thiophenyl moiety available for addition to the alkene). Examples reported in Table 1 show that the much slower additions in the absence of added metal salts nevertheless afford good yields of trifluoroacetoxysulphides. Under nitrogen the addition is substantially retarded. Although details of the mechanism of this oxidative addition remain obscure, the probability that reaction proceeds *via* an electrophilic attack on the alkene rather than a radical addition is supported by a number of points. Additions to cyclohexene in the absence of added metal salts proceed in trifluoroacetic acid but not in acetic acid. As discussed more fully in the following paper[3] cross-over experiments show that two symmetrical diaryl disulphides (PhSSPh and *p*-$MeC_6H_4SSC_6H_4Me$-*p*) readily equilibrate to give a mixture of three diaryl disulphides in trifluoroacetic acid, but not in acetic acid. Previous studies have established[4] that different electrophiles (*e.g.*, H^+) or metal ions assist in the nucleophilic cleavage of the disulphide bond. Although reaction of diphenyl disulphide with lead(IV) salts in the absence of an alkene in trifluoroacetic acid gives, after work-up, recovered diphenyl disulphide and the thiol-sulphonate (**26**), no thiol-sulphonate (**26**) is observed when diphenyl disulphide in trifluoroacetic acid is exposed to air. These observations fail to discriminate between the three intermediates (**27**)—(**29**) previously considered[1] as likely intermediates in the lead(IV)-promoted additions. Mechanistic aspects are further discussed in the following paper. In summary, preparation of these vicinal trifluoroacetoxysulphides requires either a metal salt as oxidant or exposure to air with much longer reaction times.

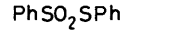
Table 2. Direct preparation of vicinal acetamidosulphides from alkenes by oxidative addition and Ritter reaction

Alkene	Disulphide	Product	Yield (%)[a]
Styrene	Dibenzyl	(**15**)	23
Cyclohexene	Dibenzyl	(**5**)	18
Cyclohexene	Diphenyl	(**6**)	39
Styrene	Diphenyl	(**16**)	100
Ethyl cinnamate	Diphenyl	(**30**)	40
trans-Stilbene	Diphenyl	(**31**)	47
Cinnamyl acetate	Diphenyl	(**32**)	99
Hexa-1,5-diene	Diphenyl	(**17**)	11
Ethene	Diphenyl	(**18**)	4

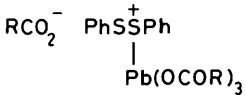
[a] Yields relative to moles of disulphide.



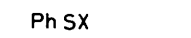
(**24**) $R^1 = OCOCF_3$, $R^2 = Ph$
(**25**) $R^1 = NHCOMe$, $R^2 = Ph$



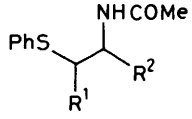
(**26**)



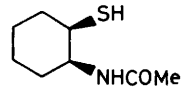
(**27**)



(**28**) X = $Pb(OCOR)_3$
(**29**) X = $OCOCF_3$



(**30**) $R^1 = CO_2Et$, $R^2 = Ph$
(**31**) $R^1 = Ph$, $R^2 = Ph$
(**32**) $R^1 = CH_2OAc$, $R^2 = Ph$
(**33**) $R^1 = CO_2H$, $R^2 = Ph$
(**34**) $R^1 = CH_2OH$, $R^2 = Ph$
(**35**) $R^1 = CH_2OCOC_6H_3(NO_2)_2$, $R^2 = Ph$



(**36**)

Efficient syntheses of the trifluoroacetoxysulphides offered an alternative route to acetamidosulphides by possible Ritter reaction. As a comparison with the direct electrochemical acetamidosulphenylation[2] we have examined both the Ritter reaction with pure trifluoroacetoxysulphides and direct conversion of alkenes into acetamidosulphides without isolation of the intermediate trifluoroacetoxysulphides. With diphenyl disulphide it is possible to achieve satisfactory conversions into acetamidosulphides. Thus the pure trifluoroacetoxysulphide (**8**) gives the acetamidosulphide (**13**) in 70% yield under Ritter conditions. Although the conversions of the pure trifluoroacetoxysulphides into acetamidosulphides [(**24**)→(**25**) in 35% yield; (**2**)→(**4**) in 35% yield; (**10**)→(**14**) in 44% yield; and (**11**)→(**15**) in 29% yield] indicate that adducts of dibenzyl disulphide give comparable yields to those of other disulphides in the Ritter reaction; in fact, the results shown in Table 2 for direct conversion of alkenes into acetamido-

disulphides are disappointing for the examples giving [(**15**) and (**5**)] from dibenzyl disulphide. Two conclusions can be drawn from the results in Table 2. Addition of diphenyl disulphide gives higher yields with the more nucleophilic alkenes; thus acetamidosulphides (**6**), (**16**), and (**30**)—(**32**) are obtained in markedly higher yields than the acetamidosulphides (**17**) and (**18**) from hexa-1,5-diene and ethene respectively. Secondly, lower yields are obtained from dibenzyl disulphide, a point we have investigated further in view of the potential importance of acetamidosulphides derived from dibenzyl disulphides as intermediates in the synthesis of aminothiols. Under a variety of reaction conditions in which the acetamidosulphide (**15**) is obtained a competitive fragmentation of the trifluoroacetoxysulphide (**11**) affords benzylacetamide. In spite of the rather mild conditions which can be used for these Ritter reactions of trifluoroacetoxysulphides the yield of acetamido(benzyl)sulphides is always reduced by formation of benzylacetamide, a problem also encountered in our electrochemical studies.[2]

The structures of the acetamidosulphides are in part assigned by comparison with samples obtained electrochemically.[2] In the case of reactions affording products not obtained electrochemically the Ritter reaction afforded a single acetamidosulphide. Formation of the *trans*-adducts (**25**) and (**4**), as indicated spectroscopically, and (**5**) and (**6**), as indicated by the above comparisons, strongly suggested participation of episulphonium ions in the Ritter reaction. The regiochemistry in formation of the adducts (**13**) and (**14**) from oct-1-ene, (**15**) and (**16**) from styrene, and (**17**) from hexa-1,5-diene, is deduced from ^{1}H n.m.r. spectra, and is consistent with both our electrochemical study and earlier results.[1,5] For adducts (**30**)—(**32**) structures are tentatively assigned with the assumption of *trans*-Markownikoff-type additions, as rigorously proved for the other cases reported in this paper. The ester (**30**) was further characterised by hydrolysis to the acid (**33**) and the ester (**32**) by hydrolysis to the alcohol (**34**), which was derivatised as the 3,5-dinitrobenzoate (**35**).

Subsequent transformations of the acetamidosulphides were briefly investigated. Under acid conditions the acetamido(phenyl)sulphide (**18**) is hydrolysed to the aminosulphide (**19**) and under basic conditions 1-acetamido-2-benzylthioethane is hydrolysed to the aminosulphide (**20**).

Reductive removal of the benzyl group in acetamido(benzyl)sulphides affords acetamidothiols. Thus reduction of compound (**5**) with sodium in liquid ammonia gives the epimeric acetamidothiols (**7**) and (**36**). The respective structures are assigned from the ^{1}H n.m.r. spectra and the epimerisation to give the *cis*-compound (**36**) under strongly basic conditions has good precedent.[6] In further examples proceeding without epimerisation the thiols (**21**)—(**23**) were obtained.

Experimental

I.r. spectra were recorded with a Perkin-Elmer 157-G spectrophotometer. N.m.r. spectra were recorded for $CDCl_3$ solutions with a Varian Associates XL-100-12 spectrometer using tetramethylsilane as internal standard. Routine and high-resolution mass spectra were obtained with a Kratos MS30 instrument fitted with the DS 505 Data System. M.p.s were determined using an Electrothermal electrically heated block, and are uncorrected. 'Flash' column chromatography refers to the method of Still[7] and was carried out using MN-Kieselgel 60 230—400 mesh silica gel. Elemental analyses were carried out at the Microanalytical Laboratory, University College, London. Compounds which were not submitted for microanalysis were homogeneous (t.l.c.). Yields are based on 1 mol equiv. of disulphide.

Materials.—Lead tetra-acetate (B.D.H. Laboratory Reagent) moist with acetic acid was partially dried by suction on filter paper under dry nitrogen. The sample was further dried over potassium hydroxide *in vacuo* and stored in a desiccator (P_2O_5). Analysis for lead(IV) (by iodometric titration using Vitex indicator) indicated a purity of 96—100% for various samples. Manganese(III) acetate was prepared as previously described. Other metal acetates, *viz* mercury(II) acetate, iron(III) acetate, and copper(II) acetate, were commercially available and used without further purification. Routinely, alkenes were purified by distillation but all disulphides were used without further purification. Acetonitrile was distilled from P_2O_5. Dichloromethane and trifluoroacetic acid (Fluorochem) were used without further purification. Light petroleum refers to the fraction boiling in the range 40—60 °C.

Typical Procedure for Trifluoroacetoxysulphenylation using Manganese(III) Acetate.—trans-1-*Phenylthio*-2-*trifluoroacetoxycyclohexane* (**1**). Manganese(III) acetate (1.15 g) was dissolved in dichloromethane (50 ml) containing trifluoroacetic acid (4 ml) at 0 °C. The solution was stirred for 10 min and first diphenyl disulphide (946 mg) and then cyclohexene (2.0 g) were added in rapid succession. Addition of the disulphide afforded a blue colour that faded on addition of the cyclohexene. The solution was stirred at 0 °C for 30 min and then poured into water (150 ml). Excess of acid was carefully neutralised by addition of solid sodium carbonate and the solution was extracted with chloroform (3 × 50 ml). The combined organic extracts were washed with water, dried over magnesium sulphate, and filtered. Removal of the solvent under reduced pressure afforded a crude product. Further purification by column chromatography (silica gel, eluant light petroleum) afforded, as an oil, trans-1-*phenylthio*-2-*trifluoroacetoxycyclohexane* (**1**) (1.30 g, 99% w.r.t. diphenyl disulphide) (Found: M^+, 304.0826. $C_{14}H_{15}F_3O_2S$ requires M, 304.0818); m/z 304 (M^+, 0.1%), 191 (38), 123 (20), 110 (30), 109 (21), and 81 (100); $\nu_{max.}$(film) 1 775 cm^{-1}; δ_H 1.1—2.2 (8 H, complex), 3.14 (1 H, dt, J 8, 8, and 4 Hz), 4.93 (1 H, dt, J 8, 8, and 4 Hz), and 7.1—7.5 (5 H, complex); δ_C 23.1, 24.5, 30.3, 31.6, 49.7, 79.2, 127.1, 127.8, 129.0, 129.1, 132.4, and 133.2 p.p.m.

1-*Phenylthio*-2-*trifluoroacetoxyoctane* (**8**). Diphenyl disulphide (1.11 g) was oxidised by lead tetra-acetate (2.4 g) in the presence of oct-1-ene (8.83 g) by the above procedure. After work-up, column chromatography (eluant light petroleum) afforded, as an oil, 1-*phenylthio*-2-*trifluoroacetoxyoctane* (**8**) (622 mg, 37% w.r.t. diphenyl disulphide) (Found: M^+, 334.1419. $C_{16}H_{21}F_3O_2S$ requires M, 334.1399); m/z 334 (M^+, 5%), 221 (91), 123 (100), 110 (46), and 109 (26); $\nu_{max.}$(film) 1 790 cm^{-1}; δ^H 0.88 (3 H, t), 1.1—1.8 (10 H, m), 3.06 (2 H, d, J 6 Hz), 5.12 (1 H, m), and 7.1—7.4 (5 H, complex); δ_C 14.2, 22.8, 24.9, 29.2, 31.8, 33.0, 37.8, 77.9, 127.1, 127.6, 127.9, 129.3, 130.6, and 132.9 p.p.m. Hydrolysis of 1-phenylthio-2-trifluoroacetoxyoctane (**8**) in methanol containing potassium hydroxide under reflux for 30 min afforded, in 97% yield after work-up and chromatography (silica gel, eluant light petroleum), 1-phenylthio-octan-2-ol (**12**), m/z 221 (100%), 123 (84), and 109 (29); $\nu_{max.}$(film) 3 400 cm^{-1}; δ_H 0.87 (3 H, t), 1.1—1.6 (10 H, complex), 2.8—3.4 (4 H, complex), and 7.1—7.4 (5 H, complex); δ_C 14.1, 22.6, 26.7, 29.0, 31.7, 32.5, 39.4, 48.3, 126.2, 127.2, 128.9, 129.8, and 132.5 p.p.m.

trans-1-*Phenylthio*-2-*trifluoroacetoxycyclopentane* (**24**). Diphenyl disulphide (1.83 g) was oxidised by lead tetra-acetate (4.34 g) in the presence of cyclopentene by the above procedure. After work-up, column chromatography [eluant light petroleum–ether (19:1)] afforded, as an oil, 1-*phenylthio*-2-*trifluoroacetoxycyclopentane* (**24**) (1.53 g, 63% w.r.t. diphenyl disulphide) (Found: M^+, 290.0689. $C_{13}H_{13}F_3O_2S$ requires M, 290.0677); m/z 290 (M^+, 1%), 177 (95), and 67 (100); $\nu_{max.}$(film) 2 960, 1 780, 1 590, 1 485, 1 440, 1 230, and 1 160 cm^{-1}; δ_H 1.5—2.0 (4 H, complex), 2.3—2.4 (2 H, m), 3.57 (1 H, m), 5.24 (1 H, m), and 7.1—7.3 (5 H, m).

trans-1-*Propylthio*-2-*trifluoroacetoxycyclohexane* (**2**). Di-n-propyl disulphide (1.50 g) was oxidised by lead tetra-acetate (5.06 g) in the presence of cyclohexene (4.9 g) by the above procedure. After work-up, column chromatography (eluant light petroleum) afforded, as an oil, 1-propylthio-2-trifluoroacetoxycyclohexane (**2**) (2.61 g, 97% w.r.t. di-n-propyl disulphide); *m/z* 157 (44%), 114 (8), 113 (8), 89 (14), and 81 (100); $\nu_{max.}$(film) 2 950, 2 880, and 1 785 cm^{-1}; δ_H 0.97 (3 H, t), 1.1—1.8 (8 H, complex), 2.25 (2 H, d), 2.56 (2 H, t), 2.77 (1 H, m), and 4.90 (1 H, m).

trans-1-*Benzylthio*-2-*trifluoroacetoxycyclohexane* (**3**). Dibenzyl disulphide (1.23 g) was oxidised by manganese(III) acetate (1.36 g) in the presence of cyclohexene (3.16 g) by the above procedure. After work-up, column chromatography (eluant light petroleum) afforded, as an oil, trans-1-*benzylthio*-2-*trifluoroacetoxycyclohexane* (**3**) (1.30 g, 82% w.r.t. dibenzyl disulphide) (Found: M^+, 318.0819. $C_{15}H_{17}F_3O_2S$ requires *M*, 318.0827); *m/z* 318 (M^+, 2%), 205 (12), 123 (25), 91 (100), and 81 (18); $\nu_{max.}$(film) 1 775 cm^{-1}; δ_H 1.1—2.2 (8 H, complex), 2.84 (1 H, m), 3.68 (2 H, s), 4.95 (1 H, m), and 7.1—7.4 (5 H, complex).

1-*Benzylthio*-2-*trifluoroacetoxyoctane* (**10**). Dibenzyl disulphide (1.65 g) was oxidised by lead tetra-acetate (3.36 g) in the presence of oct-1-ene (3.87 g) by the above procedure. After work-up, column chromatography [eluant light petroleum–ether (19:1)] afforded as an oil, 1-benzylthio-2-trifluoroacetoxyoctane (**10**) (388 mg, 17% w.r.t. dibenzyl disulphide); *m/z* 348 (M^+, 1%) and 91 (100); $\nu_{max.}$(film) 1 780 cm^{-1}; δ_H 0.6—1.8 (13 H, complex), 2.55 (2 H, d, *J* 6 Hz), 3.58 (2 H, s), 5.03 (1 H, m), and 7.1—7.3 (5 H, complex).

2-*Benzylthio*-1-*phenyl*-1-*trifluoroacetoxyethane* (**11**). Dibenzyl disulphide (1.04 g) was oxidised by lead tetra-acetate (2.12 g) in the presence of styrene (588 mg) by the above procedure. After careful work-up, column chromatography [eluant light petroleum–ether (19:1)] afforded, as an unstable oil, 2-*benzylthio*-1-*phenyl*-1-*trifluoroacetoxyethane* (**11**) (742 mg, 51% w.r.t. dibenzyldisulphide) (Found: M^+, 340.0680. $C_{17}H_{15}F_3O_2S$ requires *M*, 340.0686); *m/z* 340 (M^+, 2%), 226 ($M - CH_3CO_2H$, 4), and 91 (100); $\nu_{max.}$ 3 060, 2 950, 1 795, 1 610, 1 510, 1 470, 1 390, 1 240, and 1 170 cm^{-1}; δ_H 2.85 (2 H, dd, *J* 7 and 3 Hz), 3.60 (2 H, s), 5.85 (1 H, t, *J* 7 Hz), and 7.3 (10 H, complex).

Reaction of Disulphides with Alkenes in the Presence of Other Metal Salts.—Iron(III) acetate (1.17 g) was dissolved in dichloromethane (50 ml) containing trifluoroacetic acid (4 ml) at 0 °C. Diphenyl disulphide (1.08 g) and cyclohexene (3.16 g) were added in rapid succession. The solution was stirred at 0 °C for 30 min. Work-up and chromatography as described above afforded 1-phenylthio-2-trifluoroacetoxycyclohexane (**1**) (528 mg, 35% w.r.t. diphenyl disulphide). Similar additions were studied using copper(II) acetate and mercury(II) acetate.

Typical Procedure for Trifluoroacetoxysulphenylation by Reaction of a Disulphide with an Alkene in the Absence of Added Metal Salts.—1-*Phenyl*-2-*phenylthio*-1-*trifluoroacetoxyethane* (**9**). Diphenyl disulphide (1.29 g) was dissolved in dichloromethane (50 ml) containing trifluoroacetic acid (4 ml) at room temperature and styrene (5.62 g) was added. The solution was stirred for 3 days at room temperature and was then worked up as described above. Column chromatography of the crude product (silica gel, eluant light petroleum) afforded, as an oil, 1-*phenyl*-2-*phenylthio*-1-*trifluoroacetoxyethane* (**9**) (1.67 g, 87% w.r.t. diphenyl disulphide) (Found: M^+, 326.0726. $C_{16}H_{13}F_3O_2S$ requires *M*, 326.0712); *m/z* 326 (M^+, 3%), 213 (56), 135 (100), 123 (56), 109 (35), 104 (37), 91 (37), and 77 (31); $\nu_{max.}$(film) 1 790 cm^{-1}; δ_H 3.36 (2 H, m), 4.25 (1 H, dd, *J* 10 and 5 Hz), and 7.0—7.4 (10 H, complex); δ_C 39.5, 52.3, and 126.3—132.7 (complex).

2-*Acetamido*-1-*phenylthio*-*octane* (**13**). The trifluoroacetate (**8**) (886 mg) was heated under reflux in acetonitrile (25 ml) containing sulphuric acid (0.1 ml) for 24 h. Work-up and column chromatography (eluant ether) afforded 2-acetamido-1-phenylthio-octane (**13**) (520 mg, 70%), m.p. 60—61 °C. The sample was identical with a sample obtained by anodic oxidation.[2]

trans-1-*Acetamido*-2-*phenylthiocyclopentane* (**25**). The trifluoroacetate (**24**) (1.5 g) was heated under reflux in acetonitrile (25 ml) containing sulphuric acid (0.1 ml) for 18 h. Work-up and column chromatography (eluant ether) afforded, as an oil, trans-1-*acetamido*-2-*phenylthiocyclopentane* (**25**) (418 mg, 35%) (Found: M^+, 235.1086. $C_{13}H_{17}NOS$ requires *M*, 235.1081); *m/z* 235 (M^+, 2%), 176 ($M - CH_3CONH_2$, 100), and 67 (89); $\nu_{max.}$(film) 3 300 and 1 660 cm^{-1}; δ_H 1.5—1.8 (4 H, complex), 1.92 (3 H, s), 2.1 (2 H, m), 3.45 (1 H, dt), 4.18 (1 H, dt), and 7.1—7.5 (5 H, complex).

trans-1-*Acetamido*-2-*propylthiocyclohexane* (**4**). The trifluoroacetate (**2**) (1.8 g) was heated under reflux in acetonitrile (40 ml) containing sulphuric acid (1 ml) for 18 h. Work-up and column chromatography (eluant ether) afforded the crude title compound. Recrystallisation (dichloromethane–pentane) gave trans-1-*acetamido*-2-*propylthiocyclohexane* (**4**) (500 mg, 35%), m.p. 72.5—73 °C (Found: C, 61.3; H, 9.8; N, 6.5. $C_{11}H_{21}NOS$ requires C, 61.35; H, 9.8; N, 6.5%); *m/z* 215 (M^+, 1%), 156 (100), 114 (67), 113 (16), and 81 (50); $\nu_{max.}$($CHCl_3$) 3 300 and 1 660 cm^{-1}; δ_H 0.98 (3 H, t), 1.1—1.85 (8 H, m), 2.00 (3 H, s), 2.15 (2 H, m), 2.5 (3 H, complex), 3.70 (1 H, m), and 6.14 (1 H, br); δ_C 13.6, 23.3, 23.4, 24.5, 25.7, 31.9, 33.0, 33.3, 48.4, 51.9, and 169.9 p.p.m.

2-*Acetamido*-1-*benzylthio*-*octane* (**14**). 1-benzylthio-2-trifluoroacetoxyoctane (**10**) (1.0 g) was heated under reflux in acetonitrile (50 ml) containing sulphuric acid (0.25 ml) for 18 h. Work-up and column chromatography (eluant ether) afforded 2-acetamido-1-benzylthio-octane (**14**) (370 mg, 44%). The sample was identical with a sample obtained by anodic oxidation.[2]

1-*Acetamido*-2-*benzylthio*-1-*phenylethane* (**15**). The trifluoroacetate (**11**) (417 mg), after reaction with CH_3CN–H^+ at room temperature for 18 h, work-up, and column chromatography (eluant ether), afforded, as a white solid, 1-acetamido-2-benzylthio-1-phenylethane (**15**) (101 mg, 29%), m.p. 107—108 °C; *m/z* 285 (M^+, 0.1%), 226 ($M - CH_3CONH_2$, 32), 148 (29), and 106 (100); $\nu_{max.}$($CHCl_3$) 3 420, 3 000, 2 920, 1 665, 1 490, 1 370, 1 230, 1 200, and 1 040 cm^{-1}; δ_H 1.90 (3 H, s), 2.78 (2 H, d, *J* 7 Hz), 3.57 (2 H, s), 5.20 (1 H, m), 6.60 (1 H, br), and 7.2—7.4 (10 H, complex); δ_C 23.1, (CH_3), 36.3 (CH_2), 37.1 (CH_2), 52.3 (CH), 126.6, 127.1, 127.6, 128.6, 129.0, 138.0, and 141.0 (aromatic carbons), and 169.9 p.p.m. (CO). Further elution afforded benzylacetamide.

Dibenzyl disulphide (1.02 g) was oxidised by lead tetra-acetate (2.05 g) in the presence of styrene (700 mg). After work-up and reaction with CH_3CN–H^+, further work-up and chromatography (eluant ether) afforded compound (**15**) (314 mg, 23% w.r.t. dibenzyl disulphide) and the more polar benzylacetamide.

Typical Procedure for Acetamidosulphenylation using Lead Tetra-acetate.—trans-1-*Acetamido*-2-*phenylthiocyclohexane* (**6**). Lead tetra-acetate (2.00 g, 4.5 mmol) was dissolved in dichloromethane (50 ml) and at 0 °C trifluoroacetic acid (4 ml, 50 mmol) was added. The solution was stirred for 10 min, and diphenyl disulphide (1.00 g, 4.54 mmol) and then cyclohexene (0.51 g, 6.2 mmol) were added in rapid succession. Addition of the disulphide immediately afforded a turquoise colour but this colour rapidly faded to give a yellow solution. Addition of the cyclohexene afforded a colourless solution. The solution was stirred at 0 °C for 30 min and then poured into water (150 ml). Excess of acid was neutralised by careful addition of solid sodium carbonate and the solution was extracted with chloroform (3 × 50 ml). The combined organic extracts were washed

with water, dried over magnesium sulphate, and filtered. Removal of solvent under reduced pressure afforded a yellow oil, which was dissolved in acetonitrile (40 ml) containing concentrated sulphuric acid (0.5 ml) and the solution was kept at room temperature for 18 h. The solution was then poured into water (150 ml) and made alkaline by careful addition of solid sodium carbonate. Following extraction with chloroform (3 × 50 ml) the combined organic extracts were washed with water, dried over magnesium sulphate, and filtered. Removal of solvent under reduced pressure afforded a brown oil. Purification by 'flash' chromatography (eluant ether) afforded *trans*-1-acetamido-2-phenylthiocyclohexane (**6**) (0.445 g, 39% w.r.t. diphenyl disulphide). The product was identical (^{1}H n.m.r., i.r., m.s., t.l.c., and m.p.) with a sample obtained by anodic oxidation.[2]

1-*Acetamido*-1-*phenyl*-2-*phenylthioethane* (**16**). Diphenyl disulphide (1.03 g) was oxidised by lead tetra-acetate (2.47 g) in the presence of styrene (550 mg) by the above procedure. After work-up and reaction with CH_3CN–H^+, further work-up and column chromatography (eluant ether) afforded, as a pale oil, 1-*acetamido*-1-*phenyl*-2-*phenylthioethane* (**16**) (1.28 g, 100% w.r.t. diphenyl disulphide) (Found: M^+, 271.0924. $C_{16}H_{17}NOS$ requires M, 271.0935); m/z 271 (M^+, 1%), 212 (M − CH_3CONH_2, 56), and 106 (100); $\nu_{max.}$($CHCl_3$) 3 300, 3 080, 1 660, 1 560, 1 500, 1 450, 1 390, and 1 160 cm^{-1}; δ_H 1.87 (3 H, s), 3.28 (2 H, dd, J 7 and 2 Hz), 5.13 (1 H, m), 6.77 (1 H, d, J 7 Hz), and 7.1—7.3 (10 H, complex); δ_C 23.0 (CH_3), 42.0 (CH_2), 52.3 (CH), and 125—129 (complex).

Ethyl 3-*Acetamido*-3-*phenyl*-2-*phenylthiopropionate* (**30**). Diphenyl disulphide (1.0 g) was oxidised by lead tetra-acetate (2.07 g) in the presence of ethyl cinnamate (870 mg) by the above procedure. After work-up and reaction with CH_3CN–H^+, further work-up and column chromatography (eluant ether) afforded, as a pale oil, ethyl 3-acetamido-3-phenyl-2-phenylthiopropionate (**30**) (620 mg, 40% w.r.t. diphenyl disulphide); m/z 343 (M^+, 1%), 284 (M − CH_3CONH_2, 8), 148 (80), and 106 (100); $\nu_{max.}$($CHCl_3$) 3 300, 3 100, 3 020, 1 730, 1 660, 1 490, 1 380, 1 280, and 1 140 cm^{-1}; δ_H 0.98 (3 H, t, J 6 Hz), 1.97 (3 H, s), 4.00 (2 H, m), 4.12 (1 H, d, J 6 Hz), 5.60 (1 H, m), 7.2—7.4 (10 H, complex), and 7.69 (1 H, br). The product was further characterised by hydrolysis (2M KOH in ethanol) to afford 3-acetamido-3-phenyl-2-phenylthiopropionic acid (**33**), m.p. 143—145 °C; m/z 316 (M + 1, 1%), 175 (8), 174 (8), 148 (53), and 106 (100); δ_H 1.95 (3 H, s), 4.24 (1 H, m), 5.58 (1 H, m), and 7.1—7.3 (10 H, complex).

1-*Acetamido*1,2-*diphenyl*-2-*phenylthioethane* (**31**). Diphenyl disulphide (1.32 g) was oxidised by lead tetra-acetate (2.68 g) in the presence of *trans*-stilbene (1.18 g) by the above procedure. After work-up and reaction with CH_3CN–H^+, further work-up and column chromatography (eluant ether) afforded, as a white solid, 1-acetamido-1,2-diphenyl-2-phenylthioethane (**31**) (982 mg, 47% w.r.t. diphenyl disulphide), m.p. 112—113 °C; m/z 347 (M^+, 1%), 288 (M − CH_3CONH_2, 2), 148 (75), and 106 (100); $\nu_{max.}$($CHCl_3$) 3 420, 3 000, 1 670, 1 510, 1 490, 1 430, 1 230, 1 200, 1 070, and 1 030 cm^{-1}; δ_H 1.84 (3 H, s), 4.63 (1 H, d, J 6 Hz), 5.52 (1 H, dd, J 9 and 6 Hz), 6.56 (1 H, d, J 9 Hz), and 7.1—7.3 (15 H, complex).

A similar addition to *cis*-stilbene afforded compound (**31**) in 37% yield.

1-*Acetamido*-3-*acetoxy*-1-*phenyl*-2-*phenylthiopropane* (**32**). Diphenyl disulphide (1.08 g) was oxidised by lead tetra-acetate (2.46 g) in the presence of cinnamyl acetate (1.01 g) by the above procedure. After work-up and reaction with CH_3CN–H^+, further work-up and column chromatography (eluant ether) afforded, as an oil, 1-acetamido-3-acetoxy-1-phenyl-2-phenylthiopropane (**32**) (1.80, 99% w.r.t. diphenyl disulphide); m/z 284 (4%), 174 (46), 148 (72), 136 (46), and 106 (100); δ_H 1.94 (3 H, s), 1.97 (3 H, s), 3.86 (1 H, m), 4.18 (2 H, m), 5.49 (1 H, dd, J 8 and 5 Hz), and 7.2—7.4 (10 H, complex). Hydrolysis of compound (**32**) (2M KOH in ethanol) afforded 3-*acetamido*-3-*phenyl*-2-*phenylthiopropan*-1-*ol* (**34**), characterised as a 3,5-dinitrobenzoate with m.p. 141—142 °C (from dichloromethane–pentane) (Found: C, 58.0; H, 4.3; N, 8.3. $C_{23}H_{21}N_3O_6S$ requires C, 58.2; H, 4.3; N, 8.5%); δ_H 2.05 (3 H, s), 4.15 (1 H, dt, J 6, 5, and 5 Hz), 4.58 (2 H, d, J 6 Hz), 5.60 (1 H, dd, J 8 and 5 Hz), 6.65 (1 H, d, J 8 Hz), 7.2—7.5 (10 H, complex), 8.95 (2 H, d), and 9.20 (1 H, t).

5-*Acetamido*-6-*phenylthiohex*-1-*ene* (**17**). Diphenyl disulphide (1.05 g) was oxidised by lead tetra-acetate (2.17 g) in the presence of hexa-1,5-diene (583 mg) by the above procedure. After work-up and reaction with CH_3CN–H^+, further work-up and chromatography (eluant ether) afforded, as an oil, 5-*acetamido*-6-*phenylthiohex*-1-*ene* (**17**) (130 mg, 11% w.r.t. diphenyl-disulphide) (Found: M^+, 249.1093. $C_{14}H_{19}NOS$ requires M, 249.1102); m/z 249 (M^+, 7%), 191 (13), 190 (88), 149 (73), 126 (16), 123 (21), 110 (17), 109 (19), and 84 (100); $\nu_{max.}$(film) 3 300 and 1 660 cm^{-1}; δ_H 1.5—2.5 (7 H, complex), 3.08 (2 H, d, J 6 Hz), 4.18 (1 H, m), 4.96 (2 H, m), 5.75 (1 H, m), 6.0 (1 H, br), and 7.1—7.5 (5 H, complex).

1-*Acetamido*-2-*phenylthioethane* (**18**). Diphenyl disulphide (1.0 g) was oxidised by lead tetra-acetate (2.45 g) in the presence of ethene (bubbled continuously through the reaction mixture) by the above procedure. After work-up and reaction with CH_3CN–H^+, further work-up and column chromatography (eluant ether) afforded 1-acetamido-2-phenylthioethane (**18**) (38 mg, 4% w.r.t. diphenyl disulphide). The sample was identical with compound (**18**) obtained by anodic oxidation.[2]

trans-1-*Acetamido*-2-*benzylthiocyclohexane* (**5**). Dibenzyl disulphide (1.36 g) was oxidised by lead tetra-acetate (2.87 g) in the presence of cyclohexene (730 mg) by the above procedure. After work-up and reaction with CH_3CN–H^+, further work-up and column chromatography (eluant ether) afforded *trans*-1-acetamido-2-benzylthiocyclohexane (**5**) (260 mg, 18% w.r.t. dibenzyl disulphide). The sample was identical (^{1}H n.m.r., i.r., m.s., t.l.c., and m.p.) to a sample obtained by anodic oxidation.[2]

2-*Phenylthioethylamine* (**19**). A solution of 1-acetamido-2-phenylthioethane (**18**) (1.23 g) in propionic acid (10 ml) containing conc. hydrochloric acid (1 ml) was heated under reflux for 3 days. The reaction mixture was poured into water, neutralised with solid sodium carbonate, and the organic products were extracted into dichloromethane. Work-up afforded, as a yellow oil, 2-phenylthioethylamine (**19**) (524 mg, 54%), m/z 136 (26%), 123 (10), and 44 (100); $\nu_{max.}$(film) 3 360, 3 280, and 1 660 cm^{-1}; δ_H 3.02 (2 H, m), 3.64 (2 H, m), and 7.1—7.4 (5 H, complex).

2-*Benzylthioethylamine* (**20**). A solution of 1-acetamido-2-benzylthioethane[2] (1.65 g) in ethylene glycol (75 ml) containing potassium hydroxide (12.5 g) was heated under reflux for 4 h. The reaction mixture was poured into water and worked up *via* extraction with chloroform to afford 2-benzylthioethylamine (**20**) (900 mg, 69%) as a yellow oil (Found: M^+, 167.0666. $C_9H_{13}NS$ requires M, 167.0676); m/z 167 (M^+, 0.1%), 150 (1.5), and 91 (100); $\nu_{max.}$(film) 3 300 and 1 670 cm^{-1}; δ_H 2.80 (2 H, m), 3.7 (2 H, br), 3.58 (2 H, m), 3.97 (2 H, s), and 7.1—7.4 (5 H, complex); δ_C 32.4 (CH_2), 50.1 (CH_2), 58.9 (CH_2), and 128.4, 128.5, 129.0, and 130.2 p.p.m. (aromatic C).

Reductive Cleavage of trans-1-*Acetamido*-2-*benzylthiocyclohexane* (**5**).—To the dark blue solution of sodium (1 g) in dry liquid ammonia (100 ml) was slowly added a solution of *trans*-1-acetamido-2-benzylthiocyclohexane (**5**) (2.65 g) in tetrahydrofuran (25 ml) and t-butyl alcohol (1 ml). After the mixture had been stirred for 1 h ammonium chloride and then ether were added and the reaction mixture was allowed to warm to room temperature. Work-up and flash chromatography [eluant ether–methanol (19:1)] afforded two fractions. Recrystallis-

ation (pentane–CH_2Cl_2) of the less polar fraction afforded *cis*-2-acetamidocyclohexanethiol (**36**) (830 mg) as a white solid, m.p. 119—121 °C; $\nu_{max.}$($CHCl_3$) 3 440 and 1 670 cm^{-1}; δ_H 1.2—1.9 (8 H, complex), 2.13 (3 H, s), 2.50 (1 H, m), 3.88 (1 H, m), and 7.36 (1 H, *d*); δ_C 23.4 (CH_3), 24.8 (CH_2), 26.1 (CH_2), 33.8 (CH_2), 34.4 (CH_2), 50.0 (CH), 55.2 (CH), and 170.2 p.p.m. (CO); *m/z* 114 (98%), 81 (75), 60 (100), and 43 (55). Recrystallisation (pentane–CH_2Cl_2) of the more polar fraction afforded *trans*-2-acetamidocyclohexanethiol (**7**) (744 mg) as a white solid, m.p. 149—150 °C; $\nu_{max.}$ 3 320 and 1 660 cm^{-1}; δ_H 1.2—1.9 (8 H, complex), 2.04 (3 H, s), 2.65 (1 H, m), 3.67 (1 H, m), and 6.38 (1 H, br); δ_C 23.3 (CH_3), 25.0 (CH_2), 26.2 (CH_2), 33.5 (CH_2), 36.9 (CH_2), 43.5 (CH), 55.7 (CH), and 170.4 p.p.m. (CO); (Found: M^+, 173.0741. $C_8H_{15}NOS$ requires *M*, 173.0754); *m/z* 173 (M^+, 7%), 172 (40), 140 (93), 114 (15), 98 (100), and 60 (96).

Reductive Cleavage of 1-*Acetamido*-2-*benzylthio*-1-*phenylethane* (**15**).—1-Acetamido-2-benzylthio-1-phenylethane (**15**) (1.37 g) was reduced by the above procedure with sodium (450 mg) in liquid ammonia (100 ml). Work-up and chromatography afforded, as a yellow oil, 2-acetamido-2-phenylethanethiol (**21**) (325 mg, 35%) (Found: M^+ 195.0724. $C_{10}H_{13}NOS$ requires *M*, 195.0718); *m/z* 195 (M^+, 3%), 161 (2), 148 (64), 136 (11), 106 (100), and 43 (32); $\nu_{max.}$(film) 3 280 and 1 650 cm^{-1}; δ_H 2.00 (3 H, s), 2.88 (2 H, m), 5.04 (1 H, dt, *J* 8, 7, and 7 Hz), 7.2—7.4 (5 H, complex), and 7.5 (1 H, br); δ_C 13.5 (CH_3), 55.9 (CH), 58.4 (CH_2), 126.9, 127.5, 128.6, and 140.9 (aromatic C), and 170.4 p.p.m. (CO).

Reductive Cleavage of 2-*Acetamido*-1-*benzylthio-octane* (**14**).—2-Acetamido-1-benzylthio-octane (**14**) (830 mg) was reduced by the above procedure with sodium (250 mg) in liquid ammonia (100 ml). Work-up and purification by chromatography afforded a white solid. Recrystallisation (pentane–CH_2Cl_2) gave 2-*acetamido-octane*-1-*thiol* (**22**) (410 mg, 71%), m.p. 59—60 °C (Found: M^+, 203.1274. $C_{10}H_{21}NOS$ requires *M*, 203.1281); *m/z* 203 (M^+, 0.1%), 156 (29), and 114 (100); $\nu_{max.}$($CHCl_3$) 3 420, 3 310, and 1 660 cm^{-1}; δ_H 0.86 (3 H, t), 1.1—1.4 (10 H, complex), 1.5 (1 H, br), 2.00 (3 H, s), 2.56 (2 H, dd, *J* 9 and 5 Hz), 4.00 (1 H, m), and 6.52 (1 H, br); δ_C 14.1 (CH_3), 22.6 (CH_2), 23.3 (CH_2), 26.0 (CH_2), 29.1 (CH_2), 31.7 (CH_2), 32.7 (CH_2), 50.4 (CH), and 170.1 p.p.m. (CO).

Reductive Cleavage of 1-*Acetamido*-2-*benzylthioethane*.—1-Acetamido-2-benzylthioethane (1.78 g) was reduced by the above procedure with sodium (0.5 g) in liquid ammonia (100 ml). Work-up afforded, as a yellow oil, 2-acetamidoethanethiol[8] (**23**) (557 mg, 55%) (Found: M^+, 119.0458. Calc. for C_4H_9NOS: *M*, 119.0453); *m/z* 119 (M^+, 3%), 85 (15), 60 (52), 59 (89), and 43 (100); $\nu_{max.}$(film) 3 290 and 1 665 cm^{-1}; δ_H 2.02 (3 H, s), 2.85 (2 H, t, *J* 8 Hz), 3.55 (2 H, m), and 6.42 (1 H, br).

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