Reactions of Relevance to the Chemistry of Aminoglycoside Antibiotics. Part 9.† New Reagents for Amination of the Ethylenic Linkage

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Treatment of disulphides, especially diphenyl disulphide, with chloramine-T affords a series of reagents which react with olefins to give adducts. These reactions are electrophilic in nature, with PhS^+ initiating the reaction and a complex nitrogen anion terminating the process. Similar, but less extensive, experimentation has been carried out with diselenides, especially diphenyl diselenide. These new reagents provide a novel procedure for the amination of the ethylenic linkage.

SELENO- AND SULPHO-DI-IMIDES have recently been utilized to effect allylic amination of olefins [1-3] and 1,2-diamination of 1,3-dienes,[4] and chloramine-T (*N*-chloro-*N*-sodio-4-methylbenzenesulphonamide) in the presence of osmium tetraoxide has been shown to cause stereospecific *cis* vicinal oxyamination of olefins.[5] We now report a simple method of 1,2-*trans*-thio- and seleno-amination of olefins based on the ' oxidative imination ' of disulphides and diselenides with chloramine-T. These new methods are, in principle, applicable to partial syntheses of aminoglycoside antibiotics.

Diphenyl disulphide (1) reacted with anhydrous chloramine-T (5) in acetone to give a crystalline product $(PhSSPh)(NTs)_2$ [(6), (7), or (8)], m.p. 125—130° (decomp.) (Scheme 1), analogous to the product [(9), (10), or (11)] obtained by Levchenko *et al.*[6] from diphenyl disulphide and *N*-chloro-*N*-sodiobenzenesulphonamide. It was difficult to assign a definite structure to the latter compound.

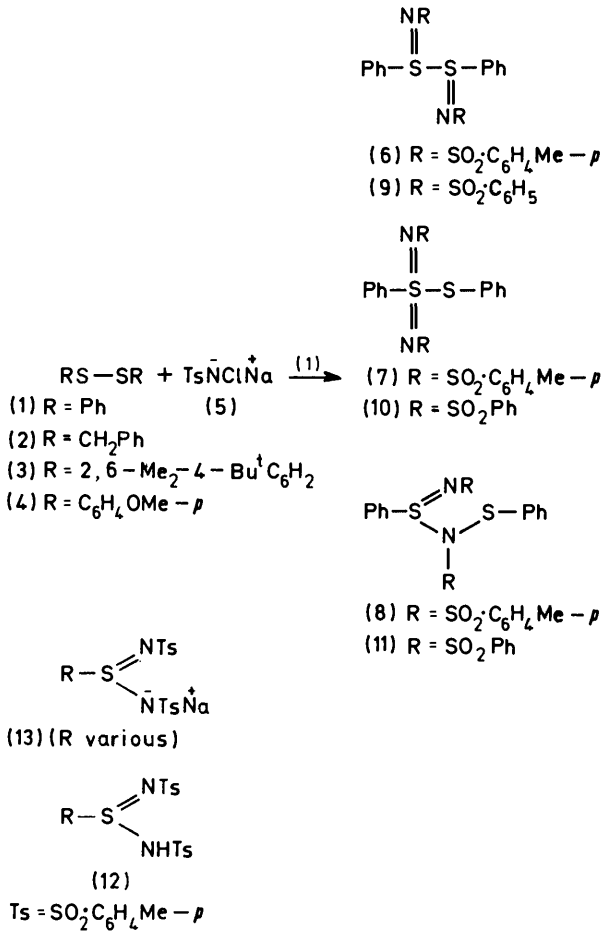
We observed the same difficulty of structural assignment with the adduct [(6), (7), or (8)]. However, the disulphimide structure (6) could be ruled out because sodium borohydride reduced the adduct to material which after reoxidation afforded diphenyl disulphide and the sodium salt of the benzenesulphinamidine [type (13)], indicating that one of the sulphur atoms had not been oxidised.

The adduct effected a stereospecific *trans*-1,2-addition to cyclohexene at room temperature, affording the phenylthiocyclohexyl-sulphinamidine (16) (40%)

† Part 8, D. H. R. Barton, P.-E. Hansen, and K. Picker, *J.C.S. Perkin I*, 1977, 1723.

[1] N. Schönberger and G. Kresze, *Annalen*, 1975, 1725.
[2] K. B. Sharpless and T. Hori, *J. Org. Chem.*, 1976, **41**, 176.
[3] K. B. Sharpless, T. Hori, L. K. Truesdale, and C. O. Dietrich, *J. Amer. Chem. Soc.*, 1976, **98**, 269.
[4] K. B. Sharpless and S. P. Singer, *J. Org. Chem.*, 1976, **41**, 2504.
[5] K. B. Sharpless, A. O. Chong, and K. Oshima, *J. Org. Chem.*, 1976, **41**, 177.
[6] E. S. Levchenko and L. V. Seleznenko, *J. Org. Chem.* (*U.S.S.R.*), 1970, **6**, 486.

(Scheme 2). The insensitivity of the reaction to molecular oxygen and the exclusive formation of the *trans*-product strongly indicated ionic addition *via* an intermediate sulphonium species (14). This suggests that the sulphinamidine ion (15) forms additional bonds on nitrogen more readily than on sulphur. We favour structure



SCHEME 1

(8) for our reagent and structure (11) for the product described earlier.

Reduction of (16) with sodium borohydride afforded the amido-sulphide (17), the structure and stereochemistry of which were established by reactions outlined in Scheme 2. Treatment of cyclohexene with *NN*-dibromo-4-methylbenzenesulphonamide (18) [7] afforded the *trans*-derivative (19), which was converted smoothly into the aziridine (20) with base.[8] Cleavage of the aziridine with phenyl sulphide ion in a 1,2-*trans*-diaxial manner gave the amido-sulphide (17) exclusively. Oxidation of the amido-sulphide with 3-chloroperbenzoic acid followed by treatment of the intermediate sulphoxide (21) with acetic anhydride [9] and hydrolysis afforded, instead of the expected cyclohexanone derivative, the vinyl sulphide (22), a result with some precedent.[10,11]

Further evidence that the sulphur reagent (8) operates ionically was obtained by reaction with cholest-2-ene (24) (Scheme 3). Preferential attack of the sulphur electrophile from the less hindered α-face and *trans*-diaxial opening [12] of the resulting sulphonium species by the sulphinamidine (15) led to the unstable intermediate (25) which, no doubt owing to steric compression, cleaved spontaneously to give the imine (26) (M^+ 647). Reduction of the latter with sodium borohydride afforded the amido-sulphide (27) (M^+ 649). Since half-band widths [13] in the n.m.r. spectrum did not permit stereochemical conclusions (chemical shifts of H-2 and H-3 coincide, δ 3.63—3.3) confirmation of structure (27) was sought by synthesis (Scheme 3).

Methyl (3α-iodocholestan-2β-yl)carbamate (29) [14] was deiodinated with tri-n-butyltin hydride [15,16] to the carbamate (30), which was hydrolysed to the 2β-amine (31).[17] Tosylation provided authentic 2β-(4-methylphenylsulphonylamino)cholestane (28), $[\alpha]_D$ +36.2°. The amido-sulphide (27) was then desulphurised [18] with Raney nickel, and the product (28) was identical with the above.

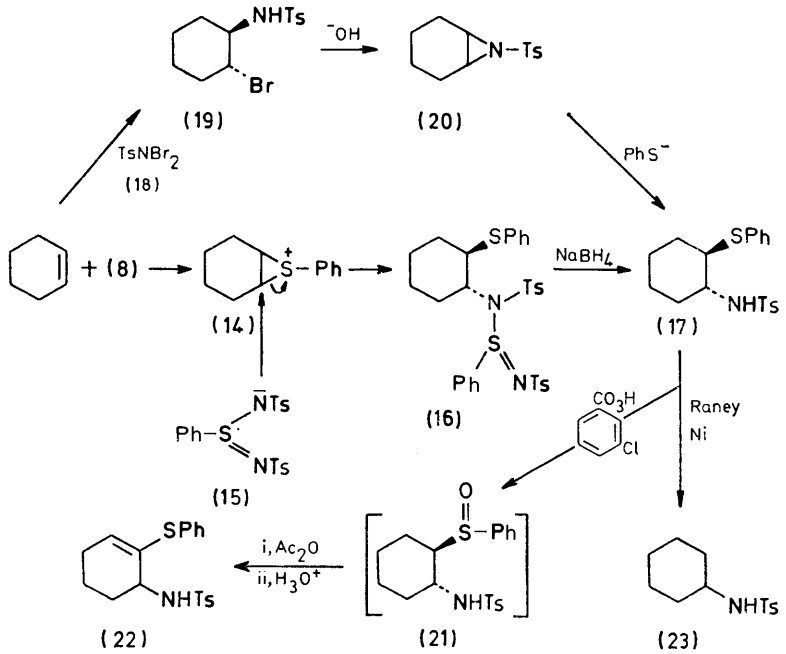
In a parallel synthesis, cholest-2-ene (24) was converted with *NN*-dibromo-4-methylbenzenesulphonamide (18) into the intermediate *N*-bromo-derivative (32) which, on reduction with iodide ion, afforded (33). The *trans*-diaxial relationship of substituents was again proved by conversion into the 2β,3β-aziridine (34) with base. A similar transformation was effected with tri-n-butyltin hydride, possibly reflecting an ionic bromide abstraction in contrast with the more commonly encountered free radical reaction.[19] α-Attack of benzenethiolate ion on the aziridine (34) gave exclusively the amido-sulphide (27), identical with that previously described. Stereochemical assignment of products in the above synthetic sequence was confirmed by reduction (lithium aluminium hydride) of the aziridine affording the 2β-derivative (28).

Reaction of the adduct (8) with 2,3-dihydropyran (35) followed by reduction of the resulting mixture with sodium borohydride afforded, rather unexpectedly, the amido-pentanol (39) [characterised as its 3,5-dinitro-

[7] Y. Ueno, S. Takemura, Y. Ando, and H. Zerauchi, *Chem. and Pharm. Bull. (Japan)*, 1967, **15**, 1193.
[8] G. L. Closs and S. J. Brois, *J. Amer. Chem. Soc.*, 1960, **82**, 6068.
[9] R. Pummerer, *Ber.*, 1909, **42**, 2282; 1910, **43**, 1401.
[10] W. E. Parhan and R. Koncos, *J. Amer. Chem. Soc.*, 1961, **83**, 4034.
[11] W. E. Parhan, L. Christensen, S. H. Groen, and R. M. Dobson, *J. Org. Chem.*, 1964, **29**, 2211.
[12] D. H. R. Barton and R. C. Cookson, *Quart. Rev.*, 1956, **10**, 44.
[13] A. Hassner and C. C. Heathcock, *Tetrahedron Letters*, 1964, 1125; *J. Org. Chem.*, 1964, **29**, 1350.
[14] A. Hassner and C. C. Heathcock, *J. Org. Chem.*, 1965, **30**, 1748.
[15] H. G. Kuivila, L. W. Menapace, and C. R. Warne, *J. Amer. Chem. Soc.*, 1962, **84**, 3854.
[16] H. G. Kuivila and L. W. Menapace, *J. Org. Chem.*, 1963, **28**, 2165.
[17] C. W. Shoppee, J. G. Feher, R. M. Hall, R. E. Lack, and L. Tarasoff, *J. Chem. Soc.* (*C*), 1968, **17**, 2211.
[18] G. M. Badger, H. J. Rodda, and W. H. F. Sasse, *J. Chem. Soc.*, 1954, 4162.
[19] H. G. Kuivilla, *J. Org. Chem.*, 1961, **25**, 284.

benzoate (42)] instead of the expected amido-sulphide (37) (Scheme 4). The initially formed intermediate sulphinamidine (36) is reduced to the anion of the amido-sulphide (37), which is reductively cleaved to the imine (38), which affords the amido-alcohol (39).

The mechanism of this borohydride-induced cleavage of N–C–O bonds is similar to the recently observed reductive rupture of N–C–N bonds during biomimetic chiral synthesis of *Cinchona* alkaloids.[20] It was also confirmed by treatment of 2-(4-methylphenylsulphonylamino)tetrahydropyran (46) with sodium borohydride to give the alcohol derivative (40) exclusively.



SCHEME 2

Desulphurisation of the 4-(phenylthio)-alcohol (39) with Raney nickel afforded the amido-alcohol (40), which was fully characterised as the crystalline ditosyl derivative (41).

The ready cleavage of the aziridines (20) and (34) with benzenethiolate ion prompted us to consider a similar approach with dihydropyran. The latter was treated with *NN*-dibromo-4-methylbenzenesulphonamide (18) to give both the *trans*- (44) and the *cis*-derivative (45), similar to the analogues obtained by Takemura *et al.*[21] on treatment of dihydropyran with *NN*-dibromobenzenesulphonamide. Both isomers were debrominated with tri-n-butyltin hydride to the sulphonamide (46).[22]

The *trans*-isomer (44) was smoothly converted into the amido-sulphide (47) with benzenethiolate ion, thus providing an efficient method of introducing C-3 nitrogen functionality into the dihydropyran nucleus. Competitive ring opening did not occur, reflecting stereochemical preference for aziridine formation and subsequent effective trapping of the latter with the sulphur nucleophile.

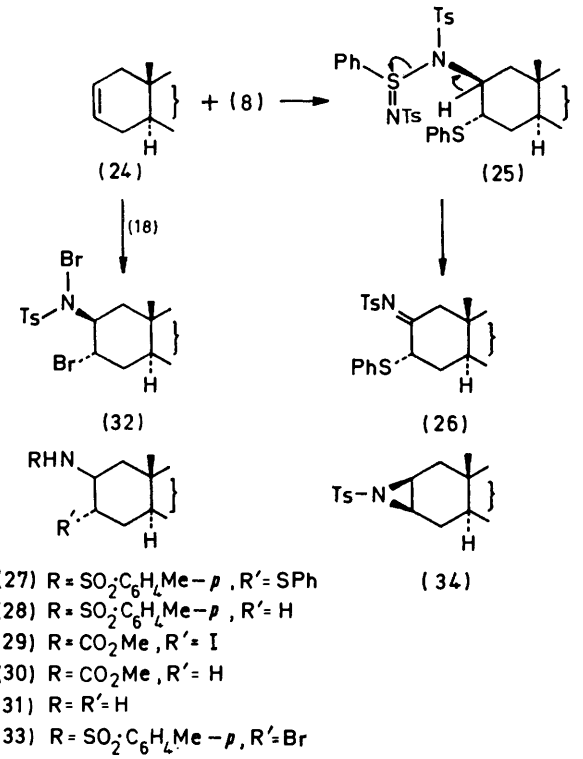
Desulphurisation of the amido-sulphide (47) with Raney nickel in ethanol gave the sulphonamide (50) and the 2-ethoxy-derivative (49). Formation of the latter reflects an ionic benzenethiolate abstraction followed by attack of ethanol on the intermediate oxonium species (48).

Treatment of the *cis*-derivative (45) with diphenyl disulphide–sodium borohydride also gave the amido-alcohol (39). The formation of this involves nucleophilic displacement of bromide by benzenethiolate ion followed by reductive cleavage of the N–C–O system or *vice versa*. The alcohol (39) was again characterised as the 3,5-dinitrobenzoate (42) and desulphurised to the 5-aminopentanol derivative (40). The terminal oxygen–nitrogen relationship was finally proved by comparing the ditosyl derivative (41) with an authentic sample, prepared by ditosylation of 5-aminopentan-1-ol (43).

In contrast with diphenyl disulphide, the disulphides (2)—(4) were oxidised by anhydrous chloramine-T to the corresponding amidinium salts of type (13) [23,24] (Scheme 1). On acidification these gave sulphinamidines of type (12).

However, stereospecific *trans*-1,2-thioamination was effected when the disulphides (2) and (4) and di-n-butyl disulphide were separately treated with chloramine-T in the presence of cyclohexene (Scheme 5). Reduction with sodium borohydride afforded the amido-sulphides (51)—(53), the structures and stereochemistry of which

[20] K. Murato, T. Shiori, and S. I. Yamada, *Chem. and Pharm. Bull.* (*Japan*), 1977, **25**, 1559.
[21] S. Takemura, K. Otsuki, K. Okamoto, and Y. Ueno, *Chem. and Pharm. Bull.* (*Japan*), 1968, **16**, 1881, 1885.
[22] A. J. Speziale, K. W. Ratts, and G. J. Maxo, *J. Org. Chem.*, 1961, **26**, 4311.
[23] I. R. Alexander and H. McCombie, *J. Chem. Soc.*, 1932, 2087.
[24] G. Bullmer and F. G. Mann, *J. Chem. Soc.*, 1945, 666.



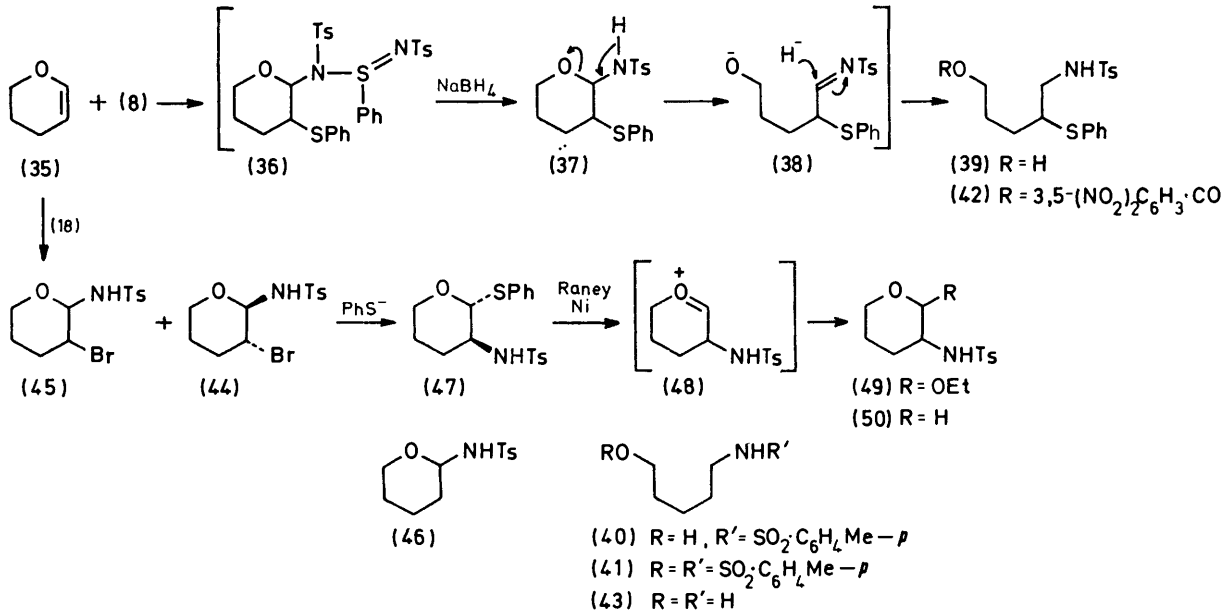
SCHEME 3

were again determined by reactions of the appropriate sulphide ion with the aziridine (20).

The oxidation of diselenides [25] invariably causes fission of the Se–Se bond. When diphenyl diselenide (54) was treated with anhydrous chloramine-T at room temperature in dichloromethane a vigorous reaction occurred, accompanied by effervescence. The products are shown in Scheme 6, suggesting that a free radical reaction was occurring.

It seems reasonable to suggest that the diselenide is oxidised twice to afford an intermediate diselenimide (55), which may fragment to give a nitrogen-centred radical (57), either directly (route i) or after rearrangement to the selenoseleninamidine (56) (route ii). Dimerisation of the radical (57) would lead to the tetrasubstituted hydrazine (58), which would decompose to afford nitrogen, phenylseleno radical, and 4-methylbenzenesulphonyl radical (59). The products formed, (60)—(62), are consistent with Scheme 6. In an attempt to trap intermediates, the reaction was performed in the presence of a number of olefins. If the radical intermediate (57) is trapped, the product of addition to the olefin would be the selenenamide (64) (Scheme 7). In this case, one would expect a mixture of *cis*- and *trans*-addition products, attachment of the amide function to the less hindered end of an unsymmetrical olefin, and sensitivity of the reaction to the presence of molecular oxygen.

Alternatively, ionic addition of the seleno-seleninamide (56) would lead to a phenylseleno-seleninamidine (66) *via* attack of seleninamidine ion on an intermediate selenonium species (65). Here one would expect exclusive Markownikoff *trans*-addition and failure of the reaction with electron-deficient olefins. The results of the reactions with a variety of alkenes are presented in the Table.

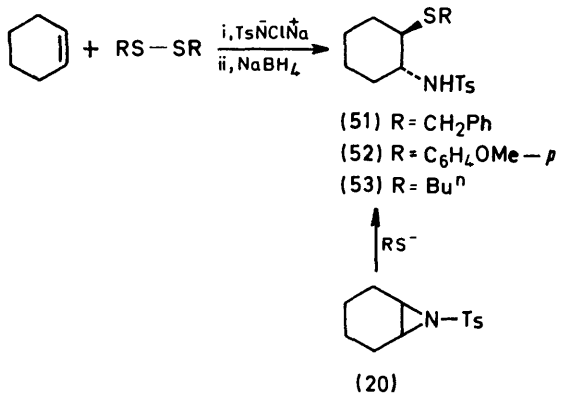


SCHEME 4

The initial product of addition to cyclohexene is a very polar, unstable compound which could not be isolated. Treatment with sodium borohydride gave the *trans*-1,2-amido-selenide (67), thus supporting a stereospecific ionic mechanism. Attempts at isolating the primary

[25] For a review, see D. S. Klayman, 'Organic Selenium Compounds: their Chemistry and Biology,' eds. D. S. Klayman and W. H. H. Günther, Wiley–Interscience, New York, 1974, p. 97.

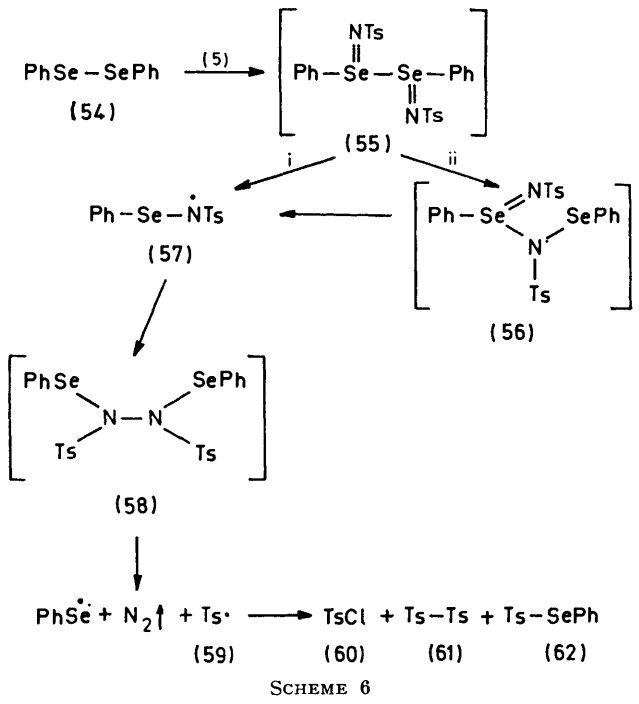
product chromatographically as in the sulphur case also led to (67), indicating decomposition of an intermediate seleninamidine of type (66) on silica to the stable amido-selenide. The reaction is not inhibited by the presence



SCHEME 5

of oxygen, nor was the yield significantly improved when the reaction was performed under an inert atmosphere. This strongly indicates that intermediate carbon radicals such as (63) are not involved.

The structure and stereochemistry of the amido-



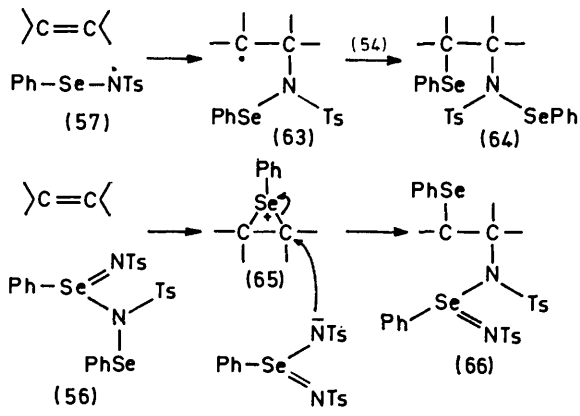
SCHEME 6

selenide (67) derived from cyclohexene were established by the reactions shown in Scheme 8. The reaction of (67) with benzoyl peroxide to give (74) on work-up is interesting.

The product (69) from oct-1-ene (68) can be compared with that obtained from the addition of sulphenyl chlorides (75) to terminal olefins (76; R′ = alkyl [26]). It

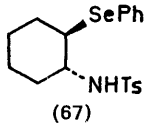
[26] W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, 1968, **90**, 2075.

is proposed that the reaction proceeds *via* an intermediate sulphonium ion (77), and that the ratio of



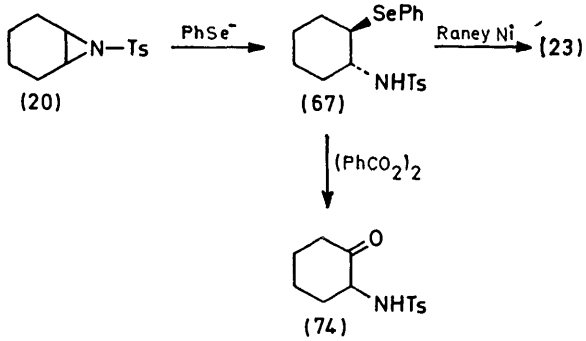
SCHEME 7

addition products (78) and (79) depends on the relative rates of reaction of chloride ion at the ring carbon positions in (77). The *anti*-Markownikoff adduct (79)

Olefin	Product	Yield (%) *
	 (67)	40
$CH_3[CH_2]_5CH{=}CH_2$ (68)	$CH_3[CH_2]_6CH_2{\cdot}NHTs$ (69)	45 †
$CH_2{=}CH{\cdot}CN$ (70)	$PhSe{\cdot}CH_2{\cdot}CH_2{\cdot}CN$ (71)	15
$PhCH{=}CH_2$ (72)	$PhCH(NHTs){\cdot}CH_2{\cdot}SePh$ (73)	62

* After reduction of primary product with sodium borohydride. † The intermediate amido-selenide was not characterised but was deselenated with nickel boride.

predominates, and the effect becomes more marked with increasing size of R′. Similar product distributions are observed with analogous reagents.[27,28]



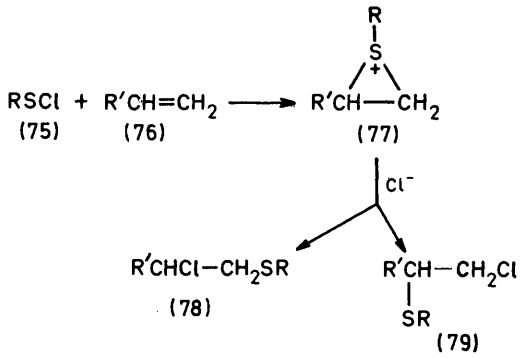
SCHEME 8

The selenium reagent adds to styrene (72) to afford a Markownikoff product (73). This is good evidence for an ionic mechanism.[26]

[27] G. H. Schmid and D. G. Garratt, ' Double Bonded Functional Groups,' Supplement A, ed. S. Patai, Wiley, New York, 1976, p. 1725.

[28] D. G. Garratt and G. H. Schmid, *J. Org. Chem.*, 1977, **42**, 1776.

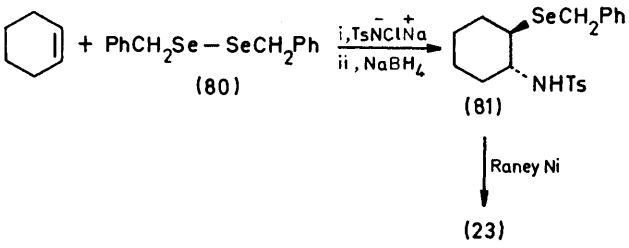
Acrylonitrile (70) would not be expected to undergo electrophilic addition. The failure of the reaction to give an amido-selenide addition product is therefore in accord with an electrophilic mechanism. The product obtained was a 3-phenylselenopropiononitrile (71), which probably arises from 1,4-Michael addition of



benseneselenolate ion, generated during work-up with sodium borohydride. This was confirmed by synthesis of (71) as above, omitting chloramine-T.

Reaction of chloramine-T with dibenzyl diselenide (80) in the presence of cyclohexene gave a seleniferous product which afforded (81) on reduction with sodium borohydride. Deselenation with nickel boride gave *N*-cyclohexyl-4-methylbenzenesulphonamide (23).

The reagents described in this paper provide novel



ways for tosylamination of the ethylenic linkage. Since tosylamides are readily converted into amines, these reagents may be useful in the chemistry of the aminoglycoside antibiotics.

EXPERIMENTAL

M.p.s were determined with a Reichert hot-stage apparatus. ^{1}H N.m.r. spectra were recorded on a Varian T60 spectrometer for solutions in $CDCl_3$ (unless stated otherwise) with Me_4Si as internal standard and mass spectral data on an A.E.I. MS9 instrument. I.r. and u.v. spectra were recorded with Perkin-Elmer 257 and Unicam SP 800B spectrophotometers, respectively. Column chromatography was performed on silica gel M.F.C. (75—150 nm; Hopkin and Williams). T.l.c. and p.l.c. were carried out on Merck Kieselgel GF_{254} (0.2 and 1 mm layers, respectively). Organic solvent extracts were washed with water (3 ×), dried ($MgSO_4$), and evaporated under reduced pressure. Disulphides and diselenides, when not available commercially, were prepared by standard methods.[29-31]

Bis-(2,6-dimethyl-4-t-butylphenyl) Disulphide (3).—2-Bromo-1,3-dimethyl-5-t-butylbenzene (2.4 g) and ethyl bromide (2.2 g) in dry ether (40 ml) were added to magnesium ribbon (0.7 g) under ether (10 ml) and the mixture was stirred under gentle reflux for 1 h. Sulphur (0.96 g) was added and refluxing continued for a further hour. The mixture was poured onto ice (100 ml) and N-hydrochloric acid (100 ml) added. The layers were separated and the aqueous layer washed with ether (100 ml). The combined etheral layers were concentrated to a yellow oil (1.8 g). Column chromatography (petroleum, b.p. 40—60 °C) gave starting material (6%), followed by the *disulphide* (3) (55%), m.p. 127—128° (from ethanol), δ(CCl_4) 6.87 (4 H, s), 2.17 (12 H, s), and 1.27 (18 H, s), *m/e* 386 (M^+) and 193 ($M - C_{12}H_{17}S$) (Found: C, 74.65; H, 8.9; S, 16.65. $C_{24}H_{34}S_2$ requires C, 74.55; H, 8.9; S, 16.6%).

Bis-(4-methoxyphenyl) Disulphide (4).—1-Bromo-4-methoxybenzene (4.65 g) was treated with magnesium (0.607 5 g) and sulphur (0.8 g) in dry ether (50 ml) as described above to afford the disulphide (4) as a yellow oil (90%) (lit.,[32] m.p. 119°; lit.,[33] 44—45°), *m/e* 278 (M^+), 246, and 139 (Found: C, 60.45; H, 4.95. Calc. for $C_{14}H_{14}O_2S_2$: C, 60.45; H, 5.05%).

Oxidations of Disulphides and Diselenides with N-Chloro-N-sodio-4-methylbenzenesulphonamide

The trivial name chloramine-T for *N*-chloro-*N*-sodio-4-methylbenzenesulphonamide (5) is used throughout.

With Diphenyl Disulphide (1).—Diphenyl disulphide (1) (2.18 g) and anhydrous chloramine-T (4.56 g) were stirred in dry acetone (50 ml) on ice for 3 h. The solvent was removed under reduced pressure, and the residue taken up in dichloromethane (50 ml) and filtered through Celite. Ether (100 ml) was added, and the solution concentrated to give a pale yellow crystalline *product* (8) (PhSSPh)$(NTs)_2$ (5.01 g, 91%), m.p. 125—130° (decomp.), $\nu_{max.}$ (Nujol) 2 990—2 890, 1 470, 1 390, 1 175, 1 155, 1 100, 1 020, 900, and 680 cm^{-1}, δ 7.9—6.9 (18 H, complex) and 2.45 (6 H, s), *m/e* 387 ($M - C_7H_7NO_2S$) (Found: C, 55.8; H, 4.7; N, 5.0. $C_{26}H_{24}N_2O_4S_4$ requires C, 56.1; H, 4.35; N, 5.05%).

Repeated crystallisation from dichloromethane–ether gave a paler yellow specimen, m.p. 121—124° (decomp.), with identical i.r., n.m.r., and mass spectra (Found: C, 56.0; H, 4.3; N, 4.95; S, 22.7%).

A suspension of the adduct (8) (278 mg) in ethanol (5 ml) was treated with sodium borohydride (20 mg) and stirred for 15 min. The clear solution was concentrated to an oil, which was taken up in dichloromethane (40 ml) and filtered through Celite. Ether (20 ml) was added and the solution concentrated to give *S*-phenyl-*S*-(*N*-sodio-4-methylphenylsulphonylamino)-*N*-(4-methylphenylsulphonyl)sulphimide (13; R = Ph) (88%), m.p. 228—230° (lit.,[34] 226°). The mother liquor was concentrated and crystallised from methanol to give diphenyl disulphide (1) (77%).

With Dibenzyl Disulphide (2).—Dibenzyl disulphide (2) (984 mg) and chloramine-T (1.824 g) in acetone (20 ml) were stirred at room temperature for 2 h. Work-up as

[29] D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Filder, *J. Amer. Chem. Soc.*, 1951, **73**, 3627.
[30] A. Schönberg, E. Singer, E. Frese, and K. Praefcke, *Chem. Ber.*, 1965, **98**, 3311.
[31] D. L. Klayman and T. S. Griffin, *J. Amer. Chem. Soc.*, 1973, **95**, 197.
[32] L. Colichman and D. L. Dove, *J. Amer. Chem. Soc.*, 1953, **75**, 5736.
[33] E. Vinkler and F. Klivenyi, *Acta Chim. Acad. Sci. Hung.*, 1954, **5**, 159.
[34] S. G. Clarke, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 1930, 1225.

above afforded a white amorphous powder which was dissolved in water (25 ml); 3N-hydrochloric acid (10 ml) was added and the mixture was extracted with dichloromethane (3 × 25 ml). Evaporation, and recrystallisation of the residue from ethanol gave *S*-benzyl-*S*-(4-methylphenylsulphonylamino)-*N*-(4-methylphenylsulphonyl)sulphimide (12; R = CH_2Ph) (941 mg, 50%), m.p. 169.5—170.5° (lit.,[24] 171—171.5°).

With Bis-(2,6-dimethyl-4-t-butylphenyl) Disulphide (3).—The disulphide (3) (386 mg) in acetone (5 ml) was treated with chloramine-T (456 mg) for 3 h at room temperature. Work-up as above afforded S-(2,6-*dimethyl*-4-*t*-*butylphenyl*)-S-(4-*methylphenylsulphonylamino*)-N-(4-*methylphenylsulphonyl*)*sulphimide* (12; R = 2,6-Me_2-4-$Bu^tC_6H_2$) (366 mg, 75%), m.p. 156—158° (from ethanol), $\nu_{max.}$ (Nujol) 3 130, 1 585, 1 545, 1 320, 1 220, 1 162, 1 130, 1 035, 920, 867, and 720 cm^{-1}, δ[$(CD_3)_2CO$] 7.68 (4 H, d, *J* 8.5 Hz), 7.27 (4 H, d, *J* 8.5 Hz), 7.3 (1 H, s), 7.18 (1 H, s), 5.6 (NH, s), 2.6 (6 H, s), 2.4 (6 H, s), and 1.29 (9 H, s), *m/e* 363 (*M* − $C_7H_7NO_2S$), 171, and 155 (Found: C, 58.6; H, 6.1; N, 5.25. $C_{26}H_{32}N_2O_4S_3$ requires C, 58.65; H, 6.05; N, 5.35%).

With Bis-(4-methoxyphenyl) Disulphide (4).—The disulphide (4) (556 mg) was treated with chloramine-T (912 mg) in acetone (10 ml) for 3 h on ice. Work-up as above gave a tan amorphous powder which was dissolved in water (20 ml); 3N-hydrochloric acid (10 ml) was added and the mixture extracted with dichloromethane (3 × 25 ml). Evaporation, and recrystallisation of the residue from ethanol afforded *S*-(4-methoxyphenyl)-*S*-(4-methylphenylsulphonylamino)-*N*-(4-methylphenylsulphonyl)sulphimide (12; R = *p*-MeO·C_6H_4) (669 mg, 70%), m.p. 98—100°, $\nu_{max.}$ (Nujol) 3 130, 1 587, 1 570, 1 340, 1 300, 1 260, 1 170, 1 140, 1 070, 980, 850, and 720 cm^{-1}, δ[$(CD_3)_2CO$] 7.73 (6 H, d, *J* 8.5 Hz), 7.3 (4 H, d, *J* 8.5 Hz), 7.1 (2 H, d, *J* 8.5 Hz), 4.71 (NH, s), 3.89 (3 H, s), and 2.43 (6 H, s).

With Diphenyl Diselenide (54).—The diselenide (54) (312 mg) in dichloromethane (5 ml) was treated with anhydrous chloramine-T (456 mg) in portions; vigorous frothing followed each addition. The mixture was concentrated under reduced pressure; p.l.c. (benzene) gave 4-methylbenzenesulphonyl chloride (60) (8% based on chloramine-T), m.p. 66—67°, mixed m.p. 65—66°; bis-(4-methylphenyl) disulphone (61) (<1%), m.p. 220—222° (lit.,[35] 222°); and Se-*phenyl* 4-*methylbenzeneselenosulphonate* (62) (37%), m.p. 77—79°, δ 7.6—7.0 (9 H, complex) and 2.42 (3 H, s), *m/e* 312 (*M*$^+$) (Found: C, 49.9; H, 4.0. $C_{13}H_{12}O_2SSe$ requires C, 50.15; H, 3.9%).

Thio- and Seleno-aminations of Olefins

Cyclohexene

NN′-*Bis*-(4-*methylphenylsulphonyl*)-N-(trans-2-*phenylthiocyclohexyl*)*benzenesulphinamidine* (16).—(PhSSPh)-$(NTs)_2$ (8) (1.112 g) was stirred with cyclohexene (164 mg) in anhydrous acetonitrile (10 ml) at room temperature for 1 h. Evaporation and crystallisation from ethanol gave the *sulphinamidine* (16) as white needles (520 mg, 40%), m.p. 127.5—128.5°, $\nu_{max.}$ (Nujol) 1 600, 1 361, 1 295, 1 160, 1 143, 1 085, 1 010, 918, 856, 820, 755, 710, and 670 cm^{-1}, δ 8.05 (4 H, d, *J* 8.5 Hz), 7.8—6.87 (14 H, complex), 3.87—3.47 (2 H, m), 2.37 (3 H, s), 2.23 (3 H, s), and 2.2—0.6 (8 H, complex), *m/e* 359, 279, 204, and 155 (Found: C, 59.95; H, 5.4; N, 4.15. $C_{32}H_{34}N_2O_4S_4$ requires C, 60.2; H, 5.35; N, 4.4%).

[35] G. Denzer, P. Allen, P. Conway, and J. M. van der Veen, *J. Org. Chem.*, 1966, **31**, 3418.

trans-1-(4-*Methylphenylsulphonylamino*)-2-*phenylthiocyclohexane* (17).—The sulphinamidine (16) (127.6 mg) in ethanol (5 ml) was stirred for 1 h at room temperature with sodium borohydride (15.2 mg). The mixture was poured onto ice containing 3N-hydrochloric acid (5 ml) and extracted with ether (3 × 25 ml). Evaporation of the extract followed by column chromatography (dichloromethane) and crystallisation from ethanol afforded the *amido-sulphide* (17) as white prisms (67 mg, 93%), m.p. 129.5—131°, $\nu_{max.}$ (Nujol) 3 360, 1 595, 1 410, 1 330, 1 160, 1 090, 1 015, 932, 881, 810, 747, and 670 cm^{-1}, δ 7.77 (2 H, d, *J* 8.5 Hz), 7.25 (2 H, d, *J* 8.5 Hz), 7.27 (5 H, s), 5.53 (NH, d, *J* 5.0 Hz), 3.3—2.73 (2 H, m), 2.43 (3 H, s), and 2.45—0.65 (8 H, complex), *m/e* 361 (*M*$^+$), 252, 206, 190, and 155 (Found: C, 63.1; H, 6.45; N, 3.6. $C_{19}H_{23}NO_2S_2$ requires C, 63.15; H, 6.4; N, 3.85%).

N-*Cyclohexyl*-4-*methylbenzenesulphonamide* (23).—The amido-sulphide (17) (180 mg) in ethanol (10 ml) was stirred with Raney nickel W2 [18] (*ca.* 1 g) for 3 h at room temperature. The mixture was filtered through Celite, the solvent evaporated off, and the residue crystallised from petroleum (b.p. 40—60 °C) to give the sulphonamide (23) (118 mg, 92%), m.p. 85° (lit.,[36] 86—87°), mixed m.p. 85—86°.

N-(2-*Phenylthiocyclohex*-2-*enyl*)-4-*methylbenzenesulphonamide* (22).—The amido-sulphide (17) (361 mg) in dichloromethane (10 ml) was treated with 3-chloroperbenzoic acid (173 mg) at room temperature for 1 h. Dichloromethane (50 ml) was added and the mixture washed with 5% sodium carbonate (3 × 25 ml), concentrated, and refluxed with acetic anhydride [9] (10 ml) for 4 h. Water (40 ml) was added, and the solution cooled to room temperature over 1 h with stirring. After extraction with ether (3 × 25 ml) and column chromatography (dichloromethane), the *vinyl sulphide* (22) was obtained as white needles (235 mg, 65%) (from ethanol), m.p. 137—138°, $\nu_{max.}$ (Nujol) 3 240, 1 590, 1 575, 1 350, 1 325, 1 285, 1 150, 1 083, 1 062, 1 000, 915, 880, 840, 810, 745, 690, and 665 cm^{-1}, δ 7.63 (2 H, d, *J* 8.5 Hz), 7.3—6.73 (7 H, complex), 6.23 (1 H, t, *J* 3.5 Hz), 4.81 (NH, d, *J* 5.0 Hz), 3.74—3.4 (1 H, m), 2.38 (3 H, s), and 2.4—1.3 (6 H, complex), *m/e* 359 (*M*$^+$), 204, 188, and 155 (Found: C, 63.7; H, 5.95; N, 3.9. $C_{19}H_{21}NO_2S_2$ requires C, 63.5; H, 5.9; N, 3.9%).

trans-1-*Benzylthio*-2-(4-*methylphenylsulphonylamino*)-*cyclohexane* (51).—Anhydrous chloramine-T (912 mg) was added in portions to a stirred solution of dibenzyl disulphide (2) (496 mg) and cyclohexene (164 mg) in acetonitrile (10 ml) at 0 °C. Stirring was continued for 1 h at 0 °C, followed by 2 h at room temperature. After addition of ethanol (10 ml) and sodium borohydride (152 mg) stirring was continued for 1 h at room temperature; the mixture was poured onto ice containing 3N-hydrochloric acid (5 ml) and extracted with ether (3 × 25 ml). Column chromatography (dichloromethane) gave the *amido-sulphide* (51) as a clear oil (175 mg, 23%), $\nu_{max.}$ (Nujol) 3 270, 1 595, 1 375, 1 325, 1 155, 1 090, 890, 815, 700, and 665 cm^{-1}, δ 7.77 (2 H, d, *J* 8.5 Hz), 7.18 (2 H, d, *J* 8.5 Hz), 7.25 (5 H, s), 5.3 (NH, d, *J* 4.5 Hz), 3.57 (2 H, s), 2.4 (3 H, s), and 3.28—0.67 (10 H, complex), *m/e* 375 (*M*$^+$), 284, 220, 155, and 91 (Found: C, 63.75; H, 6.65; N, 3.75. $C_{20}H_{25}NO_2S_2$ requires C, 64.0; H, 6.7; N, 3.75%).

trans-1-(4-*Methoxyphenylthio*)2-(4-*methylphenylsulphonylamino*)*cyclohexane* (52).—Bis-(4-methoxyphenyl) disulphide (4) (556 mg) was treated as above to afford the *amido-sulphide* (52) (283 mg, 36%), m.p. 102—102.5° (from

[36] D. M. Hall and E. E. Turner, *J. Chem. Soc.*, 1945, 694.

ethanol), $\nu_{max.}$ (Nujol) 3 270, 1 590, 1 490, 1 325, 1 280, 1 245, 1 155, 1 090, 1 025, 890, 815, and 665 cm^{-1}, δ 7.78 (2 H, d, *J* 8.5 Hz), 7.3 (2 H, d, *J* 8.5 Hz), 7.21 (2 H, d, *J* 9.0 Hz), 6.75 (2 H, d, *J* 9.0 Hz), 5.63 (NH, d, *J* 4.0 Hz), 3.78 (3 H, s), 3.3—2.57 (2 H, m), 2.4 (3 H, s), and 2.5—0.73 (8 H, complex), *m/e* 391 (M^+), 252, 155, and 140 (Found: C, 61.3; H, 6.45; N, 3.8. $C_{20}H_{25}NO_3S_2$ requires C, 61.35; H, 6.45; N, 3.6%).

trans-1-*Butylthio*-2-(4-*methylphenylsulphonylamino*)-*cyclohexane* (53).—In a manner identical to that described for dibenzyl disulphide, dibutyl disulphide (365 mg) gave the amido-sulphide (53) (152 mg, 22%) as a colourless oil, $\nu_{max.}$ (Nujol) 3 270, 1 595, 1 325, 1 155, 1 090, 890, 815, and 665 cm^{-1}, δ 7.83 (2 H, d, *J* 8.5 Hz), 7.34 (2 H, d, *J* 8.5 Hz), 5.54 (NH, d, *J* 4.5 Hz), 2.42 (3 H, s), 3.1—2.67 (2 H, m), and 2.6—0.5 (17 H, complex), *m/e* 341 (M^+), 252, 186, 170, and 155 (Found: C, 59.7; H, 8.05; N, 3.9. $C_{17}H_{27}NO_2S_2$ requires C, 59.8; H, 7.95; N, 4.1%).

trans-1-(4-*Methylphenylsulphonylamino*)-2-*phenylselenocyclohexane* (67).—Diphenyl diselenide (54) (312 mg) and cyclohexene (82 mg) in dry acetonitrile (5 ml) were cooled to −5 °C, chloramine-T (456 mg) was added, and the mixture stirred for 1 h at the bath temperature before warming to room temperature over 2 h. Ethanol (5 ml) and sodium borohydride (80 mg) were added and stirring was continued for 15 min. The mixture was poured into 3N-hydrochloric acid (25 ml) and extracted with dichloromethane (2 × 50 ml). Evaporation of the combined organic extracts followed by column chromatography (dichloromethane) and recrystallisation from ethanol gave the *amido-selenide* (67) (40%), m.p. 134—135.5°, $\nu_{max.}$ ($CHCl_3$) 3 360, 3 250, 2 910, 1 600, 1 400, 1 330, 1 155, 1 090, and 890 cm^{-1}, δ 7.78 (2 H, d, *J* 8.5 Hz), 7.5—7.1 (7 H, complex), 5.5—5.3 (NH, m), 3.3—2.9 (2 H, m), 2.41 (3 H, s), and 2.4—1.01 (8 H, complex), *m/e* 409 (M^+) and 252 ($M - C_6H_5Se$) (Found: C, 55.75; H, 5.7; N, 3.15. $C_{19}H_{23}NO_2SSe$ requires C, 55.9; H, 5.7; N, 3.45%).

N-*Cyclohexyl*-4-*methylbenzenesulphonamide* (23).—The amido-selenide (67) (204 mg) in ethanol (10 ml) was stirred with Raney nickel W2 [18] (*ca.* 1 g) for 16 h at room temperature. The mixture was filtered through Celite and the solvent carefully distilled off and analysed for benzene (82%) by g.l.c. (Carbowax; 30 °C). The residue was crystallised from petroleum (b.p. 40—60 °C) to give the cyclohexyl sulphonamide (23) (76%), m.p. 85° (lit.,[36] 86—87°).

2-(4-*Methylphenylsulphonylamino*)*cyclohexanone* (74).—The amido-selenide (67) (204 mg) in dichloromethane (10 ml) was treated with a dry solution of benzoyl peroxide [37] (360 mg) in dichloromethane (5 ml) at room temperature. The starting material was immediately consumed (t.l.c.); dichloromethane (25 ml) was added and the solution washed with 10% sodium thiosulphate (50 ml) and evaporated. The residual oil was refluxed with acetic anhydride (15 ml) for 14 h, water (50 ml) added, and the solution cooled to room temperature over 1 h with stirring. Extraction with dichloromethane followed by p.l.c. (benzene) and crystallisation from ethanol gave the cyclohexanone (74) (29%), m.p. 137—138° (lit.,[38] 136—137°), $\nu_{max.}$ ($CHCl_3$) 3 300, 2 910—2 880, 1 720, 1 605, 1 355, and 1 160 cm^{-1}, δ 7.7 (2 H, d, *J* 8.5 Hz), 7.27 (2 H, d, *J* 8.5 Hz), 6.0—5.7 (NH, m), 4.0—3.5 (1 H, m), 2.44 (3 H, s), and 2.4—1.2 (8 H, complex), *m/e* 267 (M^+) (Found: C, 58.5; H, 6.3; N, 5.25. Calc. for $C_{13}H_{17}NO_3S$: C, 58.4; H, 6.4; N, 5.25%).

[37] Y. Okamoto, K. L. Chellappa, and R. M. Homsany, *J. Org. Chem.*, 1973, **38**, 3172.

trans-1-*Benzylseleno*-2-(4-*methylphenylsulphonylamino*)-*cyclohexane* (81).—A mixture of cyclohexene (82 mg) and dibenzyl diselenide (80) (340 mg) in acetonitrile was treated with chloramine-T (456 mg) as described for cyclohexene–diphenyl diselenide. Reduction and work-up in the usual way followed by column chromatography (dichloromethane) gave the amido-selenide (81) (46%) as a yellowish oil, *m/e* 423 (M^+).

The oil was taken up in ethanol (15 ml) and water (10 ml) and treated under nitrogen with nickel(II) chloride hexahydrate (2.38 g), boric acid (6.2 g), and sodium borohydride (0.8 g).[39] After the reaction had subsided, the mixture was refluxed for 3 h, cooled, and filtered through Celite. The filtrate was extracted with ether (3 × 50 ml), and the combined etheral fractions were concentrated and crystallised from petroleum (b.p. 40—60 °C) to give *N*-cyclohexyl-4-methylbenzenesulphonamide (23) (35% overall), m.p. 85—86°.

Cholest-2-ene

2-(4-*Methylphenylsulphonylimino*)-3α-*phenylthiocholestane* (26).—Cholest-2-ene (24) (370 mg) and $(PhSSPh)(NTs)_2$ (8) (556 mg) were stirred in acetonitrile (10 ml) and petroleum (b.p. 60—80 °C; 5 ml) for 6 h at room temperature. Evaporation followed by column chromatography (benzene–dichloromethane, 1 : 1 v/v) and crystallisation from ethanol–ether gave the *imine* (26) (190 mg, 29%), m.p. 153—155°, $\nu_{max.}$ (Nujol) 1 605, 1 300, 1 148, 1 085, 805, 775, and 700 cm^{-1}, δ 7.63—7.0 (9 H, complex), 3.83—3.44 (1 H, m), 2.4 (3 H, s), 0.9 (s, 19-H_3), and 0.63 (s, 18-H_3), *m/e* 647 (M^+), 492, and 354 (Found: C, 74.1; H, 8.85; N, 2.05. $C_{40}H_{57}NO_2S_2$ requires C, 74.15; H, 8.85; N, 2.15%).

2β-(4-*Methylphenylsulphonylamino*)-3α-*phenylthiocholestane* (27).—The imine (26) (64.7 mg) in ethanol (10 ml) was stirred for 1 h at room temperature with sodium borohydride (5 mg). The mixture was poured onto ice containing N-hydrochloric acid (1 ml) and extracted with ether (3 × 25 ml). Evaporation of the extract and crystallisation from ethanol gave the *amido-sulphide* (27) (58 mg, 89%), m.p. 235—238°, $[\alpha]_D^{22}$ −11.8° (*c* 0.35 in $CHCl_3$), $\nu_{max.}$ (Nujol) 1 595, 1 580, 1 330, 1 310, 1 250, 1 180, 1 158, 1 080, 1 020, 970, 930, 890, 850, 815, 770, 740, 720, 700, 685, and 665 cm^{-1}, δ 7.78 (2 H, d, *J* 8.5 Hz), 7.57—7.0 (7 H, complex), 5.0 (NH, d, *J* 4.5 Hz), 3.63—3.3 (2 H, m), 2.58 (3 H, s), 0.9 (s, 19-H_3), and 0.63 (s, 18-H_3), *m/e* 649 (M^+), 540, 494, 478, 386, 384, 155, and 110 (Found: C, 73.9; H, 9.2; N, 2.05. $C_{40}H_{59}NO_2S_2$ requires C, 73.9; H, 9.15; N, 2.15%).

2β-(4-*Methylphenylsulphonylamino*)*cholestane* (28).—The amido-sulphide (27) (65 mg) in ethanol (10 ml) was stirred with Raney nickel W2 (*ca.* 100 mg) for 6 h at room temperature. The mixture was filtered through Celite, the solvent evaporated off, and the residue recrystallised from ethanol to give the *sulphonamide* (28) (51 mg, 94%), m.p. 153—156°, $[\alpha]_D^{22}$ +36.2° (*c* 0.3 in $CHCl_3$), $\nu_{max.}$ (Nujol) 3 320, 1 595, 1 320, 1 150, 1 090, 1 010, 925, 815, 722, 690, and 665 cm^{-1}, δ 7.78 (2 H, d, *J* 8.5 Hz), 7.3 (2 H, d, *J* 8.5 Hz), 4.71 (NH, d, *J* 6.0 Hz), 3.68—3.39 (1 H, m), 2.41 (3 H, s), 0.9 (s, 19-H_3), and 0.63 (s, 18-H_3), *m/e* 541 (M^+), 526, 386, 370, and 155 (Found: C, 75.65; H, 10.2; N, 2.5. $C_{34}H_{55}NO_2S$ requires C, 75.35; H, 10.25; N, 2.6%).

[38] A. E. Kretov, E. A. Abrazhanova, S. I. Zlotchenko, and V. P. Kukchar, *Zhur. obshchei Khim.*, 1963, **33**, 2355.

[39] R. B. Boar, D. W. Hawkins, J. F. McGhie, and D. H. R. Barton, *J.C.S. Perkin I*, 1973, 654.

2,3-Dihydropyran

5-(4-Methylphenylsulphonylamino)-4-phenylthiopentan-1-ol (39).—2,3-Dihydropyran (35) (168 mg) and (PhSSPh)-$(NTs)_2$ (8) (1.112 g) in anhydrous acetonitrile (10 ml) were stirred at room temperature for 2.5 h. Ethanol (10 ml) and sodium borohydride (152 mg) were added and stirring was continued for 2 h. The mixture was poured onto ice and extracted with ether (3 × 50 ml). Column chromatography (dichloromethane–acetone, 8 : 2 v/v) gave the *pentan-1-ol* (39) (215 mg, 30%) as a slightly yellow oil, $\nu_{max.}$ (Nujol) 3 500, 3 270, 1 595, 1 320 1 150, 1 090, 1 020, 810, 740, 690, and 660 cm^{-1}, δ 7.67 (2 H, d, 8.5 Hz), 7.23, (2 H, d, *J* 8.5 Hz), 7.2 (5 H, s), 5.63 (NH, t, *J* 6.0 Hz), 3.87—3.19 (3 H, complex), 3.2—2.84 (3 H, complex), 2.4 (3 H, s), and 2.0—1.52 (4 H, complex), *m/e* 365 (M^+), 256, 242, 194, 182, 155, 150, 135, 109, and 91 (Found: C, 59.0; H, 6.5; N, 3.65. $C_{18}H_{23}NO_3S_2$ requires C, 59.15; H, 6.35; N, 3.85%).

The *3,5-dinitrobenzoate* (42) was obtained by treatment of the alcohol (39) with 3,5-dinitrobenzoyl chloride–pyridine as a slightly yellow oil, $\nu_{max.}$ (Nujol) 3 220, 1 700, 1 335, 1 220, 1 150, 1 075, 1 025, 970, 915, 815, and 720 cm^{-1}, δ 9.1 (3 H, t, *J* 2.5 Hz), 7.59 (2 H, d, *J* 8.5 Hz), 7.21 (2 H, d, *J* 8.5 Hz), 7.2 (5 H, s), 5.31 (NH, t, *J* 6.0 Hz), 4.42 (2 H, t, *J* 7.0 Hz), 3.4—4.19 (3 H, complex), 2.4 (3 H, s), and 2.3—1.34 (4 H, complex), *m/e* 559 (M^+), 388, 376, 347, 224, 212, 192, 155, 136, and 91 (Found: C, 53.9; H, 4.5; N, 7.4. $C_{25}H_{25}N_3O_8S_2$ requires C, 53.65; H, 4.5; N, 7.5%).

5-(4-Methylphenylsulphonylamino)pentan-1-ol (40).—The 4-(phenylthio)-alcohol (39) (219 mg) in ethanol (5 ml) was stirred with an excess of Raney nickel W2 (*ca.* 1 g) for 1 h at room temperature. Filtration through Celite and evaporation followed by column chromatography (dichloromethane–acetone, 8 : 2 v/v) gave the alcohol (40) (132 mg, 85%) as a colourless oil, δ 7.74 (2 H, d, *J* 8.5 Hz), 7.33 (2 H, d, *J* 8.5 Hz), 4.5—3.28 (4 H, complex), 3.1—2.7 (2 H, complex), 2.43 (3 H, s), and 1.83—1.14 (6 H, complex), *m/e* 258, 256, 242, 240, 198, 184, 155, 102, and 91.

Treatment with 4-methylbenzenesulphonyl chloride–pyridine afforded the *ditosylate* (41) as white needles, m.p. 81—82.5° (from ethanol), $\nu_{max.}$ (Nujol) 3 220, 1 590, 1 350, 1 155, 1 090, 1 020, 955, 895, 830, and 800 cm^{-1}, δ 7.78 (2 H, d, *J* 8.5 Hz), 7.73 (2 H, d, *J* 8.5 Hz), 7.67 (2 H, d, *J* 8.5 Hz), 7.61 (2 H, d, *J* 8.5 Hz), 4.93 (NH, t, *J* 6.0 Hz), 3.94 (2 H, t, *J* 6.5 Hz), 3.08—2.73 (2 H, complex), 2.45 (6 H, s), and 1.8—1.24 (6 H, complex), *m/e* 411 (M^+), 239, 224, 155, and 91 (Found: C, 55.6; H, 6.1; N, 3.4. $C_{19}H_{25}NO_5S_2$ requires C, 55.45; H, 6.15; N, 3.4%).

The ditosylate (41) was identical (n.m.r., m.p., and mixed m.p.) with an authentic sample prepared by tosylation of 5-aminopentan-1-ol (43).

Oct-1-ene

N-Octyl-4-methylbenzenesulphonamide (69).—Diphenyl diselenide (54) (312 mg) and oct-1-ene (68) (112 mg) in acetonitrile (5 ml) were cooled in an ice-bath; chloramine-T (456 mg) was added and the mixture allowed to warm to room temperature with stirring over 2 h before reduction and work-up as for cyclohexane. Column chromatography (dichloromethane) afforded a (4-methylphenylsulphonylamino)-phenylseleno-octane as a clear oil (55%), δ 7.9—7.7 (9 H, complex), 5.3—4.9 (NH, m), 3.3—2.7 (3 H, complex), 2.42 (3 H, s), and 2.0—0.7 (13 H, complex), *m/e* 439 (M^+).

The oil was taken up in ethanol (15 ml) and water (10 ml) and treated under nitrogen with nickel(II) chloride hexahydrate (2.38 g), boric acid (6.2 g), and sodium borohydride (0.8 g).[39] After the reaction had subsided, the mixture was refluxed for 3 h, cooled, and filtered through Celite. The filtrate was extracted with ether (3 × 50 ml), and the combined etheral fractions were concentrated to give the sulphonamide (69) (45%), m.p. 49—53°, mixed m.p. 47—53° (lit.,[40] 56°), identical (i.r., n.m.r.) with an authentic sample.

Acrylonitrile

3-Phenylselenopropiononitrile (71).—A mixture of diphenyl diselenide (54) (312 mg) and acrylonitrile (70) (53 mg) was treated with chloramine-T (456 mg) as for cyclohexene. After the usual reduction and work-up, column chromatography (benzene) gave the *nitrile* (71) (15%), $\nu_{max.}$ (film) 3 030, 2 920, 2 250, 1 575, 1 475, 1 435, 1 260, 1 020, 735, and 690 cm^{-1}, δ 7.8—7.2 (5 H, complex) and 3.3—2.5 (4 H, complex symmetrical A_2B_2 system), *m/e* 211 (M^+) (Found: C, 51.35; H, 4.6; N, 6.5. C_9H_9NSe requires C, 51.45; H, 4.3; N, 6.65%).

An authentic sample of the nitrile (71) was prepared by stirring acrylonitrile (212 mg) and diphenyl diselenide (54) (624 mg) in ethanol (10 ml) with sodium borohydride [41] (80 mg) under nitrogen for 4 h at room temperature. The mixture was poured into dilute hydrochloric acid and extracted with dichloromethane (2 × 50 ml). Column chromatography (benzene) followed by distillation gave compound (71) (25%), b.p. 118—120° at 0.2 mmHg.

Styrene

1-(4-Methylphenylsulphonylamino)-1-phenyl-2-phenylselenoethane (73).—A mixture of styrene (72) (104 mg) and diphenyl diselenide (54) (312 mg) in acetonitrile (5 ml) was treated with chloramine-T (456 mg) as for cyclohexene. After the usual reduction and work-up, column chromatography (dichloromethane) and crystallisation from ethanol gave the *amido-selenide* (73) (62%), m.p. 90—92°, $\nu_{max.}$ (Nujol) 3 270, 1 330, 1 165, 795, and 710 cm^{-1}, δ 7.7—6.9 (14 H, complex), 5.9 (NH, d, *J* 6.0 Hz), 4.4 (1 H, q, *J* 6.0 Hz, collapses to t upon D_2O exchange), 3.15 (2 H, br d, *J* 6.0 Hz), and 2.25 (3 H, s), *m/e* 430 (M^+) (Found: C, 58.35; H, 4.95; N, 3.25. $C_{21}H_{21}NO_2SSe$ requires C, 58.6; H, 4.9; N, 3.25%).

The amido-selenide (73) (107 mg) reacted with Raney nickel W2 in ethanol to give 1-(4-methylphenylsulphonylamino)-1-phenylethane (42%), m.p. 79—80° (lit.,[42] 81—82°).

Synthesis of Amido-sulphides and -selenides; a Structural Corroboration

trans-2-Bromo-1-(4-methylphenylsulphonylamino)cyclohexane (19).—*NN*-Dibromo-4-methylbenzenesulphonamide (18) (3.29 g) was added in small portions to a stirred solution of cyclohexene (3.28 g) in carbon tetrachloride (1.5 ml) at 0 °C and the mixture refluxed for 1 h.[7] Concentration of the solution under reduced pressure, column chromatography (dichloromethane), and crystallisation from ethanol gave the *cyclohexane derivative* (19) (3.21 g, 88%), m.p. 105—106.5°, δ 7.81 (2 H, d, *J* 8.5 Hz), 7.29 (2 H, d, *J* 8.5 Hz), 5.6 (NH, d, *J* 6.5 Hz), 4.18—3.67 (1 H, m), 3.58—2.9 (1 H, m), 2.43 (3 H, s), and 2.62—0.95 (8 H, complex), *m/e* 333/331

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[42] P. A. Briscoe, F. Challenger, and P. S. Duckworth, *J. Chem. Soc.*, 1965, 1755.

(M^+), 252, and 155 (Found: C, 46.95; H, 5.5; N, 4.15. $C_{13}H_{18}BrNO_2S$ requires C, 47.0; H, 5.45; N, 4.2%).

7-(4-*Methylphenylsulphonyl*)-7-*azabicyclo*[4.1.0]*heptane* (20).— *trans*-2-Bromo-1-(4-methylphenylsulphonylamino)-cyclohexane (19) (640 mg) in chloroform (10 ml) was vigorously stirred with 5% sodium hydroxide (5 ml) for 1 h at room temperature.[8] Chloroform (25 ml) was added and the chloroform layer washed with cold 5% sodium hydroxide (3 × 10 ml) and water (3 × 25 ml). Evaporation and crystallisation from petroleum (b.p. 40—60 °C) gave the aziridine (20) (452 mg, 93%), m.p. 60—61° (lit.,[43] 61—62°), δ 7.83 (2 H, d, *J* 8.5 Hz), 7.34 (2 H, d, *J* 8.5 Hz), 3.03—2.87 (2 H, m), 2.43 (3 H, s), and 2.07—0.98 (8 H, complex).

trans-2-(4-*Methylphenylsulphonylamino*)-1-*phenylthiocyclohexane* (17).—Diphenyl disulphide (65 mg) and sodium borohydride (23 mg) were stirred in ethanol (5 ml) under nitrogen for 15 min at room temperature. The aziridine (20) (125 mg) was added and stirring continued for 1 h. The mixture was poured into cold dilute hydrochloric acid (25 ml) and extracted with ether (3 × 25 ml). Column chromatography (dichloromethane) followed by crystallisation from ethanol gave the amido-sulphide (17) (165 mg, 91%), identical (m.p. mixed m.p., i.r., and n.m.r.) with that obtained from cyclohexene and $(PhSSSPh)(NTs)_2$.

The amido-sulphides (51)—(53) and the amidoselenide (67) were prepared by an identical procedure (46, 94, 43, and 88% yield, respectively) except for (51) and (53) where the reaction time had to be extended to 22 h.

3α-*Bromo*-2β-(4-*methylphenylsulphonylamino*)*cholestane* (33).—Cholest-2-ene (24) (370 mg) in carbon tetrachloride (5 ml) was added dropwise to a stirred suspension of *NN*-dibromo-4-methylbenzenesulphonamide (18) (329 mg) in carbon tetrachloride (5 ml) at 0 °C. After 6 h at room temperature, ethanol (25 ml) and sodium iodide (150 mg) were added and stirring continued for 2 h. The mixture was poured into water (100 ml) and 5% sodium thiosulphate added until complete decolouration had occurred. Extraction with ether (4 × 25 ml), column chromatography (benzene), and recrystallisation from ethanol afforded starting material (181 mg) and the *cholestanylsulphonamide* (33) (231 mg, 37%), m.p. 174—177°, $\nu_{max.}$ (Nujol), 3 300, 1 595, 1 335, 1 310, 1 155, 1 090, 1 010, 950, 825, 725, and 670 cm^{-1}, δ 7.78 (2 H, d, *J* 8.5 Hz), 7.3 (2 H, d, *J* 8.5 Hz), 5.31 (NH, d, *J* 6.0 Hz), 4.58—4.39 (1 H, m), 3.91—2.43 (1 H, m), 2.44 (3 H, s), 0.92 (s, 19-H_3), and 0.62 (s, 18-H_3), *m/e* 621, 619 (M^+), 539, 524, 475, 414, 384, and 155 (Found: C, 66.0; H, 9.0; N, 2.05. $C_{34}H_{54}BrNO_2S$ requires C, 65.8; H, 8.75; N, 2.25%).

N-(4-*Methylphenylsulphonyl*)-2β,3β-*iminocholestane* (34).—The bromocholestanylsulphonamide (33) (120 mg) in chloroform (5 ml) was vigorously stirred with 5% sodium hydroxide (2.5 ml) for 2 h at room temperature.[8] The product was worked up as described for the aziridine (20) and recrystallised from ethanol to give the *aziridine* (34) (102 mg, 98%), m.p. 192—193.5°, $\nu_{max.}$ (Nujol), 1 592, 1 315, 1 240, 1 215, 1 155, 1 090, 975, 950, 885, 830, 810, 785, 725, 695, and 662 cm^{-1}, δ 7.8 (2 H, d, *J* 8.5 Hz), 7.3 (2 H, d, *J* 8.5 Hz), 3.19—2.83 (2 H, m), 2.48 (3 H, s), 0.9 (s, 19-H_3), and 0.61 (s, 18-H_3), *m/e* 539 (M^+), 524, 475, 384, 277, 258, 155, and 149 (Found: C, 75.7; H, 10.15; N, 2.6. $C_{34}H_{53}NO_2S$ requires C, 75.65; H, 10.15; N, 2.6%).

Treatment of the bromocholestanylsulphonamide (33) (124 mg) in dry tetrahydrofuran (5 ml) with tri-n-butyltin hydride (117 mg) under nitrogen for 22 h at room temperature[15,16] followed by column chromatography (benzene) also afforded the aziridine (24) (77 mg, 71%).

2β-(4-*Methylphenylsulphonylamino*)-3α-*phenylthiocholestane* (27).—The aziridine (34) (270 mg) was treated with diphenyl disulphide (65 mg) and sodium borohydride (25 mg) in ethanol (10 ml) and the product worked up as described for the aziridine (20) and diphenyl disulphide. Column chromatography (benzene–dichloromethane, 1 : 1 v/v) afforded compound (27), identical (m.p., mixed m.p., i.r., and n.m.r.) with that obtained from reduction of the cholest-2-ene–$(PhSSPh)(NTs)_2$ adduct.

2β-(4-*Methylphenylsulphonylamino*)*cholestane* (28).—The aziridine (34) (62 mg) in dry tetrahydrofuran (5 ml) was stirred with lithium aluminium hydride (10 mg) for 4 h at room temperature. Saturated aqueous sodium sulphate (5 ml) was carefully added and the mixture extracted with ether (3 × 25 ml). Column chromatography (benzene–ether, 19 : 1 v/v) and crystallisation from ethanol gave the cholestanylsulphonamide (28) (51 mg, 82%), m.p. 153—156°, $[\alpha]_D^{22}$ +36.4° (*c* 0.2 in $CHCl_3$), identical (mixed m.p., i.r., and n.m.r.) with that obtained from (27) and Raney nickel.

Methyl Cholestan-2β-*ylcarbamate* (30).—Methyl (3α-iodocholestan-2β-yl)carbamate[14] (29) (114 mg) and tri-n-butyltin hydride (582 mg) in dry tetrahydrofuran (1 ml) were stirred under nitrogen for 2.5 h at room temperature. Column chromatography (benzene–ether, 9 : 1 v/v) afforded the *carbamate* (30) (82 mg, 92%), m.p. 127—130° (from methanol), $[\alpha]_D^{22}$ +15.1° (*c* 0.65 in $CHCl_3$), $\nu_{max.}$ (Nujol) 3 300, 1 680, 1 235, 1 080, 1 010, 870, and 775 cm^{-1}, δ 4.8 (NH, d, *J* 6.0 Hz), 4.08—3.73 (1 H, m), 3.65 (3 H, s), 0.91 (s, 19-H_3), and 0.63 (s, 18-H_3), *m/e* 445 (M^+), 430, 413, 398, 370, 355, 290, 258, 230, and 215 (Found: C, 78.4; H, 11.7; N, 3.0. $C_{29}H_{51}NO_2$ requires C, 78.15; H, 11.55; N, 3.15%).

2β-*Aminocholestane* (31).—The carbamate (30) (85 mg) was refluxed for 2 h in 50% potassium hydroxide (0.2 ml) and ethanol (5 ml). Water (25 ml) and N-hydrochloric acid (5 ml) were added and the mixture was extracted with ether (3 × 25 ml). Recrystallisation from acetone gave the amine (31) (50 mg, 68%), m.p. 114—116° (as the isopropylidene derivative) (lit.,[17] m.p. 115—117°).

2β-(4-*Methylphenylsulphonylamino*)*cholestane* (28).—The amine (31) (47 mg) was stirred with 4-methylbenzenesulphonyl chloride (36 mg) in pyridine (2.5 ml) at room temperature for 6 h. The mixture was poured into an excess of cold N-hydrochloric acid and extracted with ether (3 × 25 ml), and the extract was chromatographed (column; benzene–ether, 19 : 1 v/v). Recrystallisation from ethanol gave the sulphonamide (28) (48 mg, 73%), m.p. 153—156°, $[\alpha]_D^{22}$ +36.2° (*c* 0.4 in $CHCl_3$), identical (mixed m.p., i.r., and n.m.r.) with the samples previously described.

trans- *and* cis-3-*Bromo*-2-(4-*methylphenylsulphonylamino*)-*tetrahydropyran* (44) *and* (45).—2,3-Dihydropyran (420 mg) in carbon tetrachloride (2 ml) was added dropwise to a suspension of *NN*-dibromo-4-methylbenzenesulphonamide (18) (1.65 g) in carbon tetrachloride (5 ml) at 0 °C and the mixture stirred at room temperature for 6 h. After addition of ethanol (10 ml) and sodium iodide (750 mg), stirring was continued for 2 h; the mixture was then poured into water (50 ml) and reduced with 5% sodium thiosulphate. Extraction with ether (3 × 50 ml) and column chromatography (dichloromethane–acetone, 19 : 1 v/v) gave the trans-*tetrahydropyran* (44) (1.1 g, 65%) as a clear oil, $\nu_{max.}$ (Nujol) 3 260, 1 595, 1 325, 1 155, 1 065, 940, 810, 725,

[43] W. Klötzer, *Monatsh.*, 1970, **101**, 1841.

and 665 cm^{-1}, δ 7.87 (2 H, d, *J* 8.5 Hz), 7.3 (2 H, d, *J* 8.5 Hz), 6.1 (NH, d, *J* 9.0 Hz), 4.78 (1 H, t, *J* 9.0 Hz), 4.19—3.2 (3 H, complex), 2.43 (3 H, s), and 2.6—1.3 (4 H, complex), *m/e* 335/333 (M^+), 254, and 155 (Found: C, 42.95; H, 4.65; N, 4.1. $C_{12}H_{16}BrNO_3S$ requires C, 43.15; H, 4.8; N, 4.2%), and the cis-*isomer* (45) (474 mg, 28%), m.p. 137—139° (from ethanol), $\nu_{max.}$ (Nujol) 3 280, 1 595, 1 320, 1 160, 1 070, 965, 885, 840, 810, 720, and 665 cm^{-1}, δ 7.8 (2 H, d, *J* 8.5 Hz), 7.28 (2 H, d, *J* 8.5 Hz), 5.5 (NH, d, *J* 10.0 Hz), 4.69 (1 H, q, *J* 2.0 and 10.0 Hz), 4.19—3.3 (3 H, complex), 2.4 (3 H, s), and 2.45—1.3 (4 H, complex), *m/e* 335/333 (M^+), 254, and 155 (Found: C, 42.9; H, 4.7; N, 4.05%).

trans-3-(4-*Methylphenylsulphonylamino*)-2-*phenylthiotetrahydropyran* (47).—The *trans*-bromo-sulphonamidotetrahydropyran (44) (167 mg) was treated with diphenyl disulphide (60 mg) and sodium borohydride (23 mg) as described for the aziridine (20). The mixture was poured into water (50 ml) and extracted with ether (3 × 25 ml). Column chromatography (dichloromethane) and crystallisation from ethanol afforded the *amido-sulphide* (47) (127 mg, 70%), m.p. 132—133°, $\nu_{max.}$ (Nujol) 3 270, 1 600, 1 375, 1 325, 1 155, 1 085, 995, 915, 875, 815, 750, 690, and 655 cm^{-1}, δ 7.73 (2 H, d, *J* 8.5 Hz), 7.4—7.08 (7 H, complex), 5.43 (NH, d, *J* 8.0 Hz), 4.8 (1 H, d, *J* 3.5 Hz), 4.5—3.85 (1 H, complex), 3.73—3.39 (2 H, complex), 2.41 (3 H, s), and 2.1—1.1 (4 H, complex), *m/e* 363 (M^+), 254, 210, 155, and 139 (Found: C, 59.4; H, 6.0; N, 3.8. $C_{18}H_{21}NO_3S_2$ requires C, 59.5; H, 5.85; N, 3.85%).

3-(4-*Methylphenylsulphonylamino*)*tetrahydropyran* (50) *and its* 2-*Ethoxy-derivative* (49).—The *trans*-amido-sulphide (47) (155 mg) in ethanol (5 ml) was treated with an excess of Raney nickel W2 for 20 min at room temperature. After filtering through Celite and evaporation, column chromatography (dichloromethane–acetone, 97 : 3 v/v) afforded the *amido-tetrahydropyran* (50) (65 mg, 60%), m.p. 102—104° (from ethanol), $\nu_{max.}$ (Nujol) 3 135, 1 325, 1 185, 1 150, 1 080, 1 035, 975, 925, 855, and 815 cm^{-1}, δ 7.78 (2 H, d, *J* 8.5 Hz), 7.29 (2 H, d, *J* 8.5 Hz), 5.2 (NH, d, *J* 8.0 Hz), 3.88—3.0 (5 H, complex), 2.43 (3 H, s), and 2.0—1.3 (4 H, complex), *m/e* 255 (M^+), 210, 155, and 100 (Found: C, 56.65; H, 6.75; N, 5.4. $C_{12}H_{17}NO_3S$ requires C, 56.45; H, 6.7; N, 5.5%), and the 2-*ethoxy-derivative* (49) (53 mg, 43%), m.p. 110—111.5° (from ethanol), $\nu_{max.}$ (Nujol) 3 320, 1 325, 1 160, 1 050, 1 000, 920, and 815 cm^{-1}, δ 7.78 (2 H, d, *J* 8.5 Hz), 7.29 (2 H, d, *J* 8.5 Hz), 4.89 (NH, d, *J* 11.0 Hz), 4.33 (1 H, d, *J* 3.5 Hz), 3.89—3.0 (5 H, complex), 2.43 (3 H, s), 1.83—1.4 (4 H, complex), and 1.14 (3 H, t, *J* 7.0 Hz), *m/e* 299 (M^+), 254, 155, 144, 133, 98, and 91 (Found: C, 56.15; H, 7.1; N, 4.65. $C_{14}H_{21}NO_4S$ requires C, 56.2; H, 7.05; N, 4.7%).

2-(4-*Methylphenylsulphonylamino*)*tetrahydropyran* (46).—The *trans*- and *cis*-bromo-sulphonamido-tetrahydropyran derivatives (44) and (45) (167 mg) were separately treated with tri-n-butyltin hydride (582 mg) in dry tetrahydrofuran (5 ml) under nitrogen at room temperature for 18 h. Evaporation followed by column chromatography (dichloromethane–acetone, 19 : 1 v/v) gave compound (46) (115 mg, 90%), m.p. 106—107° (from benzene) (lit.,[22] 106—107.5°), mixed m.p. 106—107°, *m/e* 255 (M^+), 155, 100, and 85.

An authentic sample of (46) was prepared by refluxing dihydropyran (420 mg) and 4-methylbenzenesulphonamide (855 mg) in benzene (25 ml) containing ether (0.5 ml) saturated with hydrogen chloride for 3 h. The mixture was poured into water (100 ml) and extracted with ether (3 × 50 ml), and the product was separated by column chromatography (dichloromethane–acetone, 19 : 1 v/v). Crystallisation from benzene gave (46) (1.09 g, 87%) (lit.,[22] 22%), m.p. 106—107°.

5-(4-*Methylphenylsulphonylamino*)-4-*phenylthiopentan*-1-*ol* (39).—Treatment of *cis*-3-bromo-2-(4-methylphenylsulphonylamino)tetrahydropyran (45) (167 mg) under nitrogen with diphenyl disulphide (66 mg) and sodium borohydride (40 mg) in ethanol (5 ml) for 6 h at room temperature followed by work-up and purification as for the dihydropyran–(PhSSPh)(NTs)$_2$ product gave the pentan-1-ol (39) (128 mg, 75%), identical (i.r. and n.m.r.) with the sample previously described.

5-(4-*Methylphenylsulphonylamino*)*pentan*-1-*ol* (40).—2-(4-Methylphenylsulphonylamino)tetrahydropyran (46) (127.5 mg) was stirred with sodium borohhdride (40 mg) in ethanol (5 ml) at room temperature for 6 h. The mixture was poured into water (50 ml) and extracted with ether (3 × 25 ml). Column chromatography (dichloromethane–acetone, 8 : 2 v/v) afforded the alcohol (40) (119 mg, 93%), identical (n.m.r. and mass spectra) with the specimen previously described.

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