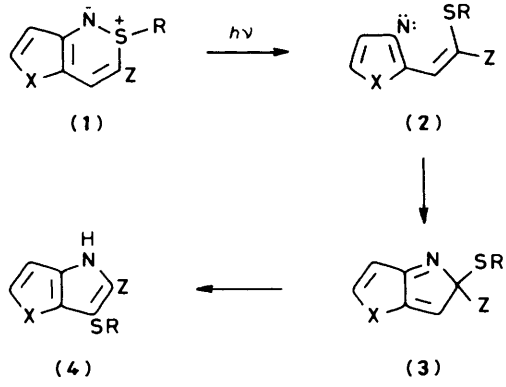
Photochemical Conversion of 3-Azido-2-vinylthiophenes into Thienopyrroles and of 2-Azidostyrenes into Indoles. High Migratory Aptitude of Sulphur Substituents

Raymond S. Gairns, Christopher J. Moody, and Charles W. Rees
Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY

On photolysis in acetonitrile 3-azido-2-vinylthiophenes (**8a—h**) give thieno[3,2-*b*]pyrroles (**10**), (**16**), (**18**)—(**20**), (**23**), (**24**), (**26**) and 2-azidostyrenes (**9a—d**) give indoles (**11**) and (**22**). A mechanism is proposed involving formation and 1,5-electrocyclisation of the corresponding nitrene, followed by sigmatropic shift of one or both of the 2-substituents (Y, Z) in the 2*H*-pyrrole thus formed (Scheme 3). Decomposition of the two series of azides thus provides a measure of the relative migratory aptitudes of these substituents which are found to decrease in the order RSO > RS > H > RSO_2 > RCO > EtO_2C. The sulphide, sulphoxide, and sulphone groups are thus remarkably mobile.

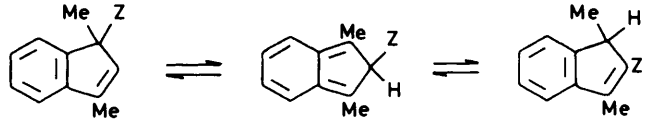
In the preceding paper,[1] we reported the photochemical rearrangement of fused 1λ^4,2-thiazines (**1**) (2-azathiabenzenes) to give fused pyrroles (**4**). Since the known photochemical reactions of sulphur–nitrogen ylides (sulphimides) almost invariably involve cleavage of the sulphur–nitrogen bond,[2] the most likely initial intermediate in the rearrangement of (**1**) to (**4**) is the nitrene (**2**), electrocyclic ring closure of which leads to the non-aromatic fused 2*H*-pyrrole (**3**) (Scheme 1). The fused



Scheme 1. X = O, S, or CH=CH; R = Ph or Me; Z = CO_2Et, COMe, or CHO

pyrrole products (**4**) then arise by successive migrations of the RS group and hydrogen. Although the exact details of these latter migrations are not known, it is clear that the observed products arise by exclusive migration of the RS group in preference to the Z group. One possibility is that the aromatisation of (**3**) occurs by 'dark' [1,5]-sigmatropic shifts.

Little is known about the sigmatropic migration of sulphur groups,[3] although the relative migratory aptitudes of a variety of other groups has been thoroughly investigated by Jones and co-workers in related carbocyclic systems.[4] The 1*H*-indene (**5**), when heated, may isomerise to the non-aromatic 2*H*-isomer (**6**) by a [1,5]-sigmatropic shift of the Z group. If the Z group migrates faster than hydrogen then aromatisation reforms the 1*H*-isomer (**5**). However, if hydrogen is the faster migrator then the isomeric 1*H*-indene (**7**) is formed on rearomatisation (Scheme 2). In a series of elegant experiments starting from optically active 1*H*-indenes (**5**) and measuring the rates of racemisation and product formation, the relative order of



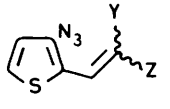
Scheme 2.

migratory aptitude for a series of Z groups was found to be alkyl < C≡CH < CN < CO_2Me < $CH=CH_2$ < H < COMe < CHO.

Since the non-aromatic fused 2*H*-pyrrole intermediate (**3**) proposed in the rearrangement of the thiazine (**1**) (Scheme 1) is isoelectronic with the 2*H*-indene intermediate (**6**) in the rearrangement of 1*H*-indenes (Scheme 2), we have now investigated a wider range of substituents in the thiazine series in order to establish the relative order of migratory aptitudes and, in particular, where sulphur substituents fall in this order.

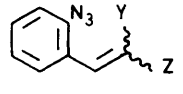
Results and Discussion

From our previous results,[1] a limited order of relative migratory aptitudes (MeS or PhS > CO_2Et, CHO, or COMe) had already been established, but clearly it was necessary to investigate a wider range of substituents. Therefore the starting materials chosen were the azides (**8**) and (**9**), rather than the



(**8**)

a; Y = COMe, Z = CO_2Et
b; Y = H, Z = COMe
c; Y = S(O)Ph, Z = CO_2Et
d; Y = $S(O)_2Ph$, Z = CO_2Et
e; Y = S(O)Me, Z = SMe
f; Y = SMe, Z = H
g; Y = S(O)Ph, Z = H
h; Y = H, Z = $S(O)_2Me$



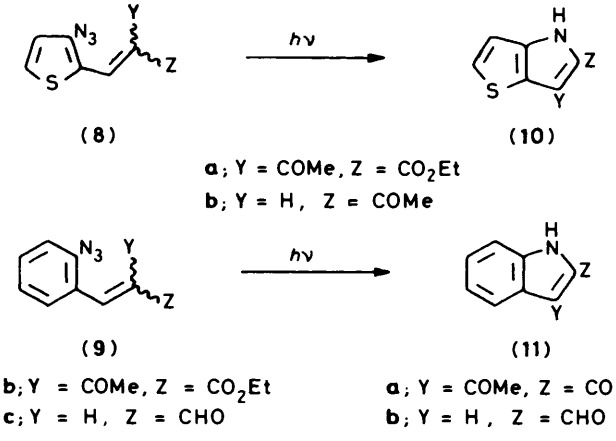
(**9**)

a; Y = SPh, Z = CO_2Et
b; Y = COMe, Z = CO_2Et
c; Y = H, Z = CHO
d; Y = SMe, Z = H

cyclic sulphimides, since it had already been shown that irradiation of the azides [*e.g.* (**8**; Y = CO_2Et, Z = SR)] gave the same fused pyrrole products as the sulphimides themselves.[1] Two series of compounds were studied; the thiophenes (**8**) which give thieno[3,2-*b*]pyrroles on irradiation, and the corresponding benzo compounds (**9**) which lead to indoles, although most of the work was done in the thiophene series.

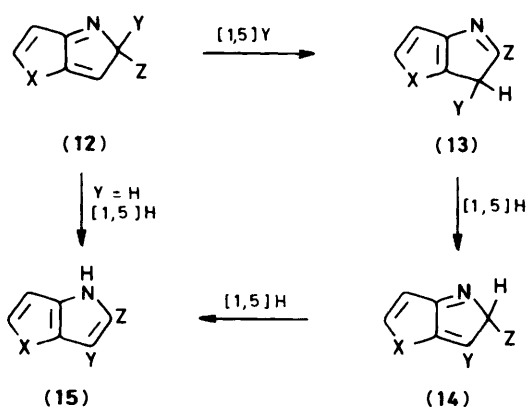
The starting azides (**8a**—**8d**) and (**9a**)[5]—(**9c**) were prepared from 3-azidothiophene-2-carbaldehyde or 2-azidobenzaldehyde by condensation with the appropriate YCH_2Z component under basic conditions. Compounds (**8e**) and (**8h**) were obtained by reaction of the thiophenealdehyde with anions derived from methyl methylsulphinylmethyl sulphide and dimethyl sulphone respectively, followed by dehydration using methanesulphonyl chloride and triethylamine. Azide (**8g**) was prepared from 3-azidothiophene-2-carbaldehyde and the anion from diethyl phenylsulphinylmethylphosphonate. The preparation of the azide (**8f**) from 3-bromothiophene-2-carbaldehyde has been described previously,[5] and the corresponding benzo derivative (**9d**) was prepared similarly from 2-bromobenzaldehyde.

Irradiation of the azides (**8a**) and (**8b**) in acetonitrile gave single thieno[3,2-*b*]pyrrole products in both cases; the structures of the products were established as (**10a**) and (**10b**) by



nuclear Overhauser effect (n.O.e.) difference experiments in the ^1H n.m.r. spectra. Pre-saturation of the NH signal produced an enhancement of the signal from the nearer group, and *vice versa*. Similar results were obtained in the benzene series, the azides (**9b**) and (**9c**) giving the indoles (**11a**) and (**11b**) on irradiation.

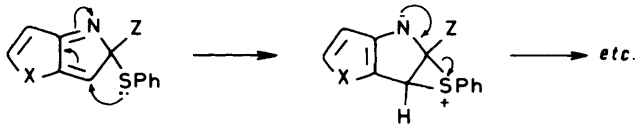
The results show that the acetyl group migrates more readily than ethoxycarbonyl, consistent with the findings in the indene series,[4] but also that hydrogen migrates faster than either acetyl or formyl, which is opposite to the results in the carbocyclic series. This difference in migratory aptitudes, with hydrogen moving more rapidly in the heterocyclic series, deserves further comment. Assuming the intermediate nitrene does collapse to give the fused 2*H*-pyrrole (**12**), then if neither Y nor Z is hydrogen, a [1,5]-shift of one of the substituents is likely to occur. Since work on 2*H*-pyrroles has shown that substituents only migrate from carbon to nitrogen when all other positions are blocked,[6] rearrangement of compounds (**12**) will give isomers (**13**) (Scheme 3). Aromatisation of (**13**) to compounds (**15**) can then occur by two successive 'dark' [1,5]-hydrogen shifts *via* intermediates (**14**) or directly by a photochemically allowed [1,3] shift. In the case where the substituent Y is hydrogen, the initial intermediate (**12**) can undergo the same process. However, a [1,5]-hydrogen shift from carbon to nitrogen in (**12**) would lead directly to the aromatic product (**15**), and it seems likely that in the heterocyclic series this extra



Scheme 3. (X = S or CH=CH)

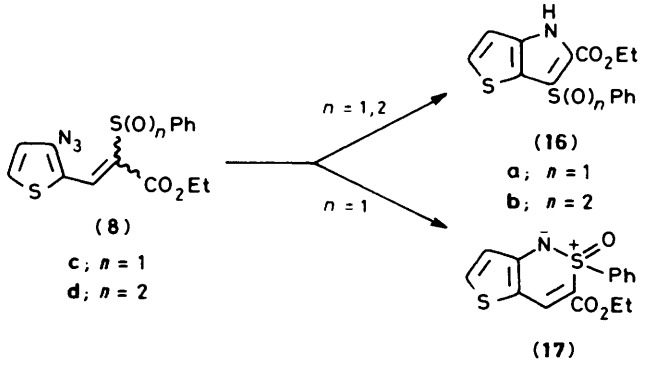
driving force of aromatisation, not applicable in the indene series, explains the rapid migration of hydrogen with respect to acetyl or formyl groups.

The present and previous [1] results taken together lead to the conclusion that, in these particular systems, both hydrogen and the sulphur groups (MeS, PhS) migrate faster than ethoxycarbonyl, acetyl or formyl groups. In order to investigate this apparently very fast migration of sulphur groups further, decomposition of the azides (**8c**—**8h**) and (**9d**) was studied with the particular aim of establishing (a) the relative migratory aptitude of the sulphur groups *vs.* hydrogen, and (b) the role, if any, of the sulphur lone pair. One possible explanation of the rapid migration of sulphur groups would involve lone-pair participation (Scheme 4).



Scheme 4.

Irradiation of the azides (**8c**) and (**8d**) led to the formation of a single thienopyrrole product (**16a**) and (**16b**) in each case, although the cyclic sulphoximide (**17**) (27%) was also formed during the photolysis of (**8c**) (Scheme 5); a product analogous to

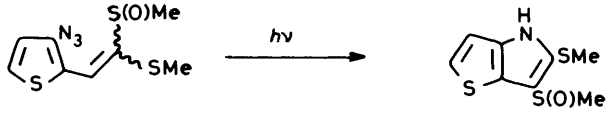


Scheme 5.

(**17**) cannot, of course, be formed from (**8d**). The structures of the thienopyrrole products (**16**) were confirmed by their in-

dependent synthesis by oxidation of the known [1] thienopyrrole (**4**, X = S, R = Ph, Z = CO_2Et).

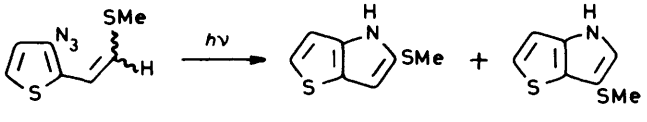
From the above results it would seem that the oxidation level of the sulphur substituent has little effect on the rate of migration, the sulphur group still migrating exclusively with respect to ethoxycarbonyl. This would appear to rule out sulphur lone-pair participation in the migration step, but as another test of the effect of oxidation levels at sulphur, an example was required in which two sulphur substituents of differing oxidation level were in competition. Irradiation of the azide (**8e**) gave a single thienopyrrole (**18**), formed by exclusive



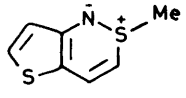
(**8e**) (**18**)

migration of the methylsulphinyl group. The structure was supported by n.O.e. experiments in which pre-saturation of the NH signal caused enhancement of the methylthio group signal (δ_H 2.40) rather than that of the methylsulphinyl (δ_H 3.00).

It thus remained to establish the relative ease of migration of hydrogen *vs.* various sulphur groups. Irradiation of the azide (**8f**) gave two products in approximately equal amounts together with much dark coloured polar material. The products were identified as the isomeric 5- and 6-methylthio-4*H*-thieno[3,2-*b*]pyrrole (**19**) and (**20**), the structure of compound (**20**) being confirmed by comparison with a sample prepared by hydrolysis and decarboxylation of the corresponding 5-ester.[1] Thermolysis of compound (**8f**) in benzene also gave a 1:1 mixture of the thienopyrroles (**19**) and (**20**), together with a very small amount of the unstable cyclic sulphimide (**21**).[5] Sulphimide (**21**), lacking an electron-withdrawing group, is thermally unstable; this probably accounts for the low yield in its formation under these mild conditions, and for the unusual formation of ring-contraction products (**19**) and (**20**), as opposed to sulphimide formation, in a *thermal* reaction.

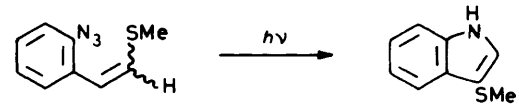


(**8f**) (**19**) (**20**)



(**21**)

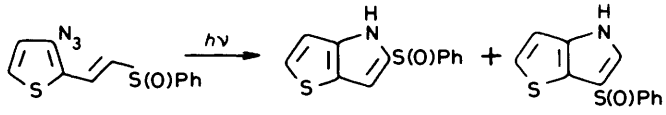
The above formation of products (**19**) and (**20**) is significant in that it demonstrates that the migration of a sulphur substituent from carbon to carbon is sufficiently fast to compete effectively with the direct aromatising hydrogen shift to nitrogen. However, in the benzene series, irradiation of the corresponding azide (**9d**) only gave a single indole product, the ^{13}C n.m.r. spectrum of which agreed with that reported[7] for 3-methylthioindole (**22**). Therefore, in this case, the SMe group migrates exclusively in preference to hydrogen, and the difference between the benzene and thiophene series is presumably related to the differences in strain and geometry



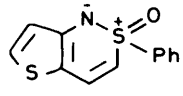
(**9d**) (**22**)

between 5,5- and 6,5-fused systems. The latter will be less strained and will rearrange less rapidly and presumably more selectively than the former. This could explain the exclusive migration of the MeS group in the benzo compound. Nevertheless, the high migratory aptitude of the sulphur substituent is again highlighted.

Since it had already been demonstrated that a methylsulphinyl group migrated faster than a methylthio, it was expected that a sulphinyl substituent would compete even more effectively with hydrogen. That this is indeed the case was demonstrated by the irradiation of the azide (**8g**) which gave, in addition to the expected cyclic sulphoximide (**25**) (22%), the thienopyrroles (**23**) and (**24**), derived by migration of hydrogen and phenylsulphinyl respectively, in the ratio 1:2.

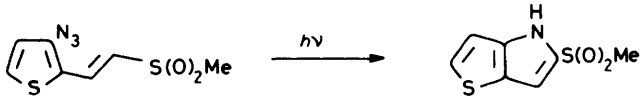


(**8g**) (**23**) (**24**)



(**25**)

In contrast, photolysis of the azido sulphone (**8h**) gave only a single product, the thienopyrrole (**26**), derived by exclusive migration of hydrogen over methylsulphonyl. Therefore a further increase in the oxidation level of sulphur decreases the rate of migration of the group.



(**8h**) (**26**)

Conclusions

Photochemical decomposition of the azidothiophenes (**8**) leads to thieno[3,2-*b*]pyrroles by migration of the substituent Y in preference to, or in competition with, the substituent Z in the presumed non-aromatic fused 2*H*-pyrrole intermediate. For the groups studied, the order of migratory aptitude is as follows:

$$RSO > RS \sim H > RSO_2 > RCO > EtO_2C$$

Although fewer examples were studied, a similar order was found for the benzene series (**9**), again illustrating the rapid migration of sulphur substituents. The exact reasons for this high migratory aptitude of sulphur groups merit further investigation.

Experimental

Ethyl 2-Acetyl-3-(3-azido-2-thienyl)propenoate (**8a**).—A mixture of 3-azidothiophene-2-carbaldehyde[8] (100 mg, 0.65 mmol) and ethyl acetoacetate (94 mg, 0.72 mmol) was added dropwise to a stirred solution of piperidinium acetate (104 mg, 0.72 mmol) in ethanol (5 ml). The mixture was stirred overnight at room temperature, and then poured into aqueous ammonium chloride, and extracted with ether. The combined extracts were washed successively with saturated aqueous sodium metabisulphite and water, dried ($MgSO_4$), and evaporated. The residue was purified by chromatography to give the *title compound* (**8a**) (147 mg, 85%), m.p. 63—64 °C (Found: C, 49.8; H, 4.1; N, 15.7. $C_{11}H_{11}N_3O_3S$ requires C, 49.8; H, 4.2; N, 15.9%); $\nu_{max.}$(CCl_4) 2 100, 1 710, and 1 690 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.36 (3 H, t), 2.40 (3 H, s), 4.40 (2 H, q), 6.97 (1 H, d, *J* 6 Hz), 7.50 (1 H, d, *J* 6 Hz), and 7.70 (1 H, s); *m/z* 265 (M^+), 237, and 221 (base).

4-(3-*Azido*-2-*thienyl*)*but*-3-*en*-2-*one* (**8b**).—Prepared by the literature procedure[9] by condensation of 3-azidothiophene-2-carbaldehyde with acetone, m.p. 104 °C (lit.,[9] 105 °C).

Ethyl 3-(3-*Azido*-2-*thienyl*)-2-*phenylsulphinylpropenoate* (**8c**).—3-Azidothiophene-2-carbaldehyde (100 mg, 0.65 mmol) was condensed with ethyl (phenylsulphinyl)acetate[10] (152 mg, 0.72 mmol) in the presence of piperidinium acetate as described for compound (**8a**) to give the *title compound* (**8c**) (109 mg, 48%), m.p. 125—126 °C (decomp.) (Found: C, 51.8; H, 3.7; N, 12.0. $C_{15}H_{13}N_3O_3S_2$ requires C, 51.9; H, 3.8; N, 12.1%); $\nu_{max.}$(Nujol) 2 100 and 1 710 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.21 (3 H, t), 4.20 (2 H, q), 7.03 (1 H, d, *J* 6.4 Hz), 7.4—7.8 (6 H, m), and 8.28 (1 H, s); *m/z* 347 (M^+), 319, 274, 242, and 222 (base).

Ethyl 3-(3-*Azido*-2-*thienyl*)-2-*phenylsulphonylpropenoate* (**8d**).—3-Azidothiophene-2-carbaldehyde (100 mg, 0.65 mmol) was condensed with ethyl (phenylsulphonyl)acetate[11] (164 mg, 0.72 mmol) in the presence of piperidinium acetate as described above to give the *title compound* (**8d**) (190 mg, 80%), m.p. 128—130 °C (decomp.) (Found: C, 49.7; H, 3.5; N, 11.4. $C_{15}H_{13}N_3O_4S_2$ requires C, 49.6; H, 3.6; N, 11.6%); $\nu_{max.}$(CCl_4) 2 100 and 1 705 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.17 (3 H, t), 4.20 (2 H, q), 7.05 (1 H, d, *J* 5 Hz), 7.45—7.63 (3 H, m), 7.75 (1 H, dd, *J* 5, 0.9 Hz), 8.00—8.50 (2 H, m), and 8.56 (1 H, d, *J* 0.9 Hz); *m/z* 363 (M^+), 335, 318, and 77 (base).

2-(3-*Azido*-2-*thienyl*)-1-(*methylthio*)*vinyl Methyl Sulphoxide* (**8e**).—Butyl-lithium (0.65 mmol) was added to a stirred solution of methyl methylsulphinylmethyl sulphide (81 mg, 0.65 mmol) in tetrahydrofuran (THF) (20 ml) at −78 °C. After 20 min, a solution of 3-azidothiophene-2-carbaldehyde (100 mg, 0.65 mmol) in THF (10 ml) was added, and the mixture was allowed to warm to room temperature. Methanesulphonyl chloride (115 mg, 1 mmol) and triethylamine (1 ml) were added, and the mixture was stirred overnight. Aqueous work-up and chromatography gave the *title compound* (**8e**) (68 mg, 40%) as an unstable oil which darkened rapidly (Found: M^+, 258.9897. $C_8H_9N_3OS_3$ requires *M*, 258.9908); $\nu_{max.}$(CCl_4) 2 100 and 1 580 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 2.38 (3 H, s), 2.71 (3 H, s), 6.96 (1 H, d, *J* 5 Hz), 7.45 (1 H, d, *J* 5 Hz), and 7.85 (1 H, s); *m/z* 259 (M^+), 244, and 231 (base).

2-(3-*Azido*-2-*thienyl*)*vinyl Methyl Sulphide* (**8f**).—Prepared as described previously.[5]

2-(3-*Azido*-2-*thienyl*)*vinyl Phenyl Sulphoxide* (**8g**).—Butyl-lithium (0.65 mmol) was added to a stirred solution of diethyl (phenylsulphinylmethyl)phosphonate[12] (179 mg, 0.65 mmol) in THF (20 ml) at −78 °C. After 20 min, a solution of 3-azidothiophene-2-carbaldehyde (100 mg, 0.65 mmol) in THF (10 ml) was added, and the mixture was stirred at −78 °C for a further 2 h before being allowed to warm to room temperature overnight. Aqueous work-up and chromatography gave the *title compound* (**8g**) (116 mg, 65%) as an unstable oil (Found: M^+, 275.0233. $C_{12}H_9N_3OS_2$ requires *M*, 275.0223); $\nu_{max.}$(neat) 2 100 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 6.65 (1 H, d, *J* 15 Hz), 6.90 (1 H, d, *J* 5 Hz), 7.23—7.35 (2 H, m), and 7.40—7.65 (5 H, m); *m/z* 275 (M^+), 247, 227, and 199 (base).

2-(3-*Azido*-2-*thienyl*)*vinyl Methyl Sulphone* (**8h**).—Butyl-lithium (0.65 mmol) was added to a stirred solution of dimethyl sulphone (61 mg, 0.65 mmol) in THF (20 ml) at −78 °C. After 20 min a solution of 3-azidothiophene-2-carbaldehyde (100 mg, 0.65 mmol) in THF (10 ml) was added, and the mixture was stirred at −78 °C for 1 h before being allowed to warm to room temperature. Methanesulphonyl chloride (115 mg, 1 mmol) and triethylamine (1 ml) was added, and the mixture was stirred overnight. Aqueous work-up and chromatography gave the *title compound* (**8h**) (97 mg, 65%) as an oil (Found: M^+, 228.9972. $C_7H_7N_3O_2S_2$ requires *M*, 228.9979); $\nu_{max.}$(CCl_4) 2 100 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 2.97 (3 H, s), 6.70 (1 H, d, *J* 15 Hz), 6.95 (1 H, d, *J* 5 Hz), 7.45 (1 H, d, *J* 5 Hz), and 7.55 (1 H, d, *J* 15 Hz); *m/z* 229 (M^+), 201, and 122 (base).

Ethyl 3-(2-*Azidophenyl*)-2-(*phenylthio*)*propenoate* (**9a**).—Prepared as described previously.[5]

Ethyl 2-*Acetyl*-3-(2-*azidophenyl*)*propenoate* (**9b**).—2-Azidobenzaldehyde[13] (100 mg, 0.68 mmol) was condensed with ethyl acetoacetate (97 mg, 0.75 mmol) in the presence of piperidinium acetate as described for compound (**8a**) to give the *title compound* (**9b**) (141 mg, 80%) as an *E*/*Z*-mixture, an oil (Found: C, 60.4; H, 5.0; N, 16.1. $C_{13}H_{13}N_3O_3$ requires C, 60.2; H, 5.05; N, 16.2%); $\nu_{max.}$(CCl_4) 2 120, 1 720, and 1 695 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.16 and 1.30 (3 H, 2 × t), 2.22 and 2.38 (3 H, 2 × s), 4.23 and 4.30 (2 H, 2 × q), 7.0—7.4 (4 H, m), and 7.68 and 7.76 (1 H, 2 × s); *m/z* 259 (M^+), 231, 217, 202, 189, 170, and 143 (base).

3-(2-*Azidophenyl*)*propenal* (**9c**).—A mixture of 2-azidobenzaldehyde (100 mg, 0.68 mmol), acetaldehyde (33 mg, 0.75 mmol), and aqueous potassium hydroxide (3% w/v; 2 ml) was stirred at room temperature for 3 h. Aqueous work-up and chromatography gave the title compound (**9c**) (92 mg, 78%), δ_H (90 MHz; $CDCl_3$) 6.69 (1 H, dd, *J* 7 and 16 Hz), 7.05—7.59 (4 H, m), 7.68 (1 H, d, *J* 16 Hz), and 9.60 (1 H, d, *J* 7 Hz); *m/z*; 173 (M^+), 145, 144, 117, and 90 (base).

2-(2-*Azidophenyl*)*vinyl Methyl Sulphide* (**9d**).—Butyl-lithium (0.54 mmol) was added to a stirred solution of methylthiomethyl(triphenyl)phosphonium chloride[14] (194 mg, 0.54 mmol) in THF (25 ml) at 0 °C. The solution was cooled to −78 °C and treated with a solution of 2-bromobenzaldehyde (100 mg, 0.54 mmol) in THF (10 ml). After 1 h, the mixture was allowed to warm to room temperature overnight. Aqueous work-up gave an *E*/*Z*-mixture of 2-(2-bromophenyl)vinyl methyl sulphide (89 mg, 72%) as an oil, $\nu_{max.}$(neat) 1 590 cm^{-1}; δ_H(90 MHz; $CDCl_3$) 2.30 and 2.35 (3 H, 2 × s), 6.3—6.7 (2 H, m), and 7.0—7.6 (4 H, m).

Butyl-lithium (0.37 mmol) was added to a stirred solution of the above bromo compound (85 mg, 0.37 mmol) in THF (10 ml) at −78 °C. After 20 min, a solution of tosyl azide (79 mg, 0.4 mmol) in THF (5 ml) was added, and the mixture was stirred at −78 °C for 2 h. After the mixture had warmed to room temperature, aqueous work-up and chromatography gave the title compound (**9d**) (40 mg, 57%) as an unstable oil, $\nu_{max.}$(neat)

2 120 and 1 590 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 2.35 (3 H, s) and 6.8—7.35 (6 H, m); *m/z* 191 (M^+), 163, and 148 (base).

Photolysis of Azides. General Procedure.—A solution of the azide in acetonitrile (150 ml per 100 mg azide) in a quartz tube was irridiated whilst a stream of nitrogen was bubbled through the solution. The irradiation was continued until t.l.c. indicated that the starting azide had been consumed. The solvent was evaporated off, and the residue was purified by chromatography.

Azide (**9a**). Irradiation of the azide (**9a**) (100 mg) at 300 nm gave ethyl 3-(phenylthio)indole-2-carboxylate (69 mg, 75%), m.p. 135 °C (lit.,[1] 135 °C).

Azide (**8a**). Irradiation of the azide (**8a**) (100 mg) at 350 nm gave *ethyl 6-acetyl-4H-thieno*[3,2-b]*pyrrole-5-carboxylate* (**10a**) (80 mg, 90%), m.p. 110 °C (Found: C, 55.7; H, 4.6; N, 5.85. $C_{11}H_{11}NO_3S$ requires C, 55.7; H, 4.7; N, 5.9%); $\nu_{max.}$(CCl_4) 3 420, 1 720, 1 680, and 1 640 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.43 (3 H, t), 2.83 (3 H, s), 4.45 (2 H, q), 6.96 (1 H, d, *J* 5 Hz), 7.42 (1 H, d, *J* 5 Hz), and 9.75 (1 H, br s); pre-irradiation of the NH proton (δ_H 9.75) caused enhancements at δ_H 6.96 (3-H) and at δ_H 4.45 and 1.43 (ethyl group); δ_C($CDCl_3$) 14.3, 30.8, 61.6, 110.4, 122.2, 125.0, 128.0, 132.2, 138.2, 160.1, and 194.2 p.p.m.; *m/z* 237 (M^+), 222, 191 (base), and 176.

Azide (**8b**). Irradiation of the azide (**8b**) (100 mg) at 350 nm gave 5-acetyl-4*H*-thieno[3,2-*b*]pyrrole (**10b**) (77 mg, 90%), m.p. 161—162 °C (lit.,[9] 160.5—163 °C); δ_H (250 MHz; $CDCl_3$) 2.52 (3 H, s), 6.98 (1 H, dd, *J* 1 and 5 Hz), 7.13 (1 H, d, *J* 1 Hz), 7.38 (1 H, d, *J* 5 Hz), and 9.90 (1 H, br s); pre-irradiation of the NH proton (δ_H 9.90) caused enhancements at δ_H 6.98 (3-H) and 2.52 (acetyl).

Azide (**9b**). Irradiation of the azide (**9b**) (100 mg) at 350 nm gave ethyl 3-acetylindole-2-carboxylate (**11a**) (79 mg, 88%), m.p. 96—97 °C (lit.,[15] 96—97 °C).

Azide (**9c**). Irradiation of the azide (**9c**) (100 mg) at 300 nm gave indole-2-carbaldehyde (**11b**) (75 mg, 90%), m.p. 141 °C (lit.,[16] 140—142 °C).

Azide (**8c**). Irradiation of the azide (**8c**) (100 mg) at 350 nm gave (i) *ethyl 6-phenylsulphinyl-4H-thieno*[3,2-b]*pyrrole-5-carboxylate* (**16a**) (48 mg, 52%), m.p. 154 °C (Found: C, 56.2; H, 4.0; N, 4.4. $C_{15}H_{13}NO_3S_2$ requires C, 56.4; H, 4.1; N, 4.4%); $\nu_{max.}$(CCl_4) 3 440 and 1 695 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.30 (3 H, t), 4.35 (2 H, q), 6.84 (1 H, d, *J* 5 Hz), 7.23 (1 H, d, *J* 5 Hz), 7.3—7.5 (3 H, m), 7.8—7.9 (2 H, m), and 10.68 (1 H, br s); δ_C($CDCl_3$) 14.3, 61.4, 110.9, 122.1, 124.1, 129.0, 130.8, 141.0, 144.9, and 160.0 p.p.m.; *m/z* 319 (M^+), 303, 271, 257, and 225 (base); and (ii) *3-ethoxycarbonyl-2-phenylthieno*[3,2-c][1,2]-*thiazin-2-ium-1-ide S-oxide* (**17**) (25 mg, 27%), m.p. 148—151 °C (Found: C, 56.3; H, 4.1; N, 4.4); $\nu_{max.}$(CCl_4) 1 705 cm^{-1}; $\lambda_{max.}$(EtOH) 318 (log ε 4.14) and 388 nm (3.79); δ_H (90 MHz; $CDCl_3$) 1.02 (3 H, t), 4.10 (2 H, qq), 6.98 (1 H, d, *J* 5.5 Hz), 7.50—7.65 (3 H, m), 7.77 (1 H, d, *J* 5.5 Hz), 7.82—8.00 (2 H, m), and 8.50 (1 H, s); δ_C($CDCl_3$) 13.8, 61.4, 101.7, 112.9, 123.7, 128.4, 129.4, 133.1, 136.9, 137.6, 141.8, 154.7, and 162.3 p.p.m.; *m/z* 319 (M^+, base).

Azide (**8d**). Irradiation of the azide (**8d**) (100 mg) at 350 nm gave *ethyl 6-phenylsulphonyl-4H-thieno*[3,2-b]*pyrrole-5-carboxylate* (**16b**) (74 mg, 80%), m.p. 171—175 °C (Found: C, 53.7; H, 3.8; N, 4.2. $C_{15}H_{13}NO_4S_2$ requires C, 53.7; H, 3.9; N, 4.2%); $\nu_{max.}$(CCl_4) 3 420 and 1 690 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 1.25 (3 H, t), 4.30 (2 H, q), 6.97 (1 H, d, *J* 5.5 Hz), 7.46—7.60 (4 H, m), 7.94—8.11 (2 H, m), and 10.02 (1 H, br s); δ_C($CDCl_3$) 14.1, 61.7, 110.9, 121.9, 124.7, 127.5, 127.8, 128.5, 132.0, 133.0, 138.2, 142.6, and 158.7 p.p.m.; *m/z* 335 (M^+, base).

Azide (**8e**). Irradiation of the azide (**8e**) (100 mg) at 350 nm gave *6-methylsulphinyl-5-methylthio-4H-thieno*[3,2-b]*pyrrole* (**18**) (49 mg, 55%) as an unstable oil (Found: M^+, 230.9845. $C_8H_9NOS_3$ requires *M*, 230.9846); $\nu_{max.}$(CCl_4) 3 440 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 2.40 (3 H, s), 3.00 (3 H, s), 6.86 (1 H, d, *J* 5 Hz), 7.20 (1 H, d, *J* 5 Hz), and 10.22 (1 H, br s); *m/z* 231 (M^+), 215, 200, 184, 169, and 154 (base).

Azide (**8f**). Irradiation of the azide (**8f**) (100 mg) at 300 nm gave (i) *5-methylthio-4H-thieno*[3,2-b]*pyrrole* (**19**) (23 mg, 27%) as an oil (Found: M^+, 169.0015. $C_7H_7NS_2$ requires *M*, 169.0020); $\nu_{max.}$(CCl_4) 3 465 cm^{-1}; δ_H (90 MHz; $CDCl_3$) 2.43 (3 H, s), 6.58 (1 H, d, *J* 1.5 Hz), 6.88 (1 H, d, *J* 5 Hz), 7.12 (1 H, d, *J* 5 Hz), and 8.20 (1 H, br); δ_C($CDCl_3$) 21.7, 107.7, 110.8, 119.0, 124.5, 127.5, and 139.7 p.p.m.; *m/z* 169 (M^+) and 154 (base); and (ii) 6-methylthio-4*H*-thieno[3,2-*b*]pyrrole (**20**) (19 mg, 22%), identical with a previously prepared specimen.[1]

Azide (**9d**). Irradiation of the azide (**9d**) (60 mg) at 300 nm gave 3-methylthioindole[7] (**22**) (28 mg, 55%), δ_H (250 MHz; $CDCl_3$) 2.46 (3 H, s), 7.15—7.30 (3 H, m), 7.36 (1 H, m), 7.77 (1 H, m), and 8.16 (1 H, s); δ_C($CDCl_3$) 20.1, 108.7, 111.5, 119.3, 120.4, 122.8, 127.6, 128.9, and 136.5 p.p.m.; *m/z* 163 (M^+) and 148 (base).

Azide (**8g**). Irradiation of the azide (**8g**) (100 mg) at 300 nm gave (i) *5-phenylsulphinyl-4H-thieno*[3,2-b]*pyrrole* (**23**) (23 mg, 26%) (Found: M^+, 247.0131. $C_{12}H_9NOS_2$ requires *M*, 247.0126); $\nu_{max.}$(CCl_4) 3 440 cm^{-1}; δ_H(90 MHz; $CDCl_3$) 6.94 (1 H, d, *J* 6 Hz), 7.00 (1 H, s), 7.32 (1 H, d, *J* 6 Hz), 7.4—7.8 (5 H, m), and 10.90 (1 H, br s); *m/z* 247 (M^+), 231, and 199 (base); (ii) 6-*phenylsulphinyl-4H-thieno*[3,2-b]*pyrrole* (**24**) (43 mg, 48%) (Found: M^+, 247.0131); δ_H [90 MHz; $(CD_3)_2SO$] 7.0 (1 H, d, *J* 4.6 Hz), 7.17 (1 H, d, *J* 4.6 Hz), 7.4—7.7 (5 H, m), 7.83 (1 H, s), and 12.91 (1 H, br s); *m/z* 247 (M^+), 231, and 199 (base); and (iii) *2-phenylthieno*[3,2-c][1,2]*thiazin-2-ium-1-ide* S-*oxide* (**25**) (20 mg, 22%) as an oil (Found: M^+, 247.0132); δ_H(90 MHz; $CDCl_3$) 6.00 (1 H, d, *J* 9 Hz), 7.0 (1 H, d, *J* 5.5 Hz), 7.50 (1 H, d, *J* 5.5 Hz), 7.58—7.68 (3 H, m), 7.79 (1 H, d, *J* 9 Hz), and 7.88—8.00 (2 H, m); *m/z* 247 (M^+, base).

Azide (**8h**). Irradiation of the azide (**8h**) (100 mg) at 300 nm gave *5-methylsulphonyl-4H-thieno*[3,2-b]*pyrrole* (**26**) (75 mg, 86%), m.p. 175—176 °C (Found: C, 41.7; H, 3.4; N, 6.85. $C_7H_7NO_2S_2$ requires C, 42.0; H, 3.0; N, 7.0%); $\nu_{max.}$(CCl_4) 3 440 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 3.20 (3 H, s), 7.00 (1 H, dd, *J* 5.5 and 0.6 Hz), 7.13 (1 H, dd, *J* 2.2 and 0.6 Hz), 7.39 (1 H, d, *J* 5.5 Hz), and 9.60 (1 H, br s); *m/z* 201 (M^+) and 108 (base).

Independent Synthesis of the Thienopyrrole (**16a**).—A solution of sodium metaperiodate (53 mg, 0.25 mmol) in a mixture of water (5 ml) and ethanol (5 ml) was added to a stirred solution of ethyl 6-phenylthio-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (50 mg, 0.17 mmol) in ethanol (10 ml). The mixture was stirred at room temperature until t.l.c. indicated that the oxidation was complete, and was then poured into water. Extraction with ether gave ethyl 6-phenylsulphinyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (**16a**) (51 mg, 98%), m.p. 154 °C.

Independent Synthesis of the Thienopyrrole (**16b**).—Ethyl 6-(phenylthio)-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (50 mg) was treated with potassium permanganate in acetic acid under the literature conditions[17] to give ethyl 6-phenylsulphonyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (**16b**) (8 mg, 15%), m.p. 171—175 °C.

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