Synthesis of Fused 1λ⁴,2-Thiazines(2-Azathiabenzenes)

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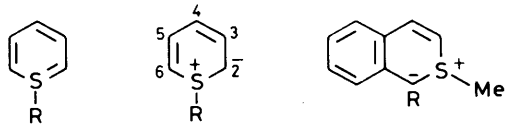
By analogy with the formation of acyclic sulphimides from sulphides and azides, mild thermolysis of aryl, hetaryl, and vinyl azides with a 1,6-related, conjugated thioether function gives the cyclic sulphimides, 1λ⁴,2-thiazines. Thus in boiling toluene the azidothiophenes (**9**), (**12**) and (**18**), the azidobenzenes (**14**), and the azidofuran (**16**) give the fused 1λ⁴,2-thiazines (**10**), (**13**), (**19**), (**15**), and (**17**) respectively. Yields are high when the products are stabilised by delocalisation of the ylidic (N^-–S^+) charges, but low when they are not. The *S*-allyl sulphimide (**10c**) is not isolable however since it rearranges spontaneously to the thienopyrrole (**11**). In contrast with azidothiophene (**12**), the 'reversed' thiophenes (**20**) do not give the corresponding 3,4-fused thienothiazines; the nitrene from the azide (**20a**) cyclises preferentially to carbon to give thienopyrrole (**21**) and that from the azide (**20b**) inserts into a methyl group to give the thienopyridine (**22**). Preferential cyclisation onto carbon rather than sulphur is also observed in the benzene series; thus azides (**24**) give 4-thio substituted indole-2-carboxylates (**25**) in good yield. The spectroscopic properties and thermal stabilities of all the 1λ⁴,2-thiazines prepared show them to be pyramidal cyclic S–N ylides rather than planar aromatic systems.

Conjugated six-membered rings containing a sulphur(IV) atom have attracted considerable interest over the last 25 years.[1] Despite earlier reports,[2] simple thiabenzenes (**1**; R = Ph) are not isolable compounds, and Mislow and co-workers[3] have demonstrated conclusively that thiabenzenes are better represented by the cyclic sulphonium ylide structure (**1A**). Thus electron-withdrawing substituents at C-2 stabilise the ring system, and the thianaphthalenes (**2**) are isolable compounds.[3,4] The ylidic structure of (**2b**) was further confirmed by an *X*-ray structure analysis.[5] Thiabenzenes lacking such electron-withdrawing substituents are highly reactive, although they can be isolated as their stable chromium-, molybdenum-, and tungsten-tricarbonyl complexes.[6]

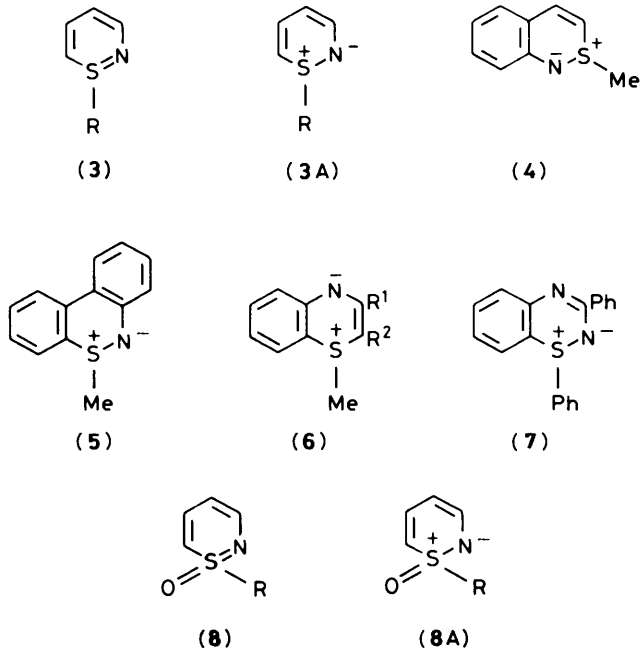


(**1**) (**1A**) (**2**)

a: R = C_6F_5
b: R = COPh
c: R = CN

2-Azathiabenzenes (**3**), the ylidic form (**3A**) of which would be expected to be more stable than the corresponding thiabenzenes because of the greater electronegativity of nitrogen, are less well described, although Hori and co-workers have prepared the azathianaphthalene (**4**) and the azathiaphenanthrene (**5**).[7] Related six-membered rings containing a sulphur(IV) atom that have been prepared include the 1λ⁴,4-thiazines (**6**),[8] and the 1λ⁴,2,4-benzothiadiazines (**7**).[9] In contrast, azathiabenzene *S*-oxides (**8**) are well known,[10] and their chemical and physical properties suggest that they are best considered as cyclic sulphoxonium ylides (**8A**).

We have been interested in open-chain sulphur-nitrogen ylides (sulphimides) for a number of years,[11,12] and in this paper, the first of a series, we report in full the preparation and properties of a range of cyclic sulphimides, fused derivatives of 2-azathiabenzene.[13]



(**3**) (**3A**) (**4**)

(**5**) (**6**) (**7**)

(**8**) (**8A**)

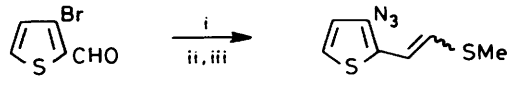
Results and Discussion

One of the standard ways of preparing acyclic sulphimides involves the decomposition of organic azides in the presence of sulphides,[11] and we therefore investigated the intramolecular version of this reaction as a route to cyclic sulphimides. Since we were already studying the decomposition of 3-azidothiophenes,[14] the initial experiments were performed in the thiophene series. Thus 3-azidothiophene-2-carbaldehyde[15] was condensed with ethyl methylthioacetate in ethanolic sodium ethoxide at −15 °C to give the azide (**9a**) in good yield. The azides (**9b—g**) were similarly prepared by condensation with the appropriate methylene compound (Scheme 1). The azide (**9h**), lacking the electron-withdrawing substituent was prepared as an *E*/*Z*-mixture by Wittig reaction of 3-bromothiophene-2-

(9)

a ; R = Me , Z = CO_2Et
b ; R = Et , Z = CO_2Et
c ; R = allyl , Z = CO_2Et
d ; R = Ph, Z = CO_2Et
e ; R = Ph, Z = COMe
f ; R = Ph, Z = CHO
g ; R = Ph, Z = CN

Scheme 1. *Reagents:* i, ZCH_2SR, NaOEt, EtOH, −15 °C



(9h)

Scheme 2. *Reagents:* i, $MeSCH{=}PPh_3$, THF; ii, BuLi, THF, −78 °C; iii, TsN_3

carbaldehyde with methylthiomethylenetriphenylphosphorane followed by lithiation and quenching with tosyl azide (Scheme 2).

The azides (**9**) decomposed in boiling toluene to give the expected cyclic sulphimides, the thieno[3,2-*c*][1λ⁴,2]thiazines (**10**) in varying yields (Table). In most cases, the sulphimides were accompanied by small amounts of other products derived from their further thermolysis.* The sulphimide (**10h**), lacking the stabilising substituent, is particularly thermally unstable and hence was only isolated in poor yield even in refluxing benzene. Likewise the *S*-ethyl sulphimide (**10b**) was only isolated in low yield because of its thermal instability which in this case is probably related to a cycloelimination reaction, a process known to occur readily in sulphimides containing a sulphur substituent with β-hydrogen atoms.[11] Thermolysis of the *S*-allyl substituted azide (**9c**) did not give the corresponding sulphimide but the thienopyrrole (**11**) (72%). This product presumably arises by initial [2,3]-sigmatropic rearrangement[11] of the *S*-allylsulphimide (**10c**) followed by further rearrangement and extrusion of sulphur, although the exact timing of these latter steps is unknown.

Attempts to prepare the isomeric thieno[3,4-*c*][1λ⁴,2]-thiazines were less successful, although thermolysis of the azide (**12a**) in toluene did give the cyclic sulphimide (**13a**) as an unstable red gum. The corresponding *S*-methylsulphimide (**13b**) could not be isolated.

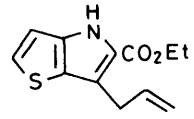
However, 1λ⁴,2-thiazines fused to rings other than thiophene could be readily prepared from the corresponding azido-aldehydes. Thus condensation of 2-azidobenzaldehyde[16] and 3-azidofuran-2-carbaldehyde[17] with the appropriate derivative of mercaptoacetic acid gave the azides (**14**) and (**16**). Thermolysis of (**14a**) and (**16**) gave the corresponding cyclic sulphimides (**15a**) and (**17**) in good yield. However, the thermolysis of the *S*-methyl compound (**14b**) gave only poor yields of a red oil which, although it was not completely characterised, had spectral properties consistent with the azathianaphthalene structure (**15b**).

* The thermal rearrangement and degradation of these sulphimides is discussed in the following paper.

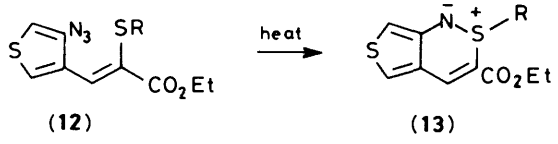
Table. Preparation of thieno[3,2-*c*][1λ⁴,2]thiazines

(9) (10)

(9)/(10)	R	Z	Yield (%)
a	Me	CO_2Et	84
b	Et	CO_2Et	30
c	$CH_2CH{=}CH_2$	CO_2Et	0
d	Ph	CO_2Et	89
e	Ph	COMe	90
f	Ph	CHO	75
g	Ph	CN	90
h	Me	H	4

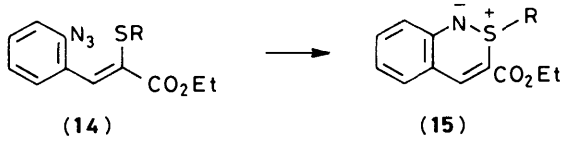


(11)



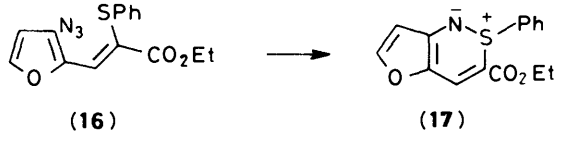
(12) (13)

a, R = Ph ; b, R = Me



(14) (15)

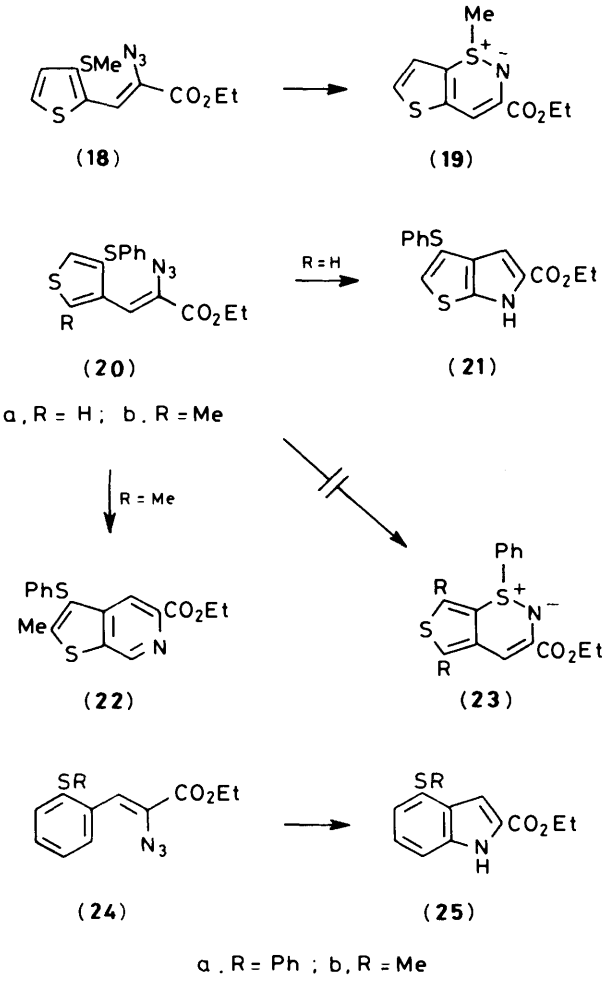
a, R = Ph; b, R = Me



(16) (17)

The successful preparation of fused 2-azathiabenzenes by thermolysis of aryl and hetaryl azides bearing sulphur containing *ortho*-substituents prompted an investigation into the 'reversed' cyclic sulphimides, *i.e.* where the positions of the sulphur and nitrogen atoms are interchanged. Again the initial work was performed in the thiophene series, and condensation of 3-(methylthio)thiophene-2-carbaldehyde[18] with ethyl azidoacetate gave the required precursor (**18**). Thermolysis of azide (**18**) in boiling toluene gave the cyclic sulphimide (**19**) in 89% yield.

The corresponding 3,4-fused thiophene derivatives could not be prepared by this method owing to preferential cyclisation of the nitrene derived from the vinyl azide to the thiophene



2-position.[19] Thus 4-bromothiophene-3-carbaldehyde ethylene acetal[20] was lithiated and quenched with diphenyl disulphide to give, after deprotection, 4-(phenylthio)thiophene-3-carbaldehyde, which was condensed with ethyl azidoacetate to give the azide (**20a**). Thermolysis of (**20a**) gave the thienopyrrole (**21**) in 98% yield with no trace of the cyclic sulphimide (**23a**).

Introduction of blocking methyl groups into the thiophene 2- and 5-positions still did not induce cyclisation onto sulphur. The product isolated from the thermolysis of the azide (**20b**) was the thienopyridine (**22**), presumably formed by attack of the vinyl-nitrene on the methyl group followed by oxidation on work-up.[21]

Preferential cyclisation of the vinylnitrene onto a ring carbon atom rather than onto the sulphur atom was also observed in the benzene series. Thermolysis of the azides (**24**) resulted in good yields of the corresponding 4-sulphur substituted indole-2-carboxylates (**25**) rather than cyclic sulphimides.

All the 2-azathiabenzenes prepared in the present study have properties which support their formulation as cyclic sulphur-nitrogen ylides, their thermal stability being increased by structural elements which can stabilise or delocalise a positive charge on sulphur and/or a negative charge on nitrogen. Therefore, in general, the *S*-phenyl cyclic sulphimides are more stable than the corresponding *S*-methyl compounds. The sulphimide (**10h**) lacking an electron-withdrawing group is particularly unstable, and of the isomeric sulphimides (**10d**) and (**13a**), the former is more stable. Any delocalisation of the negative charge into the ester carbonyl in the latter case would require the intervention of non-classical thiophene tautomers. This difference in delocalisation is reflected in the i.r. and ^{13}C n.m.r. spectra of the two sulphimides (**10d**) and (**13a**), the ester carbonyl stretch appearing at 1 670 and 1 690 cm^{-1}, and the carbon resonance for C-3 appearing at 85.5 and 113.8 p.p.m. (or 125.4, 143.4, 148.7; exact assignment uncertain) respectively.

The isomeric pair of *S*-methyl sulphimides (**10a**) and (**19**) also show marked differences in their spectral properties, reflecting the fact that in (**10a**) the negative charge can be fully delocalised into the ester carbonyl. The carbonyl stretching frequencies and C-3 carbon resonances for (**10a**) and (**19**) are 1 675 and 1 695 cm^{-1} and 85.2 and 143.4 (or 144.7) p.p.m. respectively.

The ylidic nature and non-planarity of the 2-azathiabenzene ring system and the pyramidal geometry of the sulphur atom is also evidenced by the ^1H n.m.r. spectra of some of the cyclic sulphimides. In the ethyl esters (**10d**), (**15**), (**17**), and (**19**), the ester methylene groups appear as quartets of quartets indicating the prochiral nature of the CH_2 group which results from the non-planarity of the adjacent sulphur atom. The effect is even more marked in the *S*-ethyl sulphimide (**10b**) where the prochiral methylene of the ethyl group is attached directly to the sulphur atom. It had been hoped to use the n.m.r. properties of the ethyl group in (**10b**) to measure the inversion barrier at sulphur, but the thermal instability of the compound precluded its use in the appropriate variable-temperature n.m.r. experimental procedure.

Final confirmation of the ylidic nature of the azathiabenzene derivatives came from an *X*-ray crystal structure determination of the *S*-phenyl derivative (**10d**), the details of which have already been published.[13]

In conclusion, we have prepared several fused derivatives of the $1\lambda^4$,2-thiazine ring system by the decomposition of azides bearing suitably positioned sulphur atoms to intercept the intermediate nitrenes. Although these could be considered as fused derivatives of 2-azathiabenzene, their properties indicate that they are ylidic and are best considered as cyclic sulphimides. The thermal and photochemical rearrangements and decomposition of these novel cyclic ylides are discussed in the following papers.

Experimental

For general points see ref. 14.

Starting Materials

(a) *Aldehydes.*—3-Azidothiophene-2-carbaldehyde,[15] 3-bromothiophene-2-carbaldehyde,[15] 4-azidothiophene-3-carbaldehyde,[20] 2-azidobenzaldehyde,[16] 3-azidofuran-2-carbaldehyde,[17] 3-(methylthio)thiophene-2-carbaldehyde,[18] 2-(phenylthio)benzaldehyde,[22] and 2-(methylthio)benzaldehyde[23] were prepared by literature methods.

4-(*Phenylthio*)*thiophene*-3-*carbaldehyde.* Butyl-lithium (4.25 mmol) was added to a solution of 4-bromothiophene-3-carbaldehyde ethylene acetal[20] (1.00 g, 4.25 mmol) in dry ether (5 ml) at −78 °C. The solution was stirred for 35 min before being added to a solution of diphenyl disulphide (0.93 g, 4.3 mmol) in dry ether (5 ml). After being stirred for 3 h, the mixture was poured into water, and extracted with ether (2 × 150 ml). The combined ether extracts were washed with aqueous sodium hydroxide and water, and evaporated. The crude product was dissolved in dilute hydrochloric acid, and then extracted with ether. The ether extracts were washed with aqueous sodium hydrogen carbonate, dried, evaporated, and the residue chromatographed to give the *title compound* as an oil (750 mg, 80%) (Found: C, 59.7; H, 3.95. $C_{11}H_8OS_2$ requires C, 60.0; H, 3.7%); $\nu_{max.}$ 1 695 cm^{-1}; δ (60 MHz, $CDCl_3$) 7.0 (1 H, d, *J* 3.2 Hz), 7.15—7.30 (5 H, m), 8.10 (1 H, d, *J* 3.2 Hz), and 9.90 (1 H, s); *m/z* 220 (M^+, base).

2,5-*Dimethyl*-4-(*phenylthio*)*thiophene*-3-*carbaldehyde*. Butyl-lithium (0.75 mmol) was added to a solution of 3,4-dibromo-2,5-dimethylthiophene[24] (200 mg, 0.74 mmol) in dry THF (25 ml) at −78 °C. The solution was stirred for 45 min before being added to a solution of diphenyl disulphide (165 mg, 0.76 mmol) in THF (50 ml) at −78 °C. The mixture was stirred for 2 h, allowed to warm to room temperature, and then poured into saturated aqueous ammonium chloride. Extraction with ether and chromatography gave 3-bromo-2,5-dimethyl-4-(phenylthio)thiophene (188 mg, 85%).

The above bromo compound (150 mg, 0.5 mmol) was dissolved in dry THF (25 ml), cooled to −78 °C, and treated with butyl-lithium (0.5 mmol). After 45 min, dimethylformamide (0.1 ml) was added, and the mixture stirred for a further 2 h at −78 °C. After being warmed to room temperature, the mixture was poured into saturated aqueous ammonium chloride, and extracted with ether. The combined ether extracts were dried, evaporated, and the residue chromatographed to give the title compound (93 mg, 75%), δ (90 MHz, CCl_4) 2.45 (3 H, s), 2.72 (3 H, s), 7.1 (5 H, m), and 9.95 (1 H, s), used without further purification.

(b) *'Active Methylene Compounds'*.—Ethyl (methylthio)-acetate,[25] ethyl (ethylthio)acetate,[26] ethyl 2-(allylthio)-acetate,[27] ethyl (phenylthio)acetate,[25] (phenylthio)acetone,[25] (phenylthio)acetaldehyde,[28] (phenylthio)acetonitrile,[29] and ethyl azidoacetate[30] were prepared by the literature methods.

Condensation of Aldehydes with Active Methylene Compounds. General Procedure.—A mixture of the aldehyde (1 equiv.) and the active methylene compound (1.1 equiv.)* was added dropwise to a stirred solution of sodium ethoxide [from sodium (1.1 equiv.)*] in ethanol (100 ml per 1 g sodium) at −15 °C. The mixture was stirred at −15 °C for 2 h, and then allowed to warm to room temperature overnight, care being taken to protect the reaction mixture from light at all times. The mixture was poured into aqueous ammonium chloride and extracted with ether (2 × 150 ml). The combined ether extracts were washed with saturated aqueous sodium metabisulphite and water, dried ($MgSO_4$), evaporated, and the residue purified by chromatography on silica gel.

The following compounds were prepared by this procedure: *Ethyl* 3-(3-*azido*-2-*thienyl*)-2-(*methylthio*)*propenoate* (**9a**) (82%) from 3-azidothiophene-2-carbaldehyde and ethyl (methylthio)-acetate, m.p. 54—55 °C (from light petroleum) (Found: C, 44.5; H, 4.0; N, 15.5. $C_{10}H_{11}N_3O_2S_2$ requires C, 44.6; H, 4.1; N, 15.6%); $\nu_{max.}$(Nujol) 2 120, 2 100, and 1 700 cm^{-1}; δ (250 MHz, $CDCl_3$), 1.38 (3 H, t), 2.37 (3 H, s), 4.33 (2 H, q), 6.99 (1 H, d, *J* 5.4 Hz), 7.55 (1 H, dd, *J* 5.4, 0.8 Hz), and 8.15 (1 H, d, *J* 0.8 Hz); *m/z* 269 (M^+), 241, 226, 212, 198 (base), 154, and 101.

Ethyl 3-(3-*azido*-2-*thienyl*)-2-(*ethylthio*)*propenoate* (**9b**) (50%) from 3-azidothiophene-2-carbaldehyde and ethyl (ethylthio)-acetate, unstable yellow oil, $\nu_{max.}$(neat) 2 120 and 1 710 cm^{-1}; δ (90 MHz, $CDCl_3$), 1.22 (3 H, t), 1.35 (3 H, t), 2.83 (2 H, q), 4.26 (2 H, q), 6.95 (1 H, d, *J* 5 Hz), 7.50 (1 H, d, *J* 5 Hz), and 8.20 (1 H, s).

Ethyl 3-(3-*azido*-2-*thienyl*)-2-(*allylthio*)*propenoate* (**9c**) (57%) from 3-azidothiophene-2-carbaldehyde and ethyl (allylthio)-acetate as a pale yellow oil (Found: C, 48.7; H, 4.35; N, 14.0. $C_{12}H_{13}N_3O_2S_2$ requires C, 48.8; H, 4.4; N, 14.2%); $\nu_{max.}$(neat) 2 100 and 1 700 cm^{-1}; δ (90 MHz, $CDCl_3$) 1.37 (3 H, t), 3.50 (2 H, d, *J* 6.4 Hz), 4.33 (2 H, q), 4.90—5.25 (2 H, m), 5.58—6.05 (1 H, m), 6.99 (1 H, d, *J* 5.3 Hz), 7.53 (1 H, dd, *J* 5.3, 0.9 Hz), and 8.24 (1 H, d, *J* 0.9 Hz).

Ethyl 3-(3-*azido*-2-*thienyl*)-2-(*phenylthio*)*propenoate* (**9d**) (91%) from 3-azidothiophene-2-carbaldehyde and ethyl (phenylthio)acetate, m.p. 106—108 °C (decomp.) (from light petroleum–dichloromethane) (Found: C, 54.3; H, 3.9; N, 12.65. $C_{15}H_{13}N_3O_2S_2$ requires C, 54.4; H, 3.95; N, 12.7%); $\nu_{max.}$(Nujol) 2 135, 2 120, and 1 700 cm^{-1}; δ (250 MHz, $CDCl_3$) 1.13 (3 H, t), 4.18 (2 H, q), 7.00 (1 H, d, *J* 5.0 Hz), 7.12—7.38 (5 H, m), 7.53 (1 H, dd, *J* 5.0, 0.8 Hz), and 8.43 (1 H, d, *J* 0.8 Hz); *m/z* 331 (M^+), 303, 274, 230, 226 (base), and 198.

4-(3-*Azido*-2-*thienyl*)-3-(*phenylthio*)*but*-3-*en*-2-*one* (**9e**) (75%) from 3-azidothiophene-2-carbaldehyde and (phenylthio)-acetone, m.p. 96 °C (from light petroleum–dichloromethane) (Found: C, 55.8; H, 3.7; N, 13.9. $C_{14}H_{11}N_3OS_2$ requires C, 55.8; H, 3.7; N, 13.9%); $\nu_{max.}$(CCl_4) 2 100 and 1 675 cm^{-1}; δ (90 MHz, $CDCl_3$) 2.38 (3 H, s), 7.00 (1 H, d, *J* 5.5 Hz), 7.21 (5 H, m), 7.53 (1 H, dd, *J* 5.5, 0.9 Hz), and 8.37 (1 H, d, *J* 0.9 Hz); *m/z* 301 (M^+), 273, 257, 231, and 196 (base).

3-(3-*Azido*-2-*thienyl*)-2-(*phenylthio*)*propenal* (**9f**) (50%) from 3-azidothiophene-2-carbaldehyde and (phenylthio)acet-aldehyde, m.p. 82—83 °C (from light petroleum–dichloro-methane) (Found: C, 54.5; H, 3.2; N, 14.5. $C_{13}H_9N_3OS_2$ requires C, 54.3; H, 3.2; N, 14.6%); $\nu_{max.}$(CCl_4) 2 100 and 1 690 cm^{-1}; δ (90 MHz, $CDCl_3$) 7.05 (1 H, d, *J* 5.5 Hz), 7.2—7.4 (5 H, m), 7.60 (1 H, dd, *J* 5.5, 0.9 Hz), 8.15 (1 H, d, *J* 0.9 Hz), and 9.60 (1 H, s); *m/z* 287 (M^+), 259, 243 (base), and 182.

3-(3-*Azido*-2-*thienyl*)-2-(*phenylthio*)*propenonitrile* (**9g**) (80%) from 3-azidothiophene-2-carbaldehyde and (phenylthio)-acetonitrile, m.p. 98—99 °C (Found: C, 55.1; H, 2.8; N, 19.7. $C_{13}H_8N_4S_2$ requires C, 54.9; H, 2.8; N, 19.7%); $\nu_{max.}$(CCl_4) 2 210 and 2 120 cm^{-1}; δ (90 MHz, $CDCl_3$) 7.0 (1 H, d, *J* 5.4 Hz), 7.32—7.50 (5 H, m), 7.56 (1 H, dd, *J* 5.4, 1.0 Hz), and 7.70 (1 H, d, *J* 1.0 Hz); *m/z* 284 (M^+), 256, and 179 (base).

Ethyl 3-(4-*azido*-3-*thienyl*)-2-(*phenylthio*)*propenoate* (**12a**) (57%) from 4-azidothiophene-3-carbaldehyde and ethyl (phenylthio)acetate, as a pale yellow oil (Found: M^+, 331.0461. $C_{15}H_{13}N_3O_2S_2$ requires 331.0449); $\nu_{max.}$(neat) 2 140 and 1 710 cm^{-1}; δ (250 MHz, $CDCl_3$) 1.08 (3 H, t), 4.11 (2 H, q), 6.84 (1 H, d, *J* 4.0 Hz), 7.15—7.35 (5 H, m), 7.90 (1 H, d, *J* 0.8 Hz), and 8.36 (1 H, dd, *J* 4.0, 0.8 Hz); *m/z* 331 (M^+), 303, and 226 (base).

Ethyl 3-(4-*azido*-3-*thienyl*)-2-(*methylthio*)*propenoate* (**12b**) (51%) from 4-azidothiophene-3-carbaldehyde and ethyl (methylthio)acetate, as an unstable yellow oil, $\nu_{max.}$(neat) 2 120 and 1 710 cm^{-1}; δ (60 MHz, $CDCl_3$) 1.10 (3 H, t), 2.40 (3 H, s), 4.10 (2 H, q), 6.80 (1 H, d, *J* 3 Hz), 7.9 (1 H, s), and 8.3 (1 H, d, *J* 3 Hz); *m/z* 269 (M^+) and 241 (base).

Ethyl 3-(2-*azidophenyl*)-2-(*phenylthio*)*propenoate* (**14a**) (86%) from 2-azidobenzaldehyde and ethyl (phenylthio)acetate as a yellow oil, $\nu_{max.}$(neat) 2 120 and 1 710 cm^{-1}; δ (60 MHz, $CDCl_3$) 1.0 (3 H, t), 4.1 (2 H, q), 6.9—7.9 (9 H, m), and 8.1 (1 H, s); *m/z* 325 (M^+), 220, 192, and 176.

Ethyl 3-(2-*azidophenyl*)-2-(*methylthio*)*propenoate* (**14b**) (57%) from 2-azidobenzaldehyde and ethyl (methylthio)acetate, as an unstable yellow oil, $\nu_{max.}$(neat) 2 120 and 1 710 cm^{-1}; δ (90 MHz, $CDCl_3$) 1.4 (3 H, t), 2.3 (3 H, s), 4.3 (2 H, q), 7.0—7.9 (4 H, m), and 7.9 (1 H, s); *m/z* 235 (M^+), 220, 192, and 148.

Ethyl 3-(3-*azido*-2-*furyl*)-2-(*phenylthio*)*propenoate* (**16**) (60%) from 3-azidofuran-2-carbaldehyde and ethyl (phenylthio)-acetate, m.p. 81—84 °C (decomp.) (from light petroleum) (Found: C, 57.4; H, 4.1; N, 13.2. $C_{15}H_{13}N_3O_3S$ requires C, 57.1; H, 4.2; N, 13.3%); $\nu_{max.}$(Nujol) 2 130 and 1 690 cm^{-1}; δ (250 MHz, $CDCl_3$) 1.0 (3 H, t), 4.1 (2 H, q), 6.5 (1 H, d, *J* 2 Hz), 7.1—7.4 (5 H, m), 7.5 (1 H, d, *J* 2 Hz), and 7.7 (1 H, s); *m/z* 315 (M^+), 287, 258, and 210.

Ethyl 2-*azido*-3-[3-(*methylthio*)-2-*thienyl*]*propenoate* (**18**) (52%) from 3-(methylthio)thiophene-2-carbaldehyde and ethyl azidoacetate, m.p. 61—64 °C (from light petroleum) (Found: C, 44.55; H, 4.1; N, 15.4. $C_{10}H_{11}N_3O_2S_2$ requires C, 44.6; H, 4.1; N, 15.6%); $\nu_{max.}$(Nujol) 2 120 and 1 710 cm^{-1}; δ (250 MHz, $CDCl_3$) 1.40 (3 H, t), 2.47 (3 H, s), 4.38 (2 H, q), 7.07 (1 H, d, *J* 5.3 Hz), 7.46 (1 H, d, *J* 0.7 Hz), and 7.48 (1 H, dd, *J* 5.3, 0.7 Hz); *m/z* 269 (M^+), 243, 241, and 226 (base).

* In the case of ethyl azidoacetate, 4 equiv. were used.

Ethyl 2-azido-3-[4-(phenylthio)-3-thienyl]propenoate (**20a**) (40%) from 4-(phenylthio)thiophene-3-carbaldehyde and ethyl azidoacetate as an unstable yellow oil, $\nu_{max.}$(CCl_4) 2 120 and 1 690 cm^{-1}; δ (60 MHz, $CDCl_3$) 1.3 (3 H, t), 4.25 (2 H, q), 6.95 (1 H, s), 7.1—7.2 (5 H, m), 7.4 (1 H, d, *J* 3 Hz), and 8.3 (1 H, d, *J* 3 Hz); *m/z* 331 (M^+) and 303 (base).

Ethyl 2-Azido-3-[2,5-dimethyl-4-(phenylthio)-3-thienyl]-propenoate (**20b**) (60%) from 2,5-dimethyl-4-(phenylthio)thiophene-3-carbaldehyde and ethyl azidoacetate, as an unstable yellow oil, $\nu_{max.}$(neat) 2 110 and 1 690 cm^{-1}; δ (90 MHz, $CDCl_3$) 1.3 (3 H, t), 2.45 (3 H, s), 2.55 (3 H, s), 4.23 (2 H, q), 6.65 (1 H, s), and 7.0—7.2 (5 H, m); *m/z* 359 (M^+), 331, and 254 (base).

Ethyl 2-azido-3-(2-phenylthiophenyl)propenoate (**24a**) (81%) from 2-(phenylthio)benzaldehyde and ethyl azidoacetate as a yellow oil, $\nu_{max.}$(neat) 2 120 and 1 710 cm^{-1}; δ (60 MHz, $CDCl_3$) 1.3 (3 H, t), 4.3 (2 H, q), and 7.0—8.2 (10 H, m); *m/z* 325 (M^+), 297, 220, and 197.

Ethyl 2-azido-3-(2-methylthiophenyl)propenoate (**24b**) (63%) from 2-(methylthio)benzaldehyde and ethyl azidoacetate as a yellow oil, $\nu_{max.}$(neat) 2 120 and 1 710 cm^{-1}; δ (60 MHz, $CDCl_3$) 1.4 (3 H, t), 2.5 (3 H, s), 4.4 (2 H, q), and 6.7—8.2 (5 H, m).

2-(3-Azido-2-thienyl)vinyl methyl sulphide (**9h**). n-Butyl-lithium (1.05 mmol) was added to a stirred solution of methylthiomethyltriphenylphosphonium chloride[31] (376 mg, 1.05 mmol) in dry THF (30 ml). The solution was cooled to −78 °C and then treated with a solution of 3-bromothiophene-2-carbaldehyde (200 mg, 1.05 mmol) in THF (10 ml). After 1 h at this temperature, the mixture was allowed to warm to room temperature. Standard work-up gave a 1:1 mixture of E- and Z-*2-(3-bromo-2-thienyl)vinyl methyl sulphide* (214 mg, 87%) as an oil (Found: C, 35.5; H, 2.9. $C_7H_7BrS_2$ requires C, 35.75; H, 3.0); $\nu_{max.}$(neat) 1 580 cm^{-1}; *E*-isomer δ (90 MHz, $CDCl_3$) 2.38 (3 H, s), 6.52 (1 H, d, *J* 15.3 Hz), 6.75 (1 H, d, *J* 15.3 Hz), 6.88 (1 H, d, *J* 5.0 Hz), and 7.0 (1 H, d, *J* 5.0 Hz); *Z*-isomer δ (90 MHz, $CDCl_3$) 2.43 (3 H, s), 6.25 (1 H, d, *J* 11.0 Hz), 6.75 (1 H, d, *J* 11.0 Hz), 6.97 (1 H, d, *J* 5.0 Hz), and 7.3 (1 H, d, *J* 5.0 Hz).

The 1:1 mixture of the above bromo compounds (100 mg, 0.43 mmol) was dissolved in THF (20 ml), cooled to −78 °C and treated with butyl-lithium (0.43 mmol). After 20 min, a solution of toluene-*p*-sulphonyl azide (89 mg, 0.45 mmol) was added, and the mixture stirred at —78 °C for 2 h before being allowed it to warm to room temperature. Aqueous work-up and chromatography gave an *E*/*Z*-mixture of the *title compound* (**9h**) (50 mg, 60%) as an unstable oil (Found: M^+, 197.0088. $C_7H_7N_3S_2$ requires *M*, 197.0081); $\nu_{max.}$(neat) 2 100 cm^{-1}; *Z*-isomer δ (90 MHz, $CDCl_3$) 2.44 (3 H, s), 6.11 (1 H, d, *J* 10 Hz), 6.67 (1 H, d, *J* 10 Hz), 6.94 (1 H, d, *J* 5.5 Hz), and 7.33 (1 H, d, *J* 5.5 Hz); *E*-isomer δ 2.36 (3 H, s), 6.45 (1 H, d, *J* 17 Hz), 6.60 (1 H, d, *J* 17 Hz), 6.8 (1 H, d, *J* 5.5 Hz), and 7.02 (1 H, d, *J* 5.5 Hz); *m/z* 197 (M^+), 169, and 154 (base).

Thermolysis of Azides: General Procedure.—The azide was dissolved in dry toluene (or benzene or xylene) (50 ml per 100 mg azide) and the solution heated under reflux under a nitrogen atmosphere until t.l.c. indicated that all the azide had disappeared. The solvent was evaporated, and the residue chromatographed on silica gel.

Azide (**9a**). Thermolysis of the azide (**9a**) (350 mg) in toluene for 3 h gave *ethyl 2-methylthieno*[3,2-c][1λ⁴,2]*thiazine-3-carboxylate* (**10a**) (119 mg, 84%) as an orange-red gum which solidified with time, m.p. 72—73 °C (Found: C, 49.5; H, 4.6; N, 5.7. $C_{10}H_{11}NO_2S_2$ requires C, 49.8; H, 4.6; N, 5.8%); $\nu_{max.}$(Nujol) 1 675 cm^{-1}; $\lambda_{max.}$(EtOH) 217 (log ε 3.94), 268 (3.53), 321 (3.88), and 457 nm (3.64); δ (250 MHz, $CDCl_3$) 1.35 (3 H, t), 2.28 (3 H, s), 4.31 (2 H, q), 6.79 (1 H, dd, *J* 5.4, 0.8 Hz), 7.62 (1 H, d, *J* 5.4 Hz), and 8.02 (1 H, d, *J* 0.8 Hz); δ_C($CDCl_3$) 14.4, 28.5, 61.1, 85.2, 114.0, 124.2, 135.8, 136.7, 162.0, and 162.7; *m/z* 241 (M^+), 226 (base), 198, 154, and 110.

Azide (**9b**). Thermolysis of the azide (**9b**) (100 mg) in toluene gave *ethyl 2-ethylthieno*[3,2-c][1λ⁴,2]*thiazine-3-carboxylate* (**10b**) (27 mg, 30%) as a dark red gum (Found: M^+, 255.0376. $C_{11}H_{13}NO_2S_2$ requires *M*, 255.0388); $\nu_{max.}$(CCl_4) 1 690 cm^{-1}; $\lambda_{max.}$(EtOH) 220 (log ε 4.05), 270 (3.96), 323 (3.96), and 468 nm (3.72); δ (90 MHz, $CDCl_3$) 1.10 (3 H, t), 1.33 (3 H, t), 2.68 (2 H, qq), 4.30 (2 H, q), 6.8 (1 H, d, *J* 5 Hz), 7.60 (1 H, d, *J* 5 Hz), and 8.04 (1 H, s); δ_C($CDCl_3$) 6.3, 14.4, 36.4, 61.1, 83.8, 114.5, 124.0, 136.1, 136.7, 162.5, and 163.2; *m/z* 255 (M^+), 226 (base), and 198.

Azide (**9c**). Thermolysis of the azide (**9c**) (100 mg) in toluene gave *ethyl 6-allylthieno*[3,2-b]*pyrrole-5-carboxylate* (**11**) (65 mg, 72%), m.p. 96—98 °C (Found: C, 61.2; H, 5.6; N, 5.9. $C_{12}H_{13}NO_2S$ requires C, 61.25; H, 5.61; N, 5.95); $\nu_{max.}$(CCl_4) 3 460 and 1 690 cm^{-1}; δ (90 MHz, $CDCl_3$) 1.40 (3 H, t), 3.77 (2 H, m), 4.37 (2 H, q), 5.0—5.3 (2 H, m), 5.8—6.3 (1 H, m), 6.90 (1 H, d, *J* 5 Hz), 7.28 (1 H, d, *J* 5 Hz), and 9.0 (1 H, s); *m/z* 235 (M^+, base).

Azide (**9d**). Thermolysis of the azide (**9d**) (500 mg) in toluene for 2.5 h gave *ethyl 2-phenylthieno*[3,2-c][1λ⁴,2]*thiazine-3-carboxylate* (**10d**) (410 mg, 89%) as red crystals, m.p. 128—129 °C (from light petroleum–ether acetate) (Found: C, 59.3; H, 4.4; N, 4.6. $C_{15}H_{13}NO_2S_2$ requires C, 59.4; H, 4.3; N, 4.6%); $\nu_{max.}$(Nujol) 1 670 cm^{-1}; $\lambda_{max.}$(EtOH) 220 (log ε 4.15), 262sh (3.64), 326 (3.93), and 459 nm (3.63); δ (250 MHz, $CDCl_3$) 1.38 (3 H, t), 4.38 (2 H, q), 6.89 (1 H, dd, *J* 5.5, 0.8 Hz), 7.31—7.44 (3 H, m), 7.46—7.52 (2 H, m), 7.59 (1 H, d, *J* 5.5 Hz), and 8.12 (1 H, d, *J* 0.8 Hz); δ_C($CDCl_3$) 14.5, 61.3, 85.5, 116.2, 123.7, 125.5, 129.0, 130.9, 136.8, 137.0, 139.6, 163.4, and 163.7; *m/z* 303 (M^+), 258, 230, 226 (base), 198, and 154.

Azide (**9e**). Thermolysis of the azide (**9e**) (100 mg) in toluene gave *3-acetyl-2-phenylthieno*[3,2-c][1λ⁴,2]*thiazine* (**10e**) (82 mg, 90%) as red crystals, m.p. 135—136 °C (Found: C, 61.5; H, 4.0; N, 5.1. $C_{14}H_{11}NOS_2$ requires C, 61.5; H, 4.1; N, 5.1%); $\nu_{max.}$(CCl_4) 1 635 cm^{-1}; $\lambda_{max.}$(EtOH) 221 (log ε 4.20), 332 (3.96), and 478 nm (3.66); δ (90 MHz, $CDCl_3$), 2.47 (3 H, s), 6.87 (1 H, d, *J* 5.5 Hz), 7.25—7.5 (5 H, m), 7.63 (1 H, d, *J* 5.5 Hz), and 7.93 (1 H, s); δ_C($CDCl_3$) 25.1, 96.5, 115.1, 123.7, 125.3, 128.9, 130.7, 135.5, 138.3, 138.9, 164.6, and 191.5; *m/z* 273 (M^+), 257, 230, and 196 (base).

Azide (**9f**). Thermolysis of the azide (**9f**) (100 mg) in toluene gave *2-phenylthieno*[3,2-c][1λ⁴,2]*thiazine-3-carbaldehyde* (**10f**) (68 mg, 75%) as red crystals, m.p. 138—140 °C (Found: C, 60.0; H, 3.5; N, 5.4. $C_{13}H_9NOS_2$ requires C, 60.2; H, 3.5; N, 5.4%); $\nu_{max.}$(CCl_4) 1 650 cm^{-1}; $\lambda_{max.}$(EtOH) 219 (log ε 4.02), 334 (3.78), and 476 nm (3.48); δ (90 MHz, $CDCl_3$) 6.88 (1 H, d, *J* 5.6 Hz), 7.36—7.41 (5 H, m), 7.71 (1 H, d, *J* 5.6 Hz), 7.78 (1 H, s), and 9.53 (1 H, s); δ_C($CDCl_3$) 96.5, 115.9, 124.0, 125.2, 129.2, 131.1, 138.7, 139.4, 140.0, 166.2, and 184.8; *m/z* 259 (M^+), 248, and 182 (base).

Azide (**9g**). Thermolysis of the azide (**9g**) (100 mg) in toluene gave *2-phenylthieno*[3,2-c][1λ⁴,2]*thiazine-3-carbonitrile* (**10g**) (81 mg, 90%) as red crystals, m.p. 161—162 °C (Found: C, 60.9; H, 3.15; N, 10.9. $C_{13}H_8N_2S_2$ requires C, 60.8; H, 3.1; N, 10.9%); $\nu_{max.}$(CCl_4) 2 195 cm^{-1}; $\lambda_{max.}$(EtOH) 220 (log ε 4.18), 286 (3.86), 330 (3.88), and 457 (3.43); δ (90 MHz, $CDCl_3$) 6.90 (1 H, dd, *J* 5.5, 0.6 Hz), 7.25—7.55 (5 H, m), 7.63 (1 H, d, *J* 5.5 Hz), and 7.71 (1 H, d, *J* 0.6 Hz); δ_C($CDCl_3$) 64.5, 116.4, 116.8, 123.9, 125.3, 129.2, 131.5, 137.4, 138.4, 138.7, and 161.8; *m/z* 256 (M^+) and 179 (base).

Azide (**9h**). Thermolysis of the azide (**9h**) (77 mg) in benzene gave (i) 5-methylthiothieno[3,2-*b*]pyrrole[32] (12 mg, 18%); (ii) 6-methylthiothieno[3,2-*b*]pyrrole[32] (12 mg, 18%); and (iii) *2-methylthieno*[3,2-c][1λ⁴,2]*thiazine* (**10h**) (3 mg, 4%) as an oil (Found: M^+, 169.0012. $C_7H_7NS_2$ requires *M*, 169.0020); $\lambda_{max.}$(EtOH) 211 (log ε 3.35), 232 (3.36), 282 (3.29), and 392 nm (2.73); δ (250 MHz, $CDCl_3$) 2.20 (3 H, s), 4.89 (1 H, d, *J* 8.5 Hz), 6.82 (1 H, dd, *J* 5.5, 0.7 Hz), 7.30 (1 H, dd, *J* 8.5, 0.7 Hz), and 7.37 (1 H, d, *J* 5.5 Hz); *m/z* 169 (M^+) and 154 (base).

Azide (**12a**). Thermolysis of the azide (**12a**) (100 mg) in

toluene gave *ethyl* 2-*phenylthieno*[3,4-c][1λ⁴,2]*thiazine*-3-*carboxylate* (**13a**) (52 mg, 58%) as an unstable dark red gum (Found: M^+, 303.0387. $C_{15}H_{13}NO_2S_2$ requires M, 303.0388); $\nu_{max.}$(CCl_4) 1 690 cm^{-1}; $\lambda_{max.}$(EtOH) 228 (log ε 4.06), 266 (3.99), and 320 nm (3.89); δ (250 MHz, $CDCl_3$) 1.35 (3 H, t), 4.35 (2 H, q), 6.53 (1 H, dd, *J* 3.3, 0.7 Hz), 7.2—7.3 (3 H, m), 7.49 (1 H, d, *J* 3.3 Hz), 7.51—7.56 (2 H, m), and 8.16 (1 H, d, *J* 0.7 Hz); δ_C($CDCl_3$) 14.2, 61.9, 100.3, 113.8, 125.4, 125.7, 128.7, 129.2, 130.9, 137.5, 143.4, 148.7, and 162.8; *m/z* 303 (M^+), 258, and 226 (base).

Azide (**14a**). Thermolysis of the azide (**14a**) (5.7 g) in xylene gave *ethyl* 2-*phenylbenzo*[c][1λ⁴,2]*thiazine*-3-*carboxylate* (**15a**) (2.73 g, 52%) as dark red crystals, m.p. 110—112 °C (from ether–light petroleum) (Found: C, 68.5; H, 5.3; N, 4.6; S, 10.8. $C_{17}H_{15}NO_2S$ requires C, 68.7; H, 5.1; N, 4.7; S, 10.8%); $\nu_{max.}$(Nujol) 1 690 cm^{-1}; $\lambda_{max.}$(EtOH) 213 (log ε 4.33), 251 (4.33), and 310 nm (3.85); δ (250 MHz, $CDCl_3$) 1.35 (3 H, t), 4.40 (2 H, m), 6.5—7.6 (9 H, m), and 8.1 (1 H, s); *m/z* 297 (M^+), 224, 192, and 77.

Azide (**14b**). Thermolysis of the azide (**14b**) (250 mg) in toluene gave *ethyl* 2-*methylbenzo*[c][1λ⁴,2]*thiazine*-3-*carboxylate* (**15b**) (30 mg, 13%) as a dark red gum, $\nu_{max.}$($CHCl_3$) 1 690 cm^{-1}; δ (250 MHz, $CDCl_3$) 1.40 (3 H, s), 2.30 (3 H, s), 4.35 (2 H, m), 6.8—7.4 (4 H, m), and 8.0 (1 H, s); *m/z* 235 (M^+), 220, 192, and 146.

Azide (**16**). Thermolysis of the azide (**16**) (1.0 g) in toluene gave *ethyl* 2-*phenylfuro*[3,2-c][1λ⁴,2]*thiazine*-3-*carboxylate* (**17**) (640 mg, 70%), m.p. 112—113 °C (from light petroleum) (Found: C, 62.9; H, 4.5; N, 4.95; S, 11.4. $C_{15}H_{13}NO_3S$ requires C, 62.7; H, 4.6; N, 4.9; S, 11.2%); $\nu_{max.}$(Nujol) 1 660 cm^{-1}; δ (250 MHz, $CDCl_3$) 1.40 (3 H, t), 4.4 (2 H, m), 6.4 (1 H, d, *J* 2 Hz), 7.2—7.6 (5 H, m), 7.5 (1 H, d, *J* 2 Hz), and 7.9 (1 H, s); *m/z* 287 (M^+), 242, 182, and 109.

Azide (**18**). Thermolysis of the azide (**18**) (350 mg) in toluene for 10 min gave *ethyl* 1-*methylthieno*[2,3-e][1λ⁴,2]*thiazine*-3-*carboxylate* (**19**) (278 mg, 89%) as a yellow-brown gum which slowly solidified, m.p. 58—62 °C (from light petroleum–dichloromethane) (Found: C, 49.6; H, 4.5; N, 5.7; S, 26.7. $C_{10}H_{11}NO_2S_2$ requires C, 49.8; H, 4.6; N, 5.8; S, 26.6%); $\nu_{max.}$(Nujol) 1 695 cm^{-1}; $\lambda_{max.}$(EtOH) 245 (log ε 3.93) and 400 nm (3.81); δ (250 MHz, $CDCl_3$) 1.38 (3 H, t), 2.27 (3 H, s), 4.35 (2 H, qq), 6.90 (1 H, dd, *J* 5.1, 0.8 Hz), 7.17 (1 H, d, *J* 0.8 Hz), and 7.30 (1 H, d, *J* 5.1 Hz); δ_C($CDCl_3$) 14.4, 31.4, 61.5, 102.4, 105.0, 121.2, 124.5, 142.8, and 166.4; δ_C(C_6D_6) 14.3, 30.8, 61.0, 101.6, 104.5, 121.5, 123.7, 143.4, 144.7, and 166.4; *m/z* 241 (M^+), 226 (base), and 198.

Azide (**20a**). Thermolysis of the azide (**20a**) (100 mg) in toluene gave *ethyl* 3-(*phenylthio*)*thieno*[2,3-b]*pyrrole*-5-*carboxylate* (**21**) (81 mg, 88%), m.p. 163 °C (Found: C, 59.4; H, 4.3; N, 4.5. $C_{15}H_{13}NO_2S_2$ requires C, 59.4; H, 4.3; N, 4.6%); $\nu_{max.}$(CCl_4) 3 470 and 1 685 cm^{-1}; δ (90 MHz, $CDCl_3$) 1.36 (3 H, t), 4.32 (2 H, q), 6.72 (1 H, s), 6.9 (1 H, s), 7.15 (5 H, m), and 10.7 (1 H, s); *m/z* 303 (M^+), 257 (base), and 227.

Azide (**20b**). Thermolysis of the azide (**20b**) (60 mg) in toluene gave *ethyl* 2-*methyl*-3-(*phenylthio*)*thieno*[2,3-c]*pyridine*-5-*carboxylate* (**22**) (45 mg, 82%) as an oil (Found: C, 61.9; H, 4.7; N, 4.2. $C_{17}H_{15}NO_2S_2$ requires C, 62.0; H, 4.6; N, 4.25%); $\nu_{max.}$(CCl_4) 1 710 cm^{-1}; δ (90 MHz, $CDCl_3$) 1.43 (3 H, t), 2.76 (3 H, s), 4.48 (2 H, q), 6.95—7.20 (5 H, m), 8.5 (1 H, s), and 9.16 (1 H, s); *m/z* 329 (M^+) and 257 (base).

Azide (**24a**). Thermolysis of the azide (**24a**) (200 mg) in toluene for 1 h gave *ethyl* 4-(*phenylthio*)*indole*-2-*carboxylate* (**25a**) (120 mg, 66%), m.p. 151—152 °C (from light petroleum) (Found: C, 68.5; H, 5.1; N, 4.7; S, 10.5. $C_{17}H_{15}NO_2S$ requires C, 68.7; H, 5.1; N, 4.7; S, 10.8%); $\nu_{max.}$(Nujol) 3 310 and 1 685 cm^{-1}; δ (250 MHz, $CDCl_3$) 1.40 (3 H, t), 4.35 (2 H, q), 7.1—7.6 (9 H, m), and 11.5 (1 H, br); *m/z* 297 (M^+), 251, 222, and 190.

Azide (**24b**). Thermolysis of the azide (**24b**) (110 mg) in toluene for 2 h gave *ethyl* 4-(*methylthio*)*indole*-2-*carboxylate* (**25b**) (85 mg, 86%), m.p. 131—133 °C (from light petroleum–toluene) (Found: C, 61.1; H, 5.3; N, 6.2; S, 13.7. $C_{12}H_{13}NO_2S$ requires C, 61.3; H, 5.6; N, 6.0; S, 13.6%); $\nu_{max.}$(Nujol) 3 310 and 1 680 cm^{-1}; δ (60 MHz, $CDCl_3$) 1.40 (3 H, t), 2.5 (3 H, s), 4.30 (2 H, q), 6.7—7.4 (4 H, m), and 10.7 (1 H, br); *m/z* 235 (M^+), 221, 189, and 160.

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