Synthesis and thermal decomposition of azidovinylbenzo[*b*]thiophenes

Alessandro Degl'Innocenti,*[a] Maria Funicello,[a] Patrizia Scafato,[a] Piero Spagnolo*[b] and Paolo Zanirato[b]

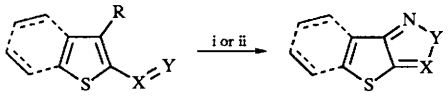
[a] *Dipartimento di Chimica, Università della Basilicata, via N. Sauro 85, 85100, Potenza, Italy*
[b] *Dipartimento di Chimica Organica 'A. Mangini', Università di Bologna, Viale Risorgimento 4, 40136, Bologna, Italy*

Condensation of 3-azidobenzo[*b*]thiophene-2-carbaldehyde **1** with acetone, diethyl malonate, ethyl acetoacetate and pentane-2,4-dione furnished the 3-azido-2-vinylic derivatives **4a–d** in fairly good yields. In refluxing toluene the azides **4a**, **b**, **d** smoothly gave solely fused pyrrole products, **5a**, **b**, **d**, whereas the azide **4c** furnished an isomeric mixture of the cyclized pyrroles **5c** and **6**. The observed 1*H*-pyrroles **5a–d** and **6** are assumed to occur through aromatization of initially formed 2*H*-pyrroles **7a–d**. Attempted condensation of 2-azidobenzo[*b*]thiophene-3-carbaldehyde **2** with acetone or pentane-2,4-dione gave no vinylic product, but instead resulted in reduction of the azide **2** to the amine **8** or in its conversion into the 1,2,3-triazole adduct **9**, respectively.

Azido group transfer of 3-styrylbenzo[*b*]thiophene with tosyl azide yielded the *ortho*-vinyl-substituted α-azide **10**, but in poor yield. Thermolysis of the azide **10** gave quantitatively the benzothiopyran **12** clearly ascribable to an initial ring-opening reaction. It is therefore inferred that, in the presence of *ortho*-vinyl substituent, an α-azidobenzo[*b*]thiophene can exhibit 'normal' ring-cleavage fragmentation, in contrast with previous deoxygenations of 2-nitro-3-vinylbenzo[*b*]thiophenes reported to yield cyclized benzothieno[2,3-*b*]pyrroles. Evidence is also presented that, upon thermolysis, the *o*-azidoaldehyde **1** cleanly affords a benzothienoisoxazole product, whereas the isomeric azide **2** essentially leads to intractable material.

Since the pioneering work of Smith in 1964,[1] especially in the last decade, remarkable attention has been dedicated to the chemistry of azides derived from five-membered heteroarene systems, though these attractive heteroaryl derivatives still remain much less investigated than their aryl counterparts.[2,3] Reported studies have uncovered the fact that the chemical reactivity of five-membered heteroaryl azides largely depends upon the position of the heterocyclic ring to which they are attached.

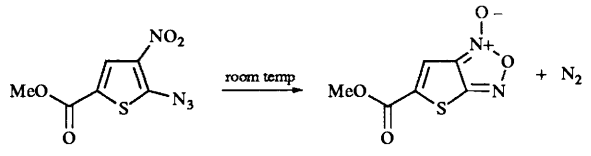
α-Azides (and -nitrenes) show a pronounced tendency to suffer ring opening leading to the formation of a nitrilic hetero-1,3-diene product. On the other hand, β-azides (and -nitrenes) can normally display chemical behaviour not dissimilar from that of the aryl analogues. In particular, in the thiophene and/or benzo[*b*]thiophene series there are several reports of β-azides bearing an adjacent aryl or α,β-unsaturated group [such as RCH=CH–, RN=CH–, O=CH–, O=N(O)–] which, on thermolysis or photolysis, lead smoothly to the formation of fused azoles by intramolecular 1,5-cyclization in a fashion strictly comparable to that of similarly substituted aryl azides[3,4] (Scheme 1). Analogous results (when available) are reported for the 'β-nitrenes' produced through triethyl phosphite deoxygenation of the corresponding 3-nitro-thiophenes and -benzo[*b*]-thiophenes[3] (Scheme 1).



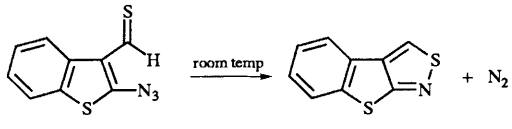
Scheme 1 i, R = N_3, heat or *hν*; ii, R = NO_2, $P(OEt)_3$

Moreover, there is general evidence that the formal generation of a nitrene at the α-position of the thiophene[5] and benzo[*b*]thiophene[3] ring instead results in the preferential or exclusive formation of a ring-opened nitrilic enethione product.

Indeed, there are only two definite examples of successful cyclization of 2-azidothiophene onto an adjacent substituent. These are represented by the very mild thermal cyclizations of methyl 2-azido-3-nitrothiophene-5-carboxylate to thieno-furazan *N*-oxide[6] (Scheme 2) and 2-azidobenzo[*b*]thiophene-3-carbothialdehyde to benzothienoisothiazole[7] (Scheme 3).



Scheme 2



Scheme 3

The successful outcome of such thermal reactions is ascribable to a pronounced ability of nitro and thioformyl groups to intercept an *ortho*-azido function. In this context, it is noteworthy that 3-vinyl-substituted 2-nitro-thiophenes[8] and -benzo[*b*]thiophenes[9] have been found to cyclize to thieno- and benzothieno-pyrroles on deoxygenation with boiling triethyl phosphite (with the absence of any ring fragmentation products), though a vinyl moiety is not expected to be especially capable of trapping an adjacent nitrene. As we already stated in a recent review,[3a] a parallel investigation of the thermal decomposition of corresponding azido derivatives would be useful for a possible comprehension of such intriguing results.

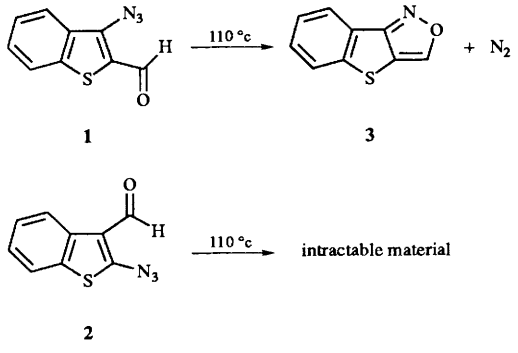
Our long interest in the chemistry of azido-thiophenes[3a,5] and -benzo[*b*]thiophenes[3a,7,10] therefore prompted us to a study of the thermal behaviour of hitherto unknown 2-azido-3-vinylbenzo[*b*]thiophenes. This study was also extended to 3-azido-2-vinylic isomers which were similarly unexplored. It was also of interest to us to compare the thermal behaviour of these latter azides with reported data on reductive cyclizations of corresponding nitro derivatives[8,9,11] and

thermal (as well as photochemical) cyclizations of 3-azidothiophene analogues.[12–14]

Results and discussion

Since various 3-azido-2-vinylthiophenes have been previously prepared by condensation of 3-azidothiophene-2-carbaldehyde with compounds containing an active methyl or methylene group,[12,13] we reasoned that a similar method might be suitably applied to the preparation of our target azidovinylbenzo[*b*]thiophenes starting from 3-azido-2-formyl- **1** and 2-azido-3-formyl-benzo[*b*]thiophene **2**. Both *o*-azido aldehydes **1**, **2** have been previously produced, but in moderate yield, through reduction of the corresponding nitro aldehydes to the amines and diazotization of the latter followed by addition of sodium azide.[15] In our hands, this synthetic route proved to be somewhat tedious and unreliable. Consequently, we developed a new, convenient, high-yielding route to the azido aldehydes **1**, **2** involving direct reaction of the nitro derivatives with sodium azide in dimethyl sulfoxide (DMSO) at room temperature.[7,10] 3-Azidobenzo[*b*]thiophene-2-carbaldehyde **1** was also prepared in almost quantitative yield from the readily available 3-bromo derivative by analogous nucleophilic aromatic substitution reaction with sodium azide in DMSO.

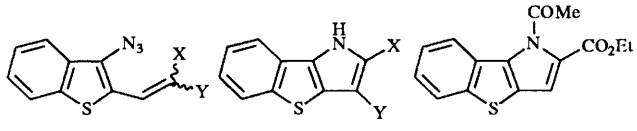
Since no data were known on decomposition reactions of the azidobenzo[*b*]thiophenes **1**, **2** we preliminarly performed a brief investigation of their thermolyses in boiling toluene. The azide **1** underwent total decomposition over *ca.* 3 h to give the hitherto unknown benzothieno[3,2-*c*]isoxazole **3** in high yield (85%). The azide **2** instead underwent slightly faster decomposition affording intractable material and none of cyclized product (Scheme 4). Thus, these findings were consistent with the thermal behaviour expected of 3-azido- and 2-azido-benzo[*b*]thiophene, despite our failure to obtain any evidence for ring-cleavage fragmentation of the azide **2**.



Scheme 4

There is a literature report[16] of thieno[3,2-*c*]isoxazole being isolated, but in low yield, from related thermolysis of 3-azidothiophene-2-carbaldehyde, whereas decomposition of isomeric 2-azidothiophene-3-carbaldehyde, very recently prepared,[10b] is unexplored. Treatment of the azido aldehyde **1** with an excess of acetone in 2% aqueous sodium hydroxide gave the expected vinylic compound **4a** in good yield. Analogous condensation of the aldehyde **1** with diethyl malonate, ethyl acetoacetate and pentane-2,4-dione in ethanol or benzene, in the presence of piperidinium acetate, furnished the vinylic compounds **4b–d** in 60–65% isolated yields.

Thermolysis of the compounds **4a**, **b**, **d** in refluxing toluene (*ca.* 2 h) gave solely benzothieno[3,2-*b*]pyrrole products, *i.e.* **5a**, **b**, **d**, in fairly high yield (70–80%), whereas under comparable conditions the azide **4c** led to an isomeric mixture of the two cyclized pyrroles **5c** and **6** in 60 and 28% yield, respectively. All new compounds **5a–d** and **6** were characterized on the basis of ^1H and ^{13}C NMR, IR and mass spectral data in addition to elemental analysis. The structures of the compounds **5a** and **5c** were also established by ^1H NMR nuclear Overhauser effect (NOE) experiments. Irradiation of the NH proton of **5a** caused enhancement of the signal of the vicinal acetyl protons, while irradiation of the NH proton of **5c** caused enhancements of the signals of the vicinal ethoxycarbonyl protons.

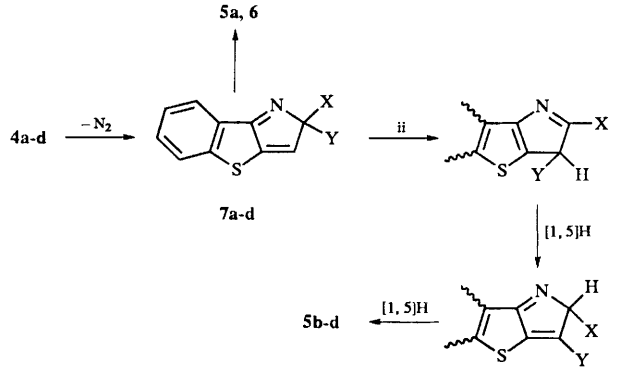


4 **5** **6**

a; X = Ac, Y = H **b**; X = Y = CO_2Et

c; X = CO_2Et, Y = Ac **d**; X = Y = Ac

In line with previous intramolecular cyclizations of analogous 3-azidothiophenes to thieno[3,2-*b*]pyrroles,[12–14] it may be assumed that the 3-azidobenzo[*b*]thiophenes **4a–d** initially led to the fused 2*H*-pyrroles **7a–d**. Aromatization of **7a** to the compound **5a** would then directly occur by [1,5]-shift of hydrogen from C-2 to nitrogen, whereas aromatization of **7b**, **d** to the compounds **5b**, **d** would proceed through a [1,5]-shift of CO_2Et or COMe group from C-2 to C-3 followed by two successive [1,5]-hydrogen shifts (Scheme 5). Instead, aromatization of the 2*H*-pyrrole **7c** to the isomers **5c** and **6** would involve competing [1,5]-shifts of the COMe group from C-2 to nitrogen and C-3, respectively (Scheme 5).

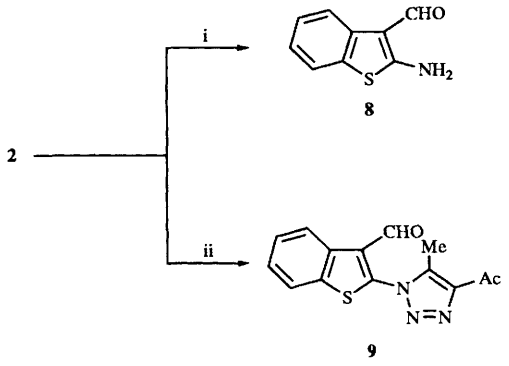


Scheme 5 i, (**7a**, **c**), [1,5]-shift of H or Ac; ii, (**7b–d**), [1,5]-shift of CO_2Et or Ac

The results show that hydrogen migrates faster than the acetyl group which, in turn, migrates faster than the ethoxycarbonyl group. Similar evidence has been provided by study of the cyclizations of 3-azido-2-vinylthiophenes.[12,13] The above postulated [1,5]-migration of an acetyl group from carbon to nitrogen in **7c** is of interest since in 2*H*-pyrroles analogous migration of a substituent other than hydrogen is (quite) unusual.[13]

In sharp contrast with 3-azidobenzo[*b*]thiophene-2-carbaldehyde **1**, the isomeric azido aldehyde **2** totally failed to afford the desired vinylic product upon attempted condensation with acetone or pentane-2,4-dione. In fact, in the presence of an excess of acetone, under basic conditions analogous to those employed with the aldehyde **1**, compound **2** furnished a rather complex reaction mixture, from which the amine **8** could be isolated as the only identifiable product (Scheme 6). Similar results were obtained when the same reaction was repeated with THF as co-solvent, in which case the amine **8** could be isolated in 75% yield. In the presence of pentane-2,4-dione and piperidinium acetate, compound **2** in ethanol solution also furnished the amine **8**, but in benzene it preferentially gave the

1,2,3-triazole **9** (Scheme 6). Thus, product **9** was clearly formed through cycloaddition of the azide **2** with the enolate anion of pentanedione and subsequent aromatization of the resulting 1,2,3-triazoline adduct by elimination of water.



Scheme 6 *Reagents:* i, acetone, OH^-; ii, pentane-2,4-dione, piperidinium acetate, benzene

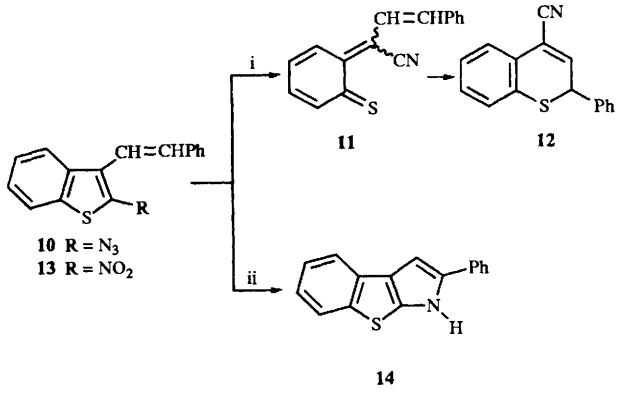
The reduction of aromatic and heteroaromatic azides, including azido aldehydes, to amines upon reaction with nucleophilic species (especially sulfur nucleophiles) is well known.[2,10b] Moreover, the reaction of azides with α-methylene β-dicarbonyl compounds, under basic conditions, is a well-established route to 1,2,3-triazolines and -triazoles,[17] though it appears to be unprecedented with azides in the benzo[*b*]-thiophene and thiophene series. The above results evidently indicate that in the case of the azido aldehyde **2** the terminal azido nitrogen is a more electrophilic site than the formyl carbon, the reverse of that encountered with the positional isomer **1**. This fact would be a consequence of the expected greater propensity of the benzo[*b*]thiophene ring to donate electron density to an electron-deficient substituent in the 3- rather than in the 2-position.

In the light of the frustrating results obtained with the azido aldehyde **2**, we were subsequently led to explore another potential synthetic approach to 2-azido-3-vinylbenzo[*b*]thiophene, namely 'azido group transfer' of 3-vinyl-substituted benzo[*b*]thiophene with tosyl azide. Indeed, in recent years various five-membered heteroaromatic α- and β-azides (especially the parent ones) have been successfully prepared through reaction of corresponding lithium derivatives with tosyl azide, followed by fragmentation of the resulting triazene salts.[3a,5,14] When this method was applied to 3-styrylbenzo-[*b*]thiophene we actually succeeded in isolating the desired α-azide **10**, but in poor yield (20%).

Unfavourable fragmentation of the suitably produced triazene salt, largely giving back tosyl azide and the original vinylic substrate, was unfortunately responsible for the low yield of the azide **10**. Upon brief thermolysis in refluxing toluene, the azide **10** cleanly gave the nitrilic benzothiopyran **12** in virtually quantitative yield. Compound **12** arises from initial ring-opening fragmentation of the azide **10** to give an *ortho*-quinoidal enethione intermediate **11** followed by electrocyclization of the latter (Scheme 7). We therefore established that the α-azide **10**, in the presence of a vinyl substituent, can undergo thermal cleavage of the thiophene moiety; this is in sharp contrast with the nitro compound **13** previously shown to cyclize to the fused pyrrole **14** upon triethyl phosphite deoxygenation[9] (Scheme 7).

Consequently, we proved that the reported reductive cyclizations of 2-nitro-3-vinylic benzo[*b*]thiophenes (and thiophenes) involve an unusual mechanism whose understanding requires further investigation.

In conclusion, in the present work we have shown that 3-azido-2-vinylbenzo[*b*]thiophenes, quite consistent with their



Scheme 7 *Reagents:* i, **10**, refluxing toluene, $-N_2$; ii, **13**, $P(OEt)_3$

thiophene analogues, can smoothly suffer intramolecular cyclization to benzothieno[3,2-*b*]pyrroles and thence, like the corresponding nitro derivatives, can be usefully employed in the preparation of these fused heterocyclic compounds. Moreover, we have provided the first definite evidence that their 2-azido-3-vinylic isomers should undergo the 'usual' ring-cleavage, the ring-opened enethione products of which would be promising synthetic precursors of the benzothiopyran ring system.

Experimental

3-Formyl-2-nitro-,[9] 2-formyl-3-nitro-[9] and 3-bromo-2-formylbenzo[*b*]thiophene[18] were prepared according to literature methods. Column chromatography was carried out on Merck silica gel (0.063–0.200 mm particle size) by elution with hexanes–diethyl ether mixtures.

3-Azidobenzo[*b*]thiophene-2-carbaldehyde 1

A solution of 3-nitrobenzo[*b*]thiophene-2-carbaldehyde (1.8 g, 8.7 mmol) in DMSO (30 cm^3) was treated with sodium azide (1.5 g, 23 mmol) and then stirred at room temperature for 1 h. The reaction mixture was poured onto water and extracted several times with diethyl ether. Evaporation of the combined ether extracts and column chromatography of the residue gave the title azide (1.55 g, 86%), mp 84–86 °C (lit.,[15] 88–90 °C). Analogous reaction of 3-bromobenzo[*b*]thiophene-2-carbaldehyde (200 mg) for 7 h gave the azide in 94% yield.

2-Azidobenzo[*b*]thiophene-3-carbaldehyde 2

2-Nitrobenzo[*b*]thiophene-3-carbaldehyde (1 g, 4.8 mmol) was similarly treated with sodium azide (0.5 g, 7.7 mmol) in DMSO (15 cm^3) for 30 min to give the title compound (650 mg, 65%), mp 90–93 °C (lit.,[15] 91–94 °C).

trans-4-(3-Azido-2-benzo[*b*]thienyl)but-3-en-2-one 4a

A suspension of 3-azidobenzo[*b*]thiophene-2-carbaldehyde **1** (490 mg, 2.41 mmol) in acetone (2.5 cm^3) was added to a solution of sodium hydroxide (75 mg) in water (3.8 cm^3). The resulting heterogeneous mixture was stirred at room temperature for 1 h and then diluted with water. Extraction with diethyl ether and column chromatography of the evaporated extract gave the *title azide* **4a** (435 mg, 74%), mp *ca.* 100 °C (decomp.) (Found: C, 58.9; H, 3.7; N, 17.4. $C_{12}H_9N_3OS$ requires C, 59.25; H, 3.7; N, 17.3%); ν_{max}/cm^{-1} 2100 and 1670; δ_H(300 MHz, $CDCl_3$) 2.40 (3 H, s), 6.45 (1 H, d, *J* 15.9), 7.4–7.5 (2 H, m), 7.7–8.0 (2 H, m) and 7.85 (1 H, d, *J* 15.9); *m*/*z* 243 (M^+) and 215 ($M^+ - N_2$).

Diethyl [(3-azido-2-benzo[*b*]thienyl)methylidene]propanedioate 4b

Diethyl malonate (160 mg, 1 mmol) was added to a stirred solution of the azido aldehyde **1** (203 mg, 1 mmol) and

piperidinium acetate (150 mg, 1 mmol) in ethanol (5 cm^3) at room temperature. After 30 h the mixture was poured into aqueous ammonium chloride and then extracted with diethyl ether. Removal of ether and chromatography of the residue gave the *title compound* **4b** (200 mg, 67%), mp *ca.* 85 °C (decomp.) (Found: C, 55.5; H, 4.3; N, 12.15. $C_{16}H_{15}N_3O_4S$ requires C, 55.65; H, 4.35; N, 12.2%); ν_{max}/cm^{-1} 2105 and 1720; δ_H(300 MHz, $CDCl_3$) 1.36 (3 H, t), 1.41 (3 H, t), 4.32 (2 H, q), 4.45 (2 H, q), 7.4–7.5 (2 H, m), 7.76 (1 H, d), 7.99 (1 H, d) and 8.12 (1 H, s); *m/z* 345 (M^+) and 317 ($M^+ - N_2$).

Ethyl 2-acetyl-3-(3-azido-2-benzo[*b*]thienyl)propenoate 4c

Ethyl acetoacetate (260 mg, 1.97 mmol) was condensed with the azido aldehyde **1** (400 mg, 1.97 mmol) in benzene (14 cm^3), in the presence of piperidinium acetate, as described above to give the *title compound* **4c** (294 mg, 60%) as an *E*/*Z* mixture, mp 90–108 °C (decomp.) (Found: C, 57.25; H, 4.15; N, 13.3. $C_{15}H_{13}N_3O_3S$ requires C, 57.25; H, 4.15; N, 13.35%); ν_{max}/cm^{-1} 2110 and 1715; δ_H(300 MHz, $CDCl_3$) 1.36 (3 H, t), 1.41 (3 H, t), 2.46 (3 H, s), 2.56 (3 H, s), 4.39 (2 H, q), 4.46 (2 H, q), 7.41–7.51 (4 H, m), 7.74–7.80 (2 H, m), 7.97–8.02 (2 H, m), 8.0 (1 H, s) and 8.06 (1 H, s); *m/z* 287 ($M^+ - N_2$).

3-Acetyl-4-(3-azido-2-benzo[*b*]thienyl)but-3-en-2-one 4d

Pentane-2,4-dione (50 mg, 0.5 mmol) was condensed with the azido aldehyde **1** (100 mg, 0.493 mmol) in ethanol, in the presence of piperidinium acetate, as described above to give the *title compound* **4d** (67 mg, 58%), mp 95–100 °C (decomp.) (Found: C, 59.1; H, 3.85; N, 14.7. $C_{14}H_{11}N_3O_2S$ requires C, 58.95; H, 3.85; N, 14.75%); ν_{max}/cm^{-1} 2115, 1700 and 1674; δ_H(300 MHz, $CDCl_3$) 2.5 (6 H, s), 7.47 (2 H, m), 7.83 (1 H, s), 7.75 (1 H, d) and 8.05 (1 H, d); *m/z* 257 ($M^+ - N_2$) and 215.

2-Azido-3-styrylbenzo[*b*]thiophene 10

Already known 3-styrylbenzo[*b*]thiophene[19] was prepared in 70% yield as a *ca.* 55:45 *Z*/*E*-mixture through Wittig reaction of benzo[*b*]thiophene-3-carbaldehyde with benzylidenetriphenylphosphorane following a standard procedure[9] [δ_H(300 MHz, $CDCl_3$) 6.71 (1 H, d, *J* 12.6), 6.78 (1 H, d, *J* 12.6) and 7.18–8.12 (20 H, m, aromatic protons of *Z*-isomer and vinylic and aromatic protons of *E*-isomer); GC-MS analysis showed that the two isomeric components had virtually identical mass spectral peaks at *m/z* 236 (M^+), 202, 189 and 117]. To a stirred solution of this isomeric mixture (0.5 g, 2.1 mmol) in dry ether (3 cm^3) was added under nitrogen, at room temperature, butyllithium (1.6 mol dm^{-3} in hexane; 1.5 cm^3). The reaction mixture was stirred and heated under reflux for 1 h, after which it was cooled to −70 °C and added dropwise to a solution of tosyl azide (2.3 mmol) in dry ether (5 cm^3). The thus formed triazene salt was rapidly filtered off and suspended in ether. The suspension was treated with a solution of tetrasodium pyrophosphate (2.3 mmol) in water (10 cm^3). The organic layer was separated and evaporated and the residue chromatographed to give, besides tosyl azide and starting substrate, the *title azide* **10** (117 mg, 20%), as a sticky oil; ν_{max}/cm^{-1} 2110; δ_H(300 MHz, $CDCl_3$) 6.59 (1 H, d, *J* 13), 6.97 (1 H, d, *J* 13), 7.29–7.48 (8 H, m) and 7.76–7.81 (1 H, m); *m/z* 249 ($M^+ - N_2$). This azide showed a tendency to decompose at room temperature and therefore was rapidly used.

Thermolysis of azides: general procedure

A solution of the appropriate azide (0.5 mmol) in toluene (5 cm^3) was heated under reflux until the azide disappearance (monitored by TLC; 1–3 h), after which the excess of solvent was evaporated off and the residue purified by column chromatography.

Thermolysis of the azide 1. This gave *benzo*[b]*thieno*[3,2-c]*isoxazole* **3** (83%), mp 66–68 °C (Found: C, 61.6; H, 2.85; N, 8.1. C_9H_5NOS requires C, 61.7; H, 2.85; N, 8.0%); δ_H(200 MHz, $CDCl_3$) 7.40–7.60 (2 H, m), 7.64–7.7 (1 H, m), 8.13–8.20 (1 H, m) and 8.52 (1 H, s); δ_C(50 MHz, $CDCl_3$) 123.6, 124.1, 124.3, 125.6, 130.2, 147.8, 148.8, 166 and 177.7; *m/z* 175 (M^+), 146, 120 and 103.

Thermolysis of the azide 2. This gave unidentifiable material.

Thermolysis of the azide 4a. This gave 2-*acetyl*-1H-*benzo*[b]*thieno*[3,2-b]*pyrrole* **5a** (77%), mp 205–207 °C (Found: C, 67.2; H, 4.25; N, 6.55. $C_{12}H_9NOS$ requires C, 67.0; H, 4.2; N, 6.5%); ν_{max}/cm^{-1} 3260 and 1630; δ_H(200 MHz, $CDCl_3$) 2.6 (3 H, s), 7.18 (1 H, d), 7.31–7.48 (2 H, m), 7.76–7.98 (2 H, m) and 10.3 (1 H, br s) (irradiation of the NH proton at δ 10.3 caused enhancement of the acetyl protons at δ 2.6); δ_C(50 MHz, $CDCl_3$) 25.6, 109.9, 120.6, 123.6, 124.1, 124.5, 125.4, 125.9, 135.8, 138.0, 144.4 and 188.6; *m/z* 215 (M^+), 200, 172, 145 and 43.

Thermolysis of the azide 4b. This gave *diethyl* 1H-*benzo*(b]*thieno*[3,2-b]*pyrrole*-2,3-*dicarboxylate* **5b** (78%), mp 178–180 °C (Found: C, 60.6; H, 4.7; N, 4.4. $C_{16}H_{15}NO_4S$ requires C, 60.55; H, 4.75; N, 4.4%); ν_{max}/cm^{-1} 3260, 1730 and 1670; δ_H(300 MHz, $CDCl_3$) 1.47 (3 H, t), 1.49 (3 H, t), 4.4 (2 H, q), 4.5 (2 H, q), 7.3–7.5 (2 H, m), 7.8–7.9 (2 H m) and 10.5 (1 H, br s); *m/z* 317 (M^+), 272, 271 and 199.

Thermolysis of the azide 4c. This gave (i) *ethyl* 3-*acetyl*-1H-*benzo*[b]*thieno*[3,2-b]*pyrrole*-2-*carboxylate* **5c** (60%), mp 196–198 °C (Found: C, 62.6; H, 4.5; N, 4.95. $C_{15}H_{13}NO_3S$ requires C, 62.7; H, 4.55; N, 4.9%); ν_{max}/cm^{-1} 3260; δ_H(200 MHz, $CDCl_3$) 1.48 (3 H, t), 2.83 (3 H, s), 4.50 (2 H, q), 7.39–7.42 (2 H, m), 7.38–7.88 (2 H, m) and 10.0 (1 H, br s) [irradiation of the NH proton at δ 10.0 caused enhancement at δ 1.48 and 4.50 (ethyl group)]; δ_C(50 MHz, $CDCl_3$) 14.4, 30.9, 61.8, 119.6, 122.7, 124.3, 124.4, 124.5, 125.1, 125.3, 127.7, 132.9, 145.2, 159.9 and 194.4; *m/z* 287 (M^+), 272, 258 and 241; and (ii) *ethyl* 1-*acetyl*-1H-*benzo*[b]*thieno*[3,2-b]*pyrrole*-2-*carboxylate* **6** (28%), mp 183–185 °C (Found: C, 62.8; H, 4.55; N, 4.85%); ν_{max}/cm^{-1} 1730 and 1690; δ_H(200 MHz, $CDCl_3$) 1.41 (3 H, t), 2.71 (3 H, s), 4.39 (2 H, q), 7.34 (1 H, s), 7.35–7.40 (2 H, m), 7.77–7.80 (1 H, m) and 8.27–8.32 (1 H, m); δ_C(50 MHz, $CDCl_3$) 14.8, 28.4, 61.9, 115.3, 124.3, 124.9, 125.1, 126.0, 126.9, 128.6, 137.5, 145.1, 161.2 and 172.7; *m/z* 287 (M^+), 267, 245 and 199.

Thermolysis of the azide 4d. This gave 2,3-*diacetyl*-1H-*benzo*[b]*thieno*[3,2-b]*pyrrole* **5d** (71%), mp 258–260 °C (Found: C, 65.4; H, 4.3; N, 5.5. $C_{14}H_{11}NO_2S$ requires C, 65.4; H, 4.3; N, 5.45%); ν_{max}/cm^{-1} 3260, 1680 and 1630; δ_H(300 MHz, $CDCl_3$) 2.74 (3 H, s), 2.81 (3 H, s), 7.4–7.55 (2 H, m), 7.85–8.05 (2 H, m) and 10.3 (1 H, br s); *m/z* 257 (M^+) and 242.

Thermolysis of the azide 10. This gave 2-*phenyl*-2H-*benzothiopyran*-4-*carbonitrile* **12** (98%) as oil (Found: C, 77.2; H, 4.4; N, 5.65. $C_{16}H_{11}NS$ requires C, 77.1; H, 4.4; N, 5.6%); ν_{max}/cm^{-1} 2230 (CN); δ_H(300 MHz, $CDCl_3$) 5.24 (1 H, d, *J* 5.9), 7.12 (1 H, d, *J* 5.9), 7.51–7.55 (3 H, m), 7.59–7.64 (5 H, m) and 7.89–7.93 (1 H, m); δ_C(75 MHz, $CDCl_3$) 43, 115.6, 116.8, 126.5, 126.9, 127.4, 127.6, 128.6, 129.1, 130.3, 130.5, 131.0, 138.7 and 139.2; *m/z* 249 (M^+), 172 and 135.

Attempted condensation of the azido aldehyde 2 with acetone

A suspension of the aldehyde **2** (100 mg, 0.493 mmol) in acetone (2 cm^3) was treated with 2% aqueous sodium hydroxide (0.8 cm^3) as described above for the aldehyde **1**. Chromatography of the crude reaction mixture gave 2-aminobenzo[*b*]thiophene-3-carbaldehyde **8** (34 mg, 40%), identical in all respects with an authentic sample.[15]

The amine **8** was isolated in 75% yield when the aldehyde **2** and acetone mixture was instead treated with aqueous sodium hydroxide as a solution in THF (2 cm^3).

Attempted condensation of the azido aldehyde 2 with pentane-1,3-dione

Pentane-1,3-dione was treated with a solution of the aldehyde **2** (100 mg, 0.493 mmol) and piperidinium acetate in benzene (6 cm^3) as described above for the aldehyde **1**. Chromatography of the crude reaction mixture gave (i) *4-acetyl-1-(3-formyl-2-benzo*[b]*thienyl)-5-methyl-1,2,3-triazole* **9** (50 mg, 35%), mp 149–151 °C (Found: C, 59.0; H, 3.85; N, 14.8. $C_{14}H_{11}N_3O_2S$ requires C, 58.9; H, 3.85; N, 14.75%); ν_{max}/cm^{-1} 1680 and 1690; δ_H(200 MHz, $CDCl_3$) 2.65 (3 H, s), 2.80 (3 H, s), 7.6 (2 H, m), 7.90 (1 H, d), 8.73 (1 H, d) and 9.80 (1 H, s); *m/z* 285 (M^+), 257, 242, 215 and 186; and (ii) the amine **8** (10%).

When the same reaction was performed by using ethanol solvent instead of benzene, the amine **8** was formed as the major product (as monitored by TLC).

Acknowledgements

We thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, quota 40%) for financial support.

References

1 P. A. S. Smith, L. O. Krbechek and W. Resemann, *J. Am. Chem. Soc.*, 1964, **86**, 2025.
2 P. A. S. Smith, 'Aryl and Heteroaryl Azides and Nitrenes', in *Azides and Nitrenes–Reactivity and Utility*, ed. E. F. V. Scriven, Academic Press, New York, 1984, ch. 3; E. F. V. Scriven and K. Turnbull, *Chem. Rev.*, 1988, **88**, 297.
3 For comprehensive reviews concerning intramolecular cyclizations and ring-cleavage reactions of five-membered heteroaromatic azides and nitrenes see: (*a*) M. Funicello, P. Spagnolo and P. Zanirato, *Acta Chem. Scand.*, 1993, **47**, 231; (*b*) J. Becher and W. Dehaen, *Acta Chem. Scand.*, 1993, **47**, 244.
4 L. K. Dyall, P. M. Suffolk, W. Dehaen and G. L'abbé, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2115.
5 D. Spinelli and P. Zanirato, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1129; S. Gronowitz and P. Zanirato, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1815.
6 R. Noto, R. Rainieri and C. Arnone, *J. Chem. Soc., Perkin Trans. 2*, 1989, 127.
7 A. Degl'Innocenti, M. Funicello, P. Scafato and P. Spagnolo, *Chem. Lett.*, 1994, 1873.
8 K. Srinivasan, K. G. Srinivasan, K. K. Balasubramonian and S. Swaminathan, *Synthesis*, 1973, 313.
9 K. E. Chippendale, B. Iddon and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 1973, 125.
10 (*a*) A. Capperucci, A. Degl'Innocenti, P. Scafato and P. Spagnolo, *Chem. Lett.*, 1995, 147; (*b*) A. Capperucci, A. Degl'Innocenti, M. Funicello, G. Mauriello, P. Scafato and P. Spagnolo, *J. Org. Chem.*, 1995, 2254.
11 V. M. Colburn, B. Iddon and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2436.
12 S. Gronowitz, C. Westerlund and A.-B. Hørnfeldt, *Acta Chem. Scand., Ser B*, 1976, **30**, 391.
13 C. J. Moody, C. W. Rees and S. C. Tsoi, *J. Chem. Soc., Perkin Trans. 1*, 1984, 915; R. S. Gairns, C. J. Moody, C. W. Rees and S. C. Tsoi, *J. Chem. Soc., Perkin Trans. 1*, 1986, 497; R. S. Gairns, C. J. Moody and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1986, 501.
14 M. Farnier, M. Brost, B. Hanquet and R. Guilard, *J. Heterocycl. Chem.*, 1986, 513 and 517.
15 K. E. Chippendale, B. Iddon and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 1973, 129.
16 S. Gronowitz, C. Westerlund and A.-B. Hørnfeldt, *Chem. Scr.*, 1976, **10**, 165.
17 L. Benati, P. C. Montevecchi and P. Spagnolo, *Gazz. Chim. Ital.*, 1992, **122**, 249; L. Benati, P. C. Montevecchi, P. Spagnolo and E. Foresti, *J. Chem. Soc., Perkin Trans. 1*, 1992, 2845 and refs. cited therein.
18 W. Ried and H. Bender, *Chem. Ber.*, 1955, **88**, 37.
19 T. Takeda and A. Kasahara, *Yamagata Daigaku Kiyo, Kogaku*, 1975, **13**, 107 (*Chem. Abstr.* 1975, **83**, 131393s).

Paper 5/02014J
Received 30*th March* 1995
Accepted 16*th May* 1995