On the Chemical, NMR and Kinetic Properties of 2-Azido- and 3-Azidothiophene: Recent Developments

Domenico Spinelli and Paolo Zanirato *

Dipartimento di Chimica Organica 'A. Mangini', Università di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy

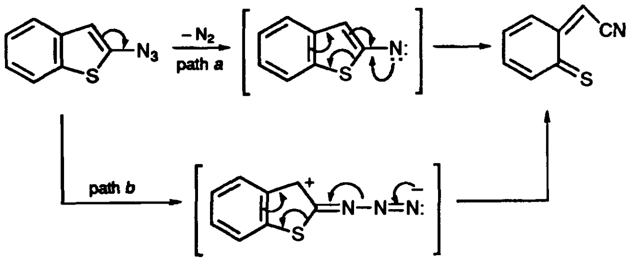
Different chemical reactivity and kinetic behaviour are observed for 2-azido- (**1**) and 3-azidothiophene (**2**) in either 1,3-cycloaddition reactions with (trimethylsilyl)acetylene and trimethyl(vinyl)silane or thermal decomposition. Compound **1** gives cyclo-A_NA_E adducts (silylated triazole and triazoline) three times faster than compound **2**. Triazolines are sensitive to silica and undergo ring-contraction on chromatography, with extrusion of nitrogen, to give the corresponding 1-(thienyl)-2-(trimethylsilyl)aziridine. Kinetic measurements of the unimolecular thermal decompositions afford distinct activation parameters: E_a = 22.6 and 30.6 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −8.2 and −0.7 cal mol^{-1} K^{-1} for **1** and **2**, respectively. The modelling of the chemical reactivity for the α- or β-azido groups in the thiophene and the consequent geometric and electronic perturbation of the azidothiophenes are qualitatively supported by measurements of either ^{1}H or ^{13}C NMR chemical shifts.

The chemistry and kinetics of organic azides, as precursors (or otherwise) of nitrenes, have been increasingly investigated this century.[1] Thermolysis and photolysis of phenyl azide, useful for many synthetic, biological and industrial applications, has been investigated primarily to understand its diverse behaviour. These reactions show a dependence on the nature of the substituents and experimental conditions, and the intermediacy of the highly reactive intermediate phenylnitrene (PhN), in either the singlet and/or triplet state, is always assumed to be responsible for the different product distributions (*i.e.* dimerization to azobenzene, ring-expansion to a dehydroazepine, ring contraction to a cyanocyclopentadienyl radical, hydrogen abstraction, or insertion into a secondary amine).[2]

With five-membered heteroaromatic azides the product distribution is dependent on the position in the ring of the azido group.[1b,3] In fact, thermolysis of α-substituted heteroaryl azides generally results in ring-opening of the heteroaromatic substrate.† On the other hand, β-substituted azides appear to behave like aryl azides, forming nitrene intermediates which cyclize onto suitable *ortho*-substituents.[7]

Recently we published papers on the thermally induced ring-opening of related 2-azidobenzo[*b*]thiophene (2-BTA),[8] 2-azido-1-methylindole and 2-azidobenzo[*b*]furan[9] which undergo ring-opening. On the basis of chemical and kinetic studies with azidobenzothiophenes (2-BTA and 3-BTA) we suggested that the unimolecular decomposition and ring-opening of 2-BTA could occur in a concerted manner (path *b*, Scheme 1).[10] Furthermore, we found that 2-BTA and 3-BTA undergo 1,3-dipolar cycloadditions with silylated alkenes at comparable rates, as expected for phenyl azides substituted with electron-withdrawing groups, and faster than azides carrying electron-donating substituents.[11]

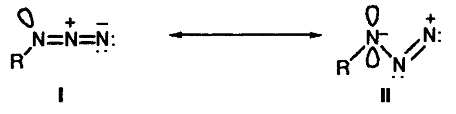
In continuation of our research in this field, we now report studies on the reactivity in the presence of (trimethylsilyl)acetylene or trimethyl(vinyl)silane (TMVS) of 2-azido- (**1**) and 3-azido-thiophene (**2**) and on their activation parameters as possible precursors of the respective nitrenes (2-ThN or 3-ThN). Experimental data together with measurements of ^{1}H and ^{13}C NMR chemical shifts ($\Delta\delta_H$ and $\Delta\delta_C$) are discussed in terms of changes in electronic structure (and geometry) of the azido-group located at either the α- or β-position of the thiophene ring.



Scheme 1

Results and Discussion

Compounds **1** and **2** were prepared by a short modification of our general procedure, previously described.[12] Their structures were confirmed by recording their IR, ^{1}H, ^{13}C NMR and exact mass spectral data. The 200 MHz ^{1}H NMR spectra of compounds **1** and **2** display three typical quartet patterns shifted considerably upfield compared with those of the corresponding bromothiophenes‡ and, especially, with those of thiophene (Table 1). In particular, in the case of compound **1** all protons are shifted upfield, while for compound **2** only the protons at the 2- and 4-positions are markedly affected.



Scheme 2

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† Deoxygenation of 2-substituted-3-nitro- and 3-substituted-2-nitrothiophenes (and -benzo-[*b*]thiophenes) with triethyl phosphite (TEP), which is the next most widely used method for generating arylnitrenes,[4] have been reported to yield a thieno (or benzo[*b*]thieno)-fused nitrogen-containing ring system without ring fragmentation.[5] The only exception appears to be 2-nitrothiophene-3-carbaldehyde anils which, in boiling *tert*-butylbenzene, undergo ring-cleavage with loss of sulfur, affording a 1-arylpyrrole-3-carbonitrile after rehybridization of the intermediate so formed.[6]

‡ For the resemblance between the physical properties of organic azides and the corresponding bromo-compounds see ref. 13.

Table 1 ^1H and ^{13}C NMR chemical shifts for azido and bromo thiophenes (Th) and azidobenzene[a]

	$\delta_H(\Delta H_n)$[b]				$\delta_C(\Delta C_n)$[b]			
Compound	H-2	H-3	H-4	H-5	C-2	C-3	C-4	C-5
Th	7.36	7.13			124.9	126.4		
2-BrTh		6.90 (−0.23)	6.87 (−0.26)	7.22 (−0.14)	112.9 (−12.0)	130.6 (4.2)	128.4 (2.0)	127.7 (2.8)
3-BrTh	7.23 (−0.13)		7.02 (−0.11)	7.27 (−0.09)	123.6 (−1.3)	110.9 (−15.5)	130.7 (4.3)	127.5 (2.6)
2-N_3Th		6.60 (−0.53)	6.83 (−0.30)	6.90 (−0.46)	143.2 (18.3)	119.8 (−6.6)	127.3 (0.9)	116.0 (−8.9)
3-N_3Th	6.78 (−0.58)		6.81 (−0.32)	7.28 (−0.08)	110.4 (−14.5)	138.3 (11.9)	121.2 (−5.2)	127.2 (2.3)
N_3Ph	7.00 (−0.26)	7.33 (0.07)	7.13 (−0.13)		119.8 (−8.7)	130.5 (2.0)	125.5 (−3.0)	

[a] In order to obtain a uniform and reliable basis for these comparisons, we used as far as possible ^1H and ^{13}C NMR spectral data obtained from solutions (*ca.* 10%, w:w) in deuteriochloroform and using TMS as internal reference; δ_H values relative to TMS and δ_C relative to $CDCl_3$ (76.9 ppm with respect to TMS). [b] (ΔH_n) and $(\Delta C_n) = \delta_H$(substrate) [or δ_C(substrate)] $-\delta_H$(reference) [or δ_C(reference)].

In aromatic (or heteroaromatic) systems there is a reasonable correlation between $\Delta\delta_H$ (or $\Delta\delta_C$) NMR parameters and the nature of the substituent.[14] Empirically, it can be assumed that the electron densities on the various protons of the thiophene ring can be given by the sum of the proton shifts produced by the substituent. Thus, if a negative value of $\Delta\delta$ (diamagnetic), determined at paragonable magnetic anisotropy, is taken as an indication of increase in electron density of the proton systems examined, our found values of $\Sigma(\Delta\delta)$ (−1.29 for **1** and −0.98 for **2**) speak in favour of a major contribution by the azido group to the conjugation in 2-azidothiophene (**1**) compared with 3-azidothiophene (**2**). This fact agrees qualitatively with simple descriptions of the electrical effects of -I + M substituted thiophenes.[15]

However, in the case of 2-azidothiophene (**1**) the observed $\Delta\delta_H$ values deviate considerably from the Swain–Lupton empirical regression analysis relating proton chemical shifts of monosubstituted thiophenes to substituent constants *F* and *R*. This fact agrees with the observed behaviour of Br, I, and SMe groups in the study carried out by Gronowitz *et al.*[16] with fourteen 2- and 3-monosubstituted thiophenes. On the other hand, compound **2** displays good linear correlation ($r = 0.996$) but with slope $m = 0.529$ presumably due to the much lower + M effect than that expected for the azido group on the basis of the resonance parameter ($R = -0.40$). The recent overhauled Hammett constants, resonance, and field parameters for the azido group ($\sigma_p = 0.08$, $R = -0.40$ and $F = 0.48$) differ significantly from those of a bromo- ($\sigma_p = 0.23$, $R = -0.22$ and $F = 0.45$) but are quite similar to those of a fluoro-substituent ($\sigma_p = 0.06$, $R = -0.39$ and $F = 0.45$).[17]

Additional information was gained by studying ^{13}C NMR chemical shifts, especially with *para*-substituent chemical shifts (para-SCS) which are considered to be related to the total and local π charge density of the molecule.[18] As expected for nitrogen-substituted carbon, both the carbon atoms carrying the azido group are shifted downfield with larger downfield shift for compound **1** than for compound **2**. Moreover, all the *ortho*-like carbon atoms are shifted upfield and a large upfield shift was observed also for C-5[19] (*para*-like) in compound **1** (Table 1).

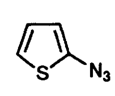
In order to find peculiarities between different nuclei we compared the SCS of azides **1** and **2** with those exerted on the thiophene ring by fluoro- and bromo-substituents. Evidence for good linear correlation was found only between 3-fluorothiophene and the corresponding 3-azidothiophene (**2**) ($r = 0.999$) with slope $m = 0.766$, thus emphasizing the basic similarity of the substituent effects particularly in this case. Furthermore, a comparison was carried out between the 3-, 4- and 5-positions in 2-substituted thiophenes and with the *ortho-*, *meta-* and *para*-positions in phenyl azide. No linear correlations were observed. On the other hand, for 3-azidothiophene (**2**) the 2- and 5-positions were compared respectively with the *ortho-* and *meta*-position of the phenyl azide, while the 4-position displays a good correlation ($r = 1.00$, $m = 2.049$ and $r = 1.00$, $m = 1.571$ for 3-fluorothiophene and compound **2**, respectively) and can be considered as a *para*-benzenic position. The resemblance observed from the SCS values between the 3-fluoro- and 3-azido-derivatives suggests that these groups exert comparable electrical effects (field/inductive plus resonance) on the thiophene ring with a major degree of interaction with this less aromatic system with respect to benzene. Thus, the nitrogen-atom attached to the ring should be in a hybridization state which makes it comparable electronically to a fluorine-atom attached to this position. On the other hand, electron release from the azido group to the thiophene ring in compound **1** appears to be still greater.

The triatomic chain of the azido group is characterized, in the valence bond description, by resonance between collinear allenyl type **I** and bent allyl type **II** canonical structures (Scheme 2).[20] The former, characterized by cylindrical symmetry, would be the most stable. However, the calculated energy involved in change of the hybridization state is low and associated with weak stabilization in the σ skeleton of the structure **II**.[21]

Moreover, the change of symmetry passing from structure **I** to **II** corresponds to the MO formalism suggested from a 1,3-dipoles cycloaddition diagram[22] which has been established using many examples.[23] This preferential bent structure of the azido group should enhance the reactivity of its 1,3-cycloaddition to carbon–carbon double (or triple) bonds. As expected, the reactions of azidothiophenes **1** and **2** with neat (trimethylsilyl)acetylene or TMVS (0.5 mol dm^{-3}) proceeded smoothly at 25 °C to afford, within 4–15 days (TLC), and after chromatographic separation, the corresponding triazoles **1a** and **2a**, or aziridines **1b** and **2b**, respectively.

Similarly to what was previously observed for the reactions of silylated dipolarophiles with some aryl azides, 2-BTA and 3-BTA,[11] aziridines **1b** and **2b** probably arise from a primary triazoline adduct which undergoes silica gel promoted ring-contraction with extrusion of nitrogen. In fact, the ^1H NMR spectrum of an aliquot of the reaction mixture obtained from compound **2**, before chromatography, revealed in addition to the peaks of the aziridine **2b** the presence of an ABX system (δ 4.21, *J* 13.6 and 9.2 Hz; δ 3.61, *J* 13.6 and 7.8 Hz; and δ 3.37, *J* 9.2 and 7.8 Hz) consistent with the presence of the triazoline adduct **2c**. The ratio **2b**:**2c** was *ca.* 1:1. The elusive triazoline **2c** was converted subsequently to the corresponding aziridine **2b** by treatment of the reaction mixture with silica gel from which dinitrogen emitted copiously.

Structural assignments of all new compounds **1a**, **2a**, **1b** and **2b** were based on IR, ^1H NMR and exact mass spectroscopic data (or elemental analysis); moreover, ^{13}C NMR spectroscopy provided evidence for the orientation of additions of azides **1** and **2** to the terminal alkyne. In fact, chemical shift assignments were obtained by recording the off-resonance



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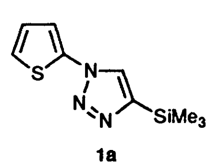
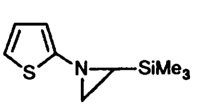
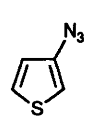


1a



1b



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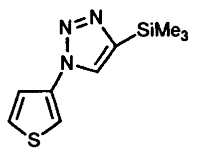
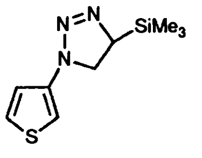
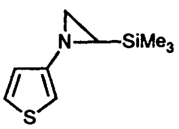


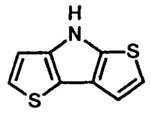
2a



2c



2b



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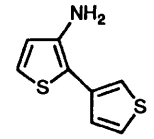

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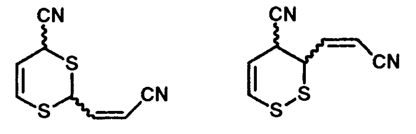

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Table 2 First-order rate constants and activation parameters for the thermolyses of the azides **1** and **2** in *p*-chlorotoluene[a]

Azide	$T/°C$	$k/10^{-4}\ s^{-1}$	E_a/kcal mol^{-1}	$\Delta S^{\neq}$/cal mol^{-1} K^{-1}
1	32.5	0.21 ± 0.01		
1	54.0	2.62 ± 0.07	22.6 ± 0.1	−8.2 ± 0.7
1	80.0	30.8 ± 0.11		
2	110.0	0.41 ± 0.01		
2	130.0	3.21 ± 0.06	30.7 ± 0.1	−0.7 ± 0.5
2	148.0	15.66 ± 0.12		

[a] 1 cal = 4.184 J.

proton decoupled spectra, which displayed a doublet at δ 129.2 (*J* 193.8) and δ 128.3 (*J* 192.4), assignable to C-5, and a singlet at δ 148.2 and 147.6, assignable to C-4 of the triazole rings **1a** and **2a**, respectively.

Compared with the approximate reaction times of phenyl azide with (trimethylsilyl)acetylene and TMVS (respectively, 35 and 40 days), the same reactions of compound **1** and 2-BTA run faster (5 and 4 or 9 and 5 days, respectively). In addition, the times required for cycloadditions of the 3-azido derivatives, **2** and 3-BTA appear nearly intermediate (16 and 12 or 28 and 15 days, respectively) between phenyl azide and the 2-azido heterocycles. As might be expected, according to the lower nucleophilic nature of an alkyne with respect to the corresponding alkene,[24] reactions of azides **1** and **2** with (trimethylsilyl)acetylene were slower than those with TMVS.

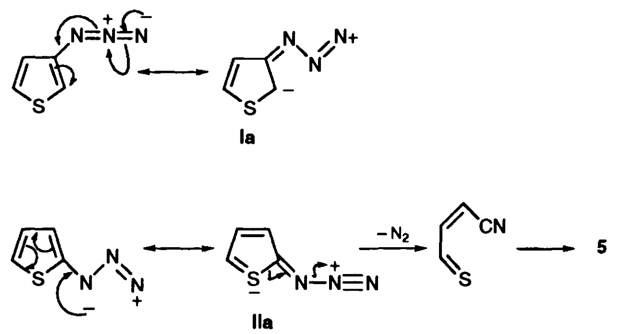
In the light of these findings, together with our previous studies[11] on the reactivity of the aryl azides 2-BTA and 3-BTA with silylated alkenes, it might be concluded that the rates of cycloadditions are strongly dependent on the degree of polarization of the azido group, as might be expected for concerted reactions initiated by the junction of the terminal azido nitrogen to the nucleophilic α-carbon of the terminal alkenes. The degree of polarization of the azido group appears to be directly dependent on the degree of its interaction by resonance with the aromatic (or heteroaromatic) substrate. In agreement with this consideration, the greater reactivity of the 2-azido derivatives (**1** and 2-BTA) compared with the 3-azido-derivatives (**2** and 3-BTA) supports a more effective conjugation for the azido group on the α-position than on the β-position of the thiophene ring.

A similar conclusion was reached by a consideration of the Arrhenius activation parameters, determined from the first-order rate constants, calculated at three different temperatures, by measuring the variation in intensity of the strong IR asymmetric stretching band of azido group as a function of time. Thermolyses of azidothiophenes **1** and **2** were carried out in inert solvents such as ethylbenzene or *p*-chlorotoluene in concentration ranges within 50–2 mmol dm^{-3}. The results, collected in Table 2, show first-order kinetics, in agreement with the most important step in decomposition of azides, which is the formation of a nitrene and nitrogen. However, a unimolecular process may arise also from a concerted rearrangement with elimination of nitrogen. In this case the activation parameters should be characterized by lower energy and larger negative entropy of activation. In fact, the calculated activation parameters for compound **1** are remarkably different from E_a and $\Delta S^{\neq}$ for compound **2** and, above all, from those reported for the thermolyses of aromatic azides to nitrenes.[25]

Analysis by GC–MS of the reaction mixtures, after complete decomposition of compound **1** or **2**, showed a difference in product distributions, which appears to be diagnostic for the different pathways involved in these reactions. Confirmation of the presence of a nitrene intermediate for compound **2** came from the detection of a trace amount of 3-aminothiophene [m/z = 99 (100), 86, 82, 72, 71] together with a major amount of 3,3′-azothiophene [m/z = 194 (66), 111 (75), 83 (100)], 1,2-bis(*p*-chlorophenyl)ethane (m/z = 252, 250), 4-chlorobenzyl alcohol (m/z = 144, 142) and, surprisingly, the 4*H*-dithieno[3,2-*b*; 2′,3′-*d*] pyrrole (**3**) [m/z = 179 (78), 98, 59]. Generation of these compounds is consistent with the intermediacy of a 3-thienyl nitrene, presumably interconverted in the triplet state, whose fate generally is dimerization to the azoderivative and/or hydrogen abstraction to give amine. Formation of compound **3** can, in principle, be ascribed to coupling of a 3-thienyl radical, presumably arising by homolytic cleavage of the C–N bond of the forerunner azide or the initially formed azothiophene, and the 2-position of 3-azido (or nitreno)thiophene. With the aim of throwing further light on this conclusion we carried out thermal decomposition of azide **2** in ethylbenzene containing a slight excess of diethylamine in a sealed tube at about 136 °C for *ca.* 4 h (until TLC showed disappearance of the starting azide), which led, after column chromatography, to the isolation of 4*H*-dithieno[3,2-*b*; 2′,3′-*d*] pyrrole (**3**) (*ca.* 26%) and 3-amino-2,3′-bithienyl (**4**) (*ca.* 8%) as the only identifiable products. Compounds **3** and **4** showed identical spectroscopic and analytical data with the same products previously reported.[7b,26] No evidence could be obtained for products arising by isomerization to ring-expanded dialkylamine nor diamino-substituted thiophene.

Diethylamine is a well-known nitrene trapping reagent[4b] and its reaction with triplet nitrene may be complicated by a single electron-transfer (SET) process involving both nitrene as well as electronically excited azide.[27] Consequently the mechanism of this reaction requires more detailed study.

On the other hand, the GC–MS analysis of the reaction mixture of compound **1** indicated the presence of a structure very close to that expected for *m*-dithiin structures (**5**). In fact, thermolysis of the azide **1** in benzene at 60 °C, after removal of the solvent, afforded unstable material whose IR spectrum showed a C≡N stretching band at *ca.* 2210 cm^{-1} and whose mass spectrum showed predominant fragmentation ions at m/z =



Scheme 3

194 ($C_8H_6N_2S_2$), 162 and 97. The ^1H NMR spectrum, though not well resolved owing to the instability of the obtained pale-yellow compound, which darkened quickly even in solution, appeared to be indicative of tautomeric structures of compound **5** (including their geometrical isomers). In accordance with expectations, largely based on ^1H and ^{13}C NMR measurements and differences in reactivity, azide **1** compared with the isomeric azide **2** is considered to have an appreciably lower aromaticity because of the higher electronic interactions between the heteroaromatic ring and the azido function showing a large +M effect. Thus, our experimental findings are interpreted in terms of different reorganization of the azido group, by conjugation of the π-electron involved in the α- or β-position of the thiophene systems, according to the path depicted in Scheme 3. This is reflected in the preferred conjugation of the carbon-bonded nitrogen-atom in structure **IIa** with lone pairs having more p-character than that of structure **Ia**. There were several striking experimental features about this assumption. The first was the large upfield ^1H NMR shift observed for all protons of compound **1** and the inability to fit $\Delta\delta_H$ (or $\Delta\delta_C$) NMR parameters with the empirical Swain–Lupton linear regression, while compound **2** behaves nearly normally. The second striking feature was the difference in reaction rates observed for the 1,3-dipolar cycloadditions to double or triple bonds. In fact, a major degree of polarization of the azido group would play a favourable role in these reactions. In addition, HMO theory predicts that the scarcely conjugated system **Ia** would be more stable than the conjugated system **IIa** (Scheme 3). Activation parameters do not account for these facts.

Experimental

Materials.—2-Azidothiophene (**1**) and 3-azidothiophene (**2**) were prepared by reacting the corresponding heteroaryllithium derivative with tosyl azide following the general procedure previously reported.[12] However, the yield of azide **1** was increased (55%) by a slight modification of our previously reported method. Tosyl azide was prepared as described in the literature.[28] (Trimethylsilyl)acetylene was purchased from Aldrich Chimica Italiana. IR spectra were recorded with a Perkin-Elmer Model 257 instrument. ^1H and ^{13}C NMR data were obtained with a Varian Gemini 200 MHz instrument for solutions in $CDCl_3$; *J* values are given in Hz and long-range coupling were not determined. Mass spectra were recorded on a VG Analytical 7070E instrument and HP 5970 GC-MS.

Preparation of 2-Azidothiophene (**1**).—A solution of thiophene (0.08 mol) in dry diethyl ether (100 cm^3) was added with stirring under nitrogen at room temperature to butyllithium (1.6 mol dm^{-3} in hexane; 50 cm^3). The reaction mixture was stirred and heated under reflux for an additional 1 h, after which it was cooled to −70 °C and added dropwise to a solution of tosyl azide (0.08 mol) in dry ether (100 cm^3). After the addition was complete the resulting mixture was stirred and allowed to reach 0 °C within 5 h. The pale yellow triazene salt which had formed was rapidly filtered off and suspended in pentane. The suspension was treated at 0 °C with a solution of tetrasodium pyrophosphate (0.08 mol) in water (200 cm^3). The yellow pentane layer was collected and the excess of solvent eliminated under vacuum to give a residue which was chromatographed on a 'Florisil' column using pentane as eluent. Chromatography gave the title compound (**1**) (0.044 mol, 55%) as an oil.

NMR and mass spectral data for 2-azidothiophene **1**: δ_H(200 MHz; $CDCl_3$) 6.90 (1 H, dd, *J* 1.5 and 5.4, H-5), 6.83 (1 H, dd, *J* 3.6 and 5.4, H-4), 6.60 (1 H, dd, *J* 1.5 and 3.6, H-3); δ_C(200 MHz; $CDCl_3$) 143.24 (C-2, s), 127.30 (C-4, d), 119.80 (C-3, d), 115.97 (C-5, d); *m/z* 125 (M$^+$, 14.3%), 97 (100, M − N_2), 96 (53.6), 70 (62.5), 57 (33.9), 45 (60.7), and 28 (76.8) (Found: M$^+$, 125.0040. $C_4H_3N_3S$ requires *M*, 125.0047).

NMR and mass spectral data for 3-azidothiophene **2**: δ_H(200 MHz; $CDCl_3$) 7.28 (1 H, dd, *J* 3.2 and 5.0, H-5), 6.81 (1 H, dd, *J* 1.4 and 5.0, H-4), 6.78 (1 N, dd, *J* 1.4 and 3.2, H-2); δ_C(200 MHz; $CDCl_3$) 138.34 (C-3, s), 127.19 (C-5, d, *J* 191.4), 121.17 (C-4, d, *J* 173.3), 110.41 (C-2, d, *J* 188.4); *m/z* 125 (M$^+$, 65.7%), 97 (62.7, M − N_2), 71 (46.3), 70 (46.3), 58 (11.9), 52 (22.0), 45 (100) and 28 (74.6) (Found: M$^+$, 125.0055).

Reactions of Thienyl Azides **1** *and* **2** *with (Trimethylsilyl)-acetylene and Trimethyl(vinyl)silane (TMVS) at* 25 °C.—*General procedure.* A solution of the thienyl azide (0.5 mol dm^{-3}) in neat (trimethylsilyl)acetylene or TMVS was allowed to react in a sealed tube at 25 °C and in the dark until TLC showed the absence of the starting azide. The residue obtained after careful elimination of the excess of silylated alkyne (or alkene) under vacuum was chromatographed on a 'Florisil' column using hexane with increasing amount of diethyl ether (up to 50%) as eluent. Triazoles **1a**, **2a** and aziridines **1b**, **2b** were isolated and characterized. Approximate reaction times at 25 °C and product yields for the reactions of thienyl azides (**1** and **2**) with silylated alkyne (or alkene) are reported in brackets. The following new triazoles **1a** and **2a** were obtained:

1-(2-Thienyl)-4-(trimethylsilyl)-1,2,3-triazole (**1a**) (5 days, 75%), m.p. 72–74 °C; ν_{max}/cm^{-1} 3140, 2960, 1250, 850 ($SiMe_3$) and 760. δ_H(200 MHz; $CDCl_3$) 7.82 (1 H, s), 7.19 (1 H, dd, *J* 1.3 and 3.6, H-3), 7.17 (1 H, dd, *J* 1.3 and 5.5, H-5), 6.99 (1 H, dd, *J* 3.6 and 5.5, H-4), 0.37 (9 H, s); δ_C(200 MHz; $CDCl_3$) 148.22 (C-4′, s), 131.73 (C-2, s), 129.26 (C-5′, d, *J* 193.8), 126.99 (C-4, d, *J* 171.8), 123.41 (C-5, d, *J* 185.5), 118.92 (C-3, d, *J* 168.8), −0.76 (q, *J* 120.7); *m/z* 195 (19.6%, M − N_2), 181 (15.0), 180 (100), 83 (37.5), 73 (34.2) and 43 (14.2) (Found: C, 48.4; H, 5.9; N, 18.5. $C_9H_{13}N_3SSi$ requires: C, 48.4; H, 5.9; N, 18.8%).

1-(3-Thienyl)-4-(trimethylsilyl)-1,2,3-triazole (**2a**) (16 days, 90%), m.p. 96–98 °C; ν_{max}/cm^{-1} 3120, 2960, 1260 and 855 ($SiMe_3$). δ_H(200 MHz; $CDCl_3$) 7.93 (1 H, s), 7.56 (1 H, dd, *J* 1.7 and 3.0, H-2), 7.47 (1 H, dd, *J* 1.7 and 5.2, H-4), 7.43 (1 H, dd, *J* 3.0 and 5.2, H-5), 0.38 (9 H, s); δ_C(200 MHz; $CDCl_3$) 147.62 (C-4′, s), 136.64 (C-3, s), 128.34 (C-5′, d, *J* 192.4), 127.77 (C-5, d, *J* 189.1), 121.77 (C-4, d, *J* 170.6), 114.69 (C-2, d, *J* 188.3), −0.79 (q, *J* 120.0); *m/z* 195 (11.8%, M − N_2), 181 (14.6), 180 (100), 83 (5.0), 73 (13.0) and 43 (10.9) (Found: C, 48.4; H, 5.9; N, 18.6).

The following new aziridines **1b** and **2b** were obtained:

1-(2-Thienyl)-2-(trimethylsilyl)aziridine (**1b**) (4 days, 75%), as an oil; ν_{max}/cm^{-1} 2960, 1250, 850 ($SiMe_3$) and 750; δ_H(200 MHz; $CDCl_3$) 6.71 (1 H, dd, *J* 3.2 and 5.5, H-4), 6.67 (1 H, dd, *J* 1.8 and 5.5, H-5), 6.40 (1 H, dd, *J* 1.8 and 3.2, H-3), 2.23 (2 H, d, *J* 6.3), 1.4 (1 H, t, *J* 6.3) and 0.13 (9 H, s); *m/z* 197 (M$^+$, 19.4%), 182 (8.2, M − CH_3), 85 (14.2), 73 (100), 59 (14.7) and 45 (15.4) (Found: M$^+$, 197.0692. $C_9H_{15}NSSi$ requires: *M*, 197.0694).

1-(3-Thienyl)-2-(trimethylsilyl)aziridine (**2b**) (12 days, 82%), as an oil; ν_{max}/cm^{-1} 2965, 1260, 850 ($SiMe_3$) and 760; δ_H(200 MHz; $CDCl_3$) 7.10 (1 H, dd, *J* 3.1 and 5.1, H-5), 6.83 (1 H, dd, *J*

1.4 and 5.1, H-4), 6.40 (1 H, dd, J 1.4 and 3.1, H-2), 2.08 (2 H, d, J 5.6), 1.22 (1 H, t, J 5.6) and 0.12 (9 H, s); m/z 197 (M^+, 46.9%), 196 (28.6, M − H), 182 (41.8), 141 (36.2), 97 (11.2), 73 (100), 59 (20.9) and 45 (19.5) (Found: M^+, 197.0694).

Rates of Decomposition of Thienyl Azides **1** *and* **2**.—A solution of the azide (0.05 mol dm^{-3}) in ethylbenzene (or *p*-chlorotoluene) (10 cm^3) was allowed to react in a thermostatic bath at the appropriate range of temperature (32.5–80.0 °C for azide **1** or 110.0–148.0 °C for **2**). The rates of decomposition of the azides as a function of time were determined by IR spectroscopic measurement of the neat N_3 band (*ca.* 2100 cm^{-1}) of spaced aliquots of solution (0.5 cm^3). Results are summarized in Table 2.

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