Preparation, Reactivity, NMR Properties and Semiempirical MNDO/PM3 Structural Calculations of 2-Azido- and 3-Azido-selenophene

Salo Gronowitz[a] **and Paolo Zanirato** *[,b]

[a] *Division of Organic Chemistry 1, Chemical Center, University of Lund, S-221 00, Lund, Sweden*

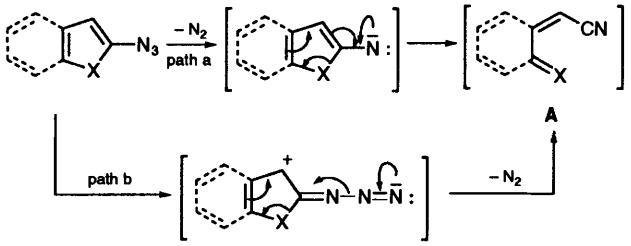
[b] *Dipartimento di Chimica Organica, 'A. Mangini', Università di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy*

The preparation, by azido-transfer reaction, of 2-azido- **1** and 3-azido-selenophene **2** using the appropriate heteroaryllithium derivatives and tosyl azide, followed by fragmentation of the intermediate triazene lithium salts is reported here. Different chemical reactivity and kinetic behaviour were observed for azides **1** and **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 or triazoline) *ca.* three times faster than compound **2**. Both the elusive triazoline adducts undergo rapid ring-contraction, with extrusion of nitrogen, to give rise to the corresponding 1-(selenophenyl)-2-(trimethylsilyl)aziridine (**1b**, **2b**). Kinetic measurements of the unimolecular thermal decompositions afford distinct activation parameters: E_a = 21.5 and 30.4 kcal mol^{-1},[†] $\Delta S^{\ddagger}$ = −10.7 and −0.9 cal mol^{-1} K^{-1} for **1** and **2**, respectively. Experimental data, as a result of geometric and electronic disturbances exerted by the azido-group located at α- or β-positions of the selenophene ring, are qualitatively supported by measurement of ^{1}H, ^{13}C and ^{77}Se NMR chemical shifts. The present experimental evidence and those previously obtained with related 2-azido- and 3-azido-thiophenes are corroborated with the determination of the structures and comparison between ^{13}C substituent chemical shift (SCS) and charge distributions by using a semiempirical computational MNDO/PM3 method.

The chemistry of aryl azides has been widely investigated mainly for their synthetic, biological and industrial applications.[1] However, less attention has been devoted to the preparation and the chemistry of five-membered heteroaromatic azides, perhaps because suitable starting azides were not readily available. Exceptions would be a few heteroaryl azides prepared from heterocycles containing a diazotizable amino group or halogen derivatives prone to nucleophilic displacement by azido ion.[2]

In heteroaromatic five-membered rings, metallation (especially halogen–metal exchange with organolithium derivatives), followed by the reaction of the heteroaryllithium derivatives with opportune electrophiles offers a most convenient route to many compounds,[3] including the formation of carbon–nitrogen bonds.[4] In fact, we show that heteroaryl azides (and their benzo-condensed systems) may be achieved easily by reaction of the appropriate heteroaryllithium with tosyl azide, followed by fragmentation of the resulting triazene salt. Moreover, the isolated heteroaryl azides may be easily reduced to the corresponding amines.[5]

Recently we reported studies into the reactivity of isomeric α- and β-azidothiophenes and benzo-condensed derivatives,[6] together with the preparation, by the same method, of the α-azides of benzofuran and 1-methylindole.[7] The general trend that emerged from those studies indicated that the formal generation of nitrenes at the α-position of the five-membered rings generally results in the opening of the ring leading to the formation of a 4-cyano-1-hetero-1,3-diene product. On the other hand, normal arylnitrene behaviour was exhibited by β-positioned nitrenes. On the basis of the observed chemical and kinetic reactivities, we suggested that the unimolecular decomposition and ring-opening of α-azidothiophene would occur in a concerted manner and the process should be dependent on the nature of the heteroatom; Scheme 1, pathway b. Therefore, the formal generation of a 2-positioned nitrene generally results in the opening of the former thiophene ring leading to the formation of the possible building-block 4-cyano enethione intermediate A (X = S).

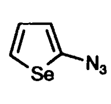


Scheme 1

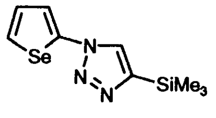
In continuation of this research and in order to detect common patterns of behaviour, we now report the syntheses of 2-azido-**1** (2-ASe) and 3-azido-selenophene **2** (3-ASe),[‡] and their thermal kinetic and chemical behaviour in the presence of silylated dipolarophiles. Thermal activation parameters and ^{1}H, ^{13}C and ^{77}Se NMR spectra are discussed in terms of diverse directing and activating effects produced by the azido-group located at the α- or β-position of the selenophene ring. Experimental data, are compared with the relative geometries and charge distributions of both isomers, calculated theoretically at MNDO/PM3 level.

[†] 1 kcal mol^{-1} = 4.184 kJ mol^{-1}.

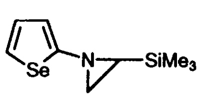
[‡] Comparative investigations on the aromaticity, based mainly on NMR parameters and mesomeric dipole moment, of furan, thiophene, selenophene and tellurophene have been carried out.[8] Furthermore, the correlation of their reactivity with NMR (^{1}H, ^{13}C and ^{77}Se) chemical shifts has been investigated[9] and the directing effects of the selenophene ring have been reviewed.[10]



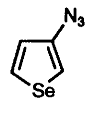
1



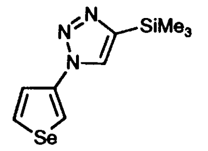
1a



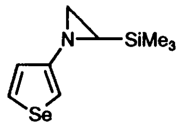
1b



2



2a



2b

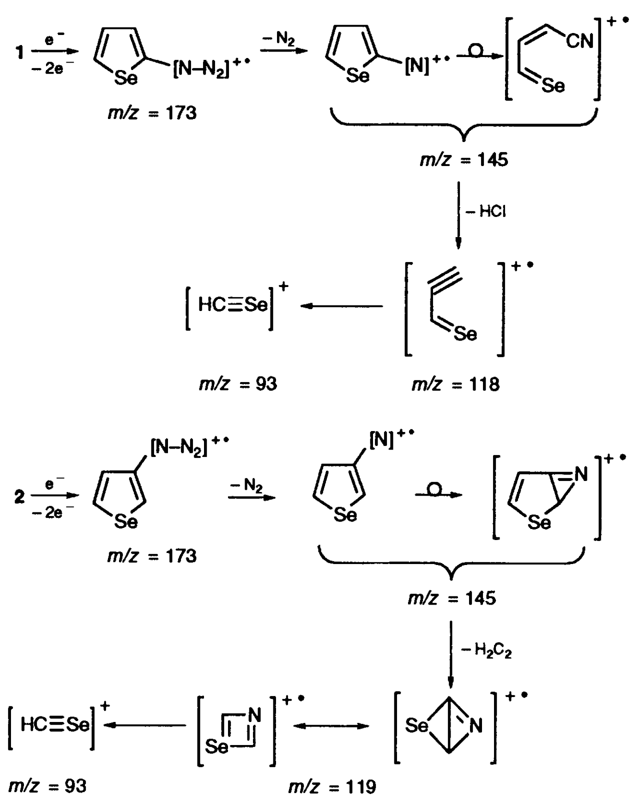
Results and Discussion

The azides **1** and **2** were obtained by reaction of tosyl azide with the appropriate heteroaryllithium, prepared by using butyllithium for direct metallation of selenophene or by halogen–lithium exchange with 3-bromoselenophene, followed by fragmentation of the resulting triazene salts. Compound **1** is less stable than isomer **2** and must be stored in a freezer.

Structures of azides **1** and **2** were confirmed by recording their IR, ^{13}C NMR and exact mass spectral data. The mass spectra of these azides are characterized by the significant abundance of the molecular ions showing characteristic isotopic peaks at m/z = 171 and 173. The first mode of fragmentation m/z = 145, corresponding to the loss of the molecular nitrogen mass unit, is common and somewhat reflects the stability of the corresponding azides. The subsequent $C_4H_3NSe^{+\bullet}$ species, has been shown to undergo a different kind of fragmentation with elimination of hydrogen cyanide and acetylene (fragment ions at m/z 118 and 119) for azides **1** or **2**, respectively. Analogous fragmentations have been observed with aryl azides but these cases generally exhibit contemporary loss of both acetylene and hydrogen cyanide from $ArN^{+\bullet}$.[11] In our case, the specific formation of neutral HCN and H_2C_2 might be dependent on the relative elimination rates occurring with the different intermediate $C_4H_3NSe^{+\bullet}$ and is diagnostic for the different pathways involved in the ion fragmentation mechanisms for selenophene[12] and compounds **1** and **2**; Scheme 2.

The ^1H NMR spectra display three typical quartet patterns which may be assigned, on the basis of the two vicinal coupling constants on the selenophene ring J_{45} = 5.9 and J_{34} = 3.9 Hz and the separated protons J_{35} = 1.4 Hz, to azide **1**, while the azido group located in the 3-position of **2**, gives rise to a vicinal coupling constant of J_{45} = 5.7 Hz and two separated proton coupling constants J_{25} = 2.8 and J_{24} = 1.5 Hz, typical for selenophene rings.[9] All protons of **1** and **2** are shifted upfield compared with those of selenophene, in particular, in the case of **1** the 3- and 5-positions ($\Delta\delta_H = -0.67$ and -0.53, respectively) on the ring, are shifted more upfield than the 4-position ($\Delta\delta_H = -0.34$). On the other hand, the proton located at the 2-position in **2** is more markedly affected ($\Delta\delta_H = -0.77$) than that of other positions ($\Delta\delta_H = -0.26$ and -0.17 for 4- and 5-H) (Table 1).

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.[13] Empirically, it can be assumed that the electron densities produced (or modified) by the substituent on the single protons are reasonably well correlated with their observed diamagnetic or paramagnetic shifts. Thus, if a negative value of $\Delta\delta_H$ (diamagnetic), determined at paragonable magnetic anisotropy, is taken as an indication of increase in electron density of the proton systems examined, the values we found speak in favour of a major degree of conjugation by the azido group through the αposition of the 2-azidoselenophene **1** compared with the β-position of 3-azidoselenophene **2**. As might have been expected, a general concordance with the $\Delta\delta_H$ trend, observed previously for both isomeric azidothiophenes occurred.[6g] In particular, all the positions of **1** are slightly shifted upfield, compared to 2-azidothiophene. On the other hand, the same comparison for **2**, relative to 3-azidothiophene, allows the observation that the 2- and 5-positions appear shifted upfield, but the 4-position does not.*



Scheme 2

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.[15] As expected for nitrogen substituted carbon, both the carbon atoms carrying the azido group are shifted downfield with a larger downfield shift for **1** than for **2**. Moreover, all the *ortho*-like carbon atoms are shifted upfield and a large upfield shift was observed also for C-5[16] (*para*-like) in compound **1** (Table 1). Thus, qualitative comparison between $\Delta\delta_H$ and $\Delta\delta_C$ for all positions of isomeric azidothiophenes and azidoselenophenes show a similar trend, and the slight differences observed between selenophene and thiophene azido-systems may be speculatively interpreted as a minor aromaticity of the selenophene, but with a greater ability to delocalize charges, with respect to the thiophene ring.[17]

The resemblance observed from the SCS and $\Delta\delta_H$ spectroscopic data between the α- and β-azidoselenophenes and the isomeric azidothiophenes suggests that the delocalized chemical bond of the heteroaromatic nucleus undergoes comparable electrical effects (field/inductive plus resonance) by the canonical structures of the azido group.[18]

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* Detailed ^1H, ^{13}C (and ^{77}Se) NMR spectroscopic data of various 2- and 3-substituted thiophenes and selenophenes, including the Swain–Lupton empirical regression analysis, have been previously reported by Gronowitz *et al.* In addition, the correlation between the relative chemical shifts ($\Delta\delta_H$, $\Delta\delta_C$ or $\Delta\delta_{Se}$) for the couple thiophene–selenophene have been carried out.[9,14]

Table 1 ^1H and ^{13}C NMR chemical shifts for selenophene (Se), thiophene (Th) and their α- and β-azides[a]

	$\delta_H(\Delta H_n)$[b]				$\delta_C(\Delta C_n)$[b]			
	2-H	3-H	4-H	5-H	C-2	C-3	C-4	C-5
Se	8.10	7.33			131.0	129.8		
2-N_3Se		6.66 (−0.67)	6.99 (−0.34)	7.57 (−0.53)	146.8 (15.8)	117.6 (−12.2)	128.7 (1.1)	124.8 (−6.2)
3-N_3Se	7.33 (−0.77)		7.07 (−0.26)	7.93 (−0.17)	113.1 (−17.9)	138.8 (9.0)	123.9 (−5.9)	131.2 (0.2)
Th	7.36	7.13			124.9	126.4		
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)

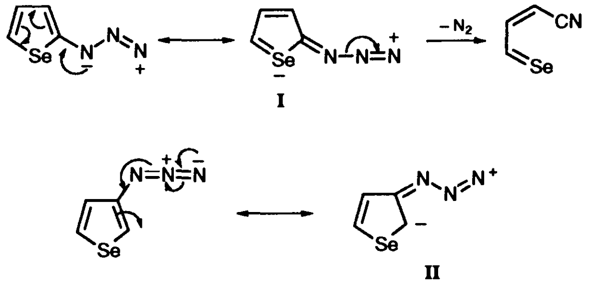
[a] In order to obtain a uniform and reliable basis for these comparison, we used as far as possible ^1H and ^{13}C NMR spectral data obtained from solutions (*ca.* 10%, w/w) in deuteriochloroform; δ_H values relative to TMS and δ_C relative to $CDCl_3$ (76.9 ppm with respect to TMS). [b] (ΔH_n) and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

With the aim of correlating the NMR spectroscopic data with the ground state charge distributions on the various carbon atoms of azides **1** and **2**, and the parent selenophene, we carried out semiempirical theoretical calculations. Computational MNDO/PM3 molecular geometries of the selenophene and their azido derivatives **1** and **2**, were determined by energy minimization using the keyword PRECISE, to allow the lowest gradient possible. We found that the comparison between the structure of the selenophene, determined by this method, and those determined by microwave spectra,[19] generally showed an accuracy of the geometrical parameters to less than ± 1%. The optimized geometry of selenophene is planar and the nearly colinear azido group showed preferential CCNN *cis*-planar conformation for **2** and SeCNN *trans*-planar conformation for **1**.

Simple HMO-type calculations illustrating geometries and charge distributions have been performed with phenyl azide,[18b] but to our knowledge similar treatment of five-membered heteroaryl azides is actually lacking. Of particular interest is the conjugative effect of the azido group located at the α- or β-position on the selenophene portion of the molecules and the π-electron populations with respect to the reaction mechanism pathways whose intermediates **I** and **II** are depicted on Scheme 3. Charge distribution and bond length data, reported in Fig. 1, suggest that the ground-state structure of α-azide **1** is close to the canonical structure **I**, characterized by a greater delocalized π-system due to conjugation with the azido group, unlike β-azides **2** with structure **II**. Conformations were made from the above reported geometrical data together with the observation that the Se–C_2 bond length of **1** is significantly elongated (1.8898 Å) with respect to that of β-azido derivative **2** (1.8788 Å), and conversely, the C–N bond has less double bond character which is indicated by the slight elongation (1.424 24 Å) with respect to the C–N bond of derivative **1** (1.397 45 Å).

The underlying semiempirical calculation includes electronic charge distribution on the various carbons of the selenophene ring, which can be correlated with the sum of the carbon shifts (SCS) produced by the substituent azido group. An illustration of these correlations was obtained by plotting the SCS values determined, for each carbon atom of **1** and **2** against the difference in charge with unsubstituted selenophene. Evidence for satisfactory linear correlations was found for **1** (r = 0.979 with slope m = 121.8, plot 1) and **2** (r = 0.919 with slope m = 99.3). In the light of these findings, it might be concluded that the degree of polarization of the azido group appears to be directly dependent on the degree of its interaction by resonance with the heteroaromatic substrate. The electron-charge distributions are consistent with contributions from the expected structures where the effects appear more pronounced at the α-position than the β-position of the heteroaryl ring (**I** and **II**, respectively) (Scheme 3).

A similar conclusion was reached by the consideration of Arrhenius activation parameters, determined from the first-order rate constants of thermolyses of azidoselenophenes **1** and **2**. Thermal decompositions were carried out in an inert solvent, such as *p*-chlorotoluene, at concentration ranges within 2–50 mmol dm^{-3} by measuring the variation in intensity of the strong IR asymmetric stretching band (*ca.* 2100 cm^{-1}) of the azido-group as a function of time. The results, collected in Table 2, show first-order kinetic rates, in agreement with the most important step in decomposition of azides, which is the formation of nitrene and nitrogen. However, a unimolecular process may also arise 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 (E_a = 21.5 kcal mol^{-1}, $\Delta S^‡$ = −10.7 cal mol^{-1} K^{-1}) for **1** are remarkably different from E_a = 30.4 kcal mol^{-1} and $\Delta S^‡$ = −0.9 cal mol^{-1} K^{-1} for **2**, and both are comparable with those previously reported for the thermolyses of corresponding



Scheme 3

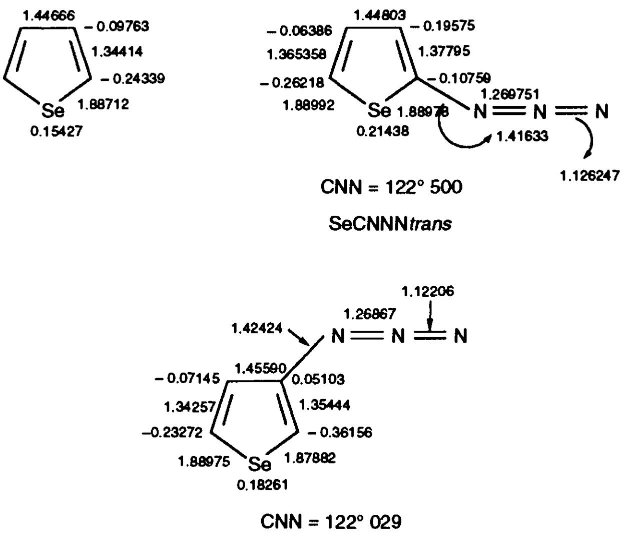


Fig. 1 Significant geometric data determined by MNDO/PM3, conformation and charge distribution for selenophene and their isomeric azido derivatives

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

Azide	T/°C	k/10^4 s^{-1}	E_a/kcal mol^{-1}	$\Delta S^\ddagger$/cal mol^{-1} K^{-1}
1	32.0	0.43 ± 0.01		
1	52.0	4.36 ± 0.07	21.5 ± 0.1	−10.7 ± 1.0
1	75.0	34.30 ± 0.11		
2	99.0	0.15 ± 0.01		
2	122.0	2.31 ± 0.06	30.4 ± 0.1	−0.9 ± 0.6
2	139.5	8.67 ± 0.12		

2-azido- and 3-azido-thiophene (E_a = 22.6 and 30.6 kcal mol^{-1}, $\Delta S^\ddagger$ = −8.2 and −0.7 cal mol^{-1} K^{-1}, respectively).[6g]

Our experimental findings, obtained from the present study of thermal reactivity of azidoselenophenes, as well as previously observed azidothiophenes, 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 five-membered heteroaryl systems. This is reflected in the preferred conjugation of the carbon-bonded nitrogen atom in structure **I**, characterized by the C–N bond with more double bond character than that of structure **II**. Thus, the bent structure which results, favoured by conjugation of the azido-group in compound **1**, should enhance the reactivity of its 1,3-cycloaddition to carbon-carbon double (or triple) bonds. As expected, the azidoselenophene **1** reacts *ca.* three times faster than **2** with neat (trimethylsilyl)acetylene or trimethyl(vinyl)-silane (TMVS) affording the corresponding triazoles **1a** and **2a**, or aziridines **1b** and **2b**, respectively.

Similarly to that previously observed for 1,3-cycloadditions to silylated dipolarophiles, chosen as a probe for the reactions with some heteroaryl azides,[6d,f,g] aziridines **1b** and **2b** presumably arise from a primary triazoline adduct which undergoes ring-contraction with expulsion of nitrogen. Structural assignments of all new compounds **1a**, **2a**, **1b** and **2b** were based on IR, ^{1}H NMR and exact mass spectroscopic data (or elemental analyses). The ^{13}C NMR spectroscopy provided evidence for the orientation of additions of azides **1** and **2** to the terminal alkyne by recording the off-resonance proton decoupled spectra, which displayed a doublet at δ 127.98 (J 191.7 Hz) and δ 127.79 (J 193.0 Hz), assignable to C-5, and a singlet at δ 148.12 and 143.38, assignable to C-4 of the triazole rings **1a** and **2a**, respectively. As might be expected, according to the lower nucleophilic nature of an alkyne with respect to the corresponding alkene,[20] reactions of azides **1** and **2** with (trimethylsilyl)acetylene were slightly slower than those with TMVS.

In the light of these findings together with our previous studies on the reactivity of the heteroaryl azides, especially azidothiophenes, with silylated olefins, it might be concluded that the rate of 1,3-cycloadditions is 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 alkene (or alkyne). The degree of polarization of the azido-group appears to be directly dependent on the degree of its interaction by resonance with the heteroaromatic substrate. In agreement with this consideration, the greater reactivity of the 2-azido-derivatives, compared with the 3-azido-derivatives, supports a more effective conjugation for the azido group on the α-position than on the β-position of the selenophene ring.

Experimental

Materials.—2-Azido, **1** and 3-azido-selenophene **2** were prepared by reacting the corresponding heteroayllithium derivative with tosyl azide mostly following the procedure previously reported for related heterocycles.[5–7] The metallations were made by reaction with butyllithium and the regioselectivity was obtained by direct reaction with selenophene for compound **1** and by metal–halogen exchange with 3-bromoselenophene for compound **2**.

(Trimethylsilyl)acetylene and TMVS were purchased from Aldrich Chimica Italiana. Tosyl azide,[21] 2,4,5-tribromoselenophene[9a] and 3-bromoselenophene[22] were prepared as described in the literture. IR spectra were recorded with a Perkin-Elmer Model 298 spectrophotometer. ^{1}H, ^{13}C and ^{77}Se NMR data for compounds **1** and **2** were obtained with Varian XL 300 or Varian Gemini 200 instruments for solutions in $CDCl_3$; J values are given in Hz and long-range coupling constants were not determined. Mass spectra were recorded on a JEOL SX-CO2 instrument.

2-*Azidoselenophene* **1**.—A solution of selenophene (0.066 mol) in dry diethyl ether (100 cm^3) was added with stirring under nitrogen at room temp. to butyllithium (2.2 mol dm^{-3} in cyclohexane; 33 cm^3). The reaction mixture was stirred and heated under reflux for an additional 10 min, after which it was cooled to −70 °C and added dropwise to a solution of tosyl azide (0.07 mol) in dry diethyl 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 (0.07 mol) in water (200 cm^3) and after 10 min with a solution of ammonium chloride (0.07 mol) in water (100 cm^3). The yellow pentane layer, which had formed, 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 azide **1** (0.022 mol, 33%) as an unstable oil; ν_{max}/cm^{-1} 3100, 3080, 2100 ($-N_3$), 1500, 1220 and 670; δ_H(300 MHz; $CDCl_3$) 7.57 (1 H, dd, J 1.4 and 5.9, 5-H), 6.99 (1 H, dd, J 3.9 and 5.9, 4-H) and 6.66 (1 H, dd, J 1.4 and 3.9, 3-H); δ_C(300 MHz; $CDCl_3$) 146.80 (C-2, s), 128.70 (C-4, J 165.5), 124.86 (C-5, J 190.2) and 117.60 (C-3, J 165.8); m/z 173 (M$^+$, 22.5%), 145 (69.5%, M − N_2), 118 (68.0), 93 (30.5), 84 (33.5), 64 (100.0) and 39 (56.5) (Found: M$^+$, 172.9490. $C_4H_3N_3Se$ requires M, 172.9492).

3-*Azidoselenophene* **2**.—A solution of 3-bromoselenophene (0.044 mol) in dry diethyl ether (80 cm^3) was added with stirring under nitrogen at −70 °C to butyllithium (2.2 mol dm^{-3} in cyclohexane; 20 cm^3). The reaction mixture was stirred for an additional 10 min, after which it was added dropwise to a solution of tosyl azide (0.044 mol) in dry diethyl 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 filtered off rapidly and suspended in pentane. The suspension was treated at 0 °C with a solution of tetrasodium pyrophosphate (0.07 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 azide **2** (0.023 mol, 52%) as an oil; ν_{max}/cm^{-1} 2980, 2100 ($-N_3$), 1530, 1370, 1200 and 750; δ_H(300 MHz; $CDCl_3$) 7.93 (1 5-H, dd, J 2.7 and 5.6), 7.33 (1 2-H, dd, J 1.5 and 2.7) and 7.07 (1 4-H, dd, J 1.5 and 5.6); δ_C(300 MHz; $CDCl_3$) 138.81 (C-3, s), 131.19 (C-5, J 189.2), 123.88 (C-4, J 167.7) and 113.10 (C-2, J 186.2); m/z 173 (M$^+$, 41.3%), 145 (92.5, M − N_2), 119 (100), 93 (75.0), 80 (18.5), 64 (7.2), 52 (14.6) and 39 (9.5) (Found: M$^+$, 172.9493).

Reactions of Azides **1** *and* **2** *with (Trimethylsilyl)acetylene and Trimethyl(vinyl)silane (TMVS) at* 25 °C.—*General procedure.* A solution of the azidoselenophene (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 consisted of almost pure triazoles **1a**, **2a** and aziridines **1b**, **2b** which were characterized. Approximate reaction times at 25 °C and product yields for the reactions of azides **1** and **2** with silylated alkyne (or alkene) are reported in parentheses. The following new triazoles **1a**, **2a** and aziridines **1b**, **2b** were obtained.

1-(*Selenophen*-2-*yl*)-4-(*trimethylsilyl*)-1,2,3-*triazole* **1a** (4 days, 83%), m.p. 42–43 °C; ν_{max}/cm^{-1} 3120, 2960, 1250, 845 ($SiMe_3$), 760 and 680; δ_H(200 MHz; $CDCl_3$) 7.87 (1 H, s, 5'-H), 7.81 (1 H, dd, *J* 1.5 and 5.9, 5-H), 7.29 (1 H, dd, *J* 1.3 and 4.0, 3-H), 7.21 (1 H, dd, *J* 4.0 and 5.9, 4-H) and 0.36 (9 H, s); δ_C(200 MHz; $CDCl_3$) 148.12 (C-4', s), 130.87 (C-2, s), 128.65 (C-5, d, *J* 193.6), 128.57 (C-4, d, *J* 176.3), 127.79 (C-5', d, *J* 193.0), 119.20 (C-3, d, *J* 167.2) and −0.70 (q, *J* 119.4); *m*/*z* 243 (18.6%, $M - N_2$), 229 (15.2), 228 (100), 177 (8.1), 138 (10.2), 118 (10.1), 93 (10.3), 83 (90.2), 80 (5.8), 73 (98.5), 45 (44.9) and 43 (70.7) (Found: C, 39.95; H, 4.8; N, 15.5. $C_9H_{13}N_3SeSi$ requires C, 40.0; H, 4.85; N, 15.55%).

1-(*Selenophen*-3-*yl*)-4-(*trimethylsilyl*)-1,2,3-*triazole* **2a** (16 days, 87%), m.p. 72–73 °C; ν_{max}/cm^{-1} 3120–3100, 2960, 1260 and 855 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 8.14 (1 H, dd, *J* 1.6 and 2.8, 2-H), 8.11 (1 H, dd, *J* 2.8 and 5.5, 5-H), 7.86 (1 H, s, 5'-H), 7.78 (1 H, dd, *J* 1.6 and 5.5, 4-H) and 0.36 (9 H, s); δ_C(200 MHz; $CDCl_3$) 143.38 (C-4', s), 138.07 (C-3, s), 132.37 (C-5, d, *J* 190.7), 127.98 (C-5', d, *J* 191.7), 124.62 (C-4, d, *J* 173.0), 119.18 (C-2, d, *J* 188.7) and −0.67 (q, *J* 119.4), *m*/*z* 271 (M^+, 0.9%), 243 (14.8, $M - N_2$), 228 (100), 224 (17.0), 200 (7.3), 186 (4.1), 177 (4.1), 138 (6.2), 123 (8.1), 93 (6.3), 84 (26.8), 73 (36.6), 45 (22.4) and 43 (30.2) (Found: C, 40.0; H, 4.85; N, 15.5%).

1-(*Selenophen*-2-*yl*)-2-(*trimethylsilyl*)*aziridine* **1b** (3 days, 77%), as an oil; ν_{max}/cm^{-1} 2960, 1250, 850 ($SiMe_3$) and 750; δ_H(200 MHz; $CDCl_3$) 7.35 (1 H, dd, *J* 1.3 and 5.9, 5-H), 6.92 (1 H, dd, *J* 3.8 and 5.9, 4-H), 6.51 (1 H, dd, *J* 1.3 and 3.8, 3-H), 2.30 (1 H, dd, *J* 1.4 and 5.2), 2.21 (1 H, dd, *J* 1.4 and 7.9), 1.41 (1 H, dd, *J* 5.2 and 7.9) and 0.12 (9 H, s); *m*/*z* 245 (M^+, 4.0%), 230 (0.8, $M - CH_3$), 177 (0.4), 145 (3.5), 118 (2.4), 100 (10.0), 85 (12.2), 73 (100), 59 (24.7) and 45 (35.4) (Found: M^+, 245.0139. $C_9H_{15}NSeSi$ requires *M*, 245.0139).

1-(*Selenophen*-3-*yl*)-2-(*trimethylsilyl*)*aziridine* **2b** (11 days, 82%), as an oil; ν_{max}/cm^{-1} 2965, 1260, 850 ($SiMe_3$) and 760; δ_H(200 MHz; $CDCl_3$) 7.79 (1 H, dd, *J* 2.6 and 5.6, 5-H), 7.18 (1 H, dd, *J* 1.5 and 5.6, 4-H), 6.93 (1 H, dd, *J* 1.5 and 2.6, 3-H), 2.12 (1 H, dd, *J* 1.3 and 5.0), 2.07 (1 H, dd, *J* 1.3 and 7.7), 1.26 (1 H, dd, *J* 5.0 and 7.7) and 0.11 (9 H, s); *m*/*z* 245 (M^+, 9.9%), 230 (5.2, $M - CH_3$), 189 (7.8), 146 (6.2), 131 (2.2), 107 (5.2), 93 (1.4), 73 (100), 59 (8.9) and 45 (12.5) (Found: M^+, 245.0139).

Rates of Decomposition of Azides **1** *and* **2**.—A solution of the azide (0.05 mol dm^{-3}) in *p*-chlorotoluene (*ca.* 10 cm^3) was allowed to react in a thermostatic bath at the appropriate range of temperature (32.0–75.0 °C for azide **1** or 99.0–139.5 °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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