Reactivity of Aryl and Heteroaryl Azides with Vinylsilane and Alkynylsilane. Formation of *C*-Silylated 1,2,3-Triazolines and 1,2,3-Triazoles

Paolo Zanirato
Dipartimento di Chimica Organica 'A. Mangini', Università di Bologna, Viale Risorgimento n° 4, 40136 Bologna, Italy

The reactions of the silylated dipolarophiles trimethyl(vinyl)silane, trimethoxy(vinyl)silane and (trimethylsilyl)acetylene, with some *para*-substituted phenyl azides, 2-azidobenzo[*b*]thiophene (2-BTA) and 3-azidobenzo[*b*]thiophene (3-BTA) have been examined. At room temperature these reactions give the respective 1-substituted 4-silylated-1,2,3-triazoline. However, only the reactions of 4-nitrophenyl and 4-cyanophenyl azide occur smoothly, furnishing triazolines in high yields; similar reactions with phenyl, 4-tolyl, 4-methoxyphenyl and 4-chlorophenyl azide are slower, affording mixtures of a 3-(*N*-arylamino)methyl-3,5-bis(trimethylsilyl)-1-pyrazoline, arising from the primary triazoline adduct through ring-opening to diazo compounds **2**, and the corresponding 1-aryl-2-(trimethylsilyl)aziridine, resulting from nitrogen extrusion from the same elusive triazoline. On the other hand reactions of 2-BTA and 3-BTA involve rapid extrusion of nitrogen to afford exclusively the corresponding 1-(benzo[*b*]thienyl)-2-silylated aziridine.

Results suggest that all these azides generally undergo 1,3-dipolar cycloadditions to terminally silylated alkenes to give triazoline adducts with the same geometrical orientation and whose thermal behaviour was found to be strongly dependent on the activating or deactivating effects exerted by N-1 substituents.

Suitable support for electronic and steric factors acting in the same direction in the orientations of the former cyclo-A_NA_E adducts has been provided by the observation that the same aryl azides, 2-BTA and 3-BTA exhibit analogous 1,3-dipolar cycloadditions with (trimethylsilyl)acetylene from which stable 1-aryl(or heteroaryl)-4-trimethylsilyl-1,2,3-triazoles are obtained in quantitative yields.

Vinylsilanes have been considered, for the most part, as reagents for electrophilic substitutions.[1] Whilst addition of 1,3-dipoles to double or triple C–C bonds to give five-membered heterocyclic compounds is well-known,[2] examples in which silylated alkenes are employed as a dipolarophilic component appear to be limited to reactions with dipolar diazoalkanes[3,*] and nitrones.[4] To our knowledge examples of related reactions with dipolar aryl azides are limited to reactions between phenyl azide[5] and 4-bromophenyl azide[6] with trimethyl(vinyl)silane (TMVS) or trimethylsilyl styrene, respectively, which give mainly aziridines in modest or moderate yield. Isolation of *C*-silylated triazolines arising from 1,3-dipolar cycloaddition of azides to a dipolarophilic vinylsilane, or from other routes, has not been reported.

Triazolines are generally unstable both under chemical and thermal conditions, undergoing different types of cycloreversion.[7] Considerable attention has been focussed upon N–N bond cleavage as a key step in a process leading to isomerization, to give the diazoalkanes **2**. There is evidence also of another competing decomposition pathway in the thermal fragmentation of triazolines which involves loss of nitrogen to give aziridines.[7b] In some cases this may predominate.

Recently we have found that both 2-azidobenzo[*b*]thiophene (2-BTA) and 3-azidobenzo[*b*]thiophene (3-BTA) react with neat TMVS, at 25 °C within 5 or 15 days, respectively, through quantitative conversion into the corresponding 1-benzo[*b*]-thienyl-2-(trimethylsilyl)aziridine, presumably arising from the unstable initial triazoline adduct formed by heteroaryl azide–alkene cycloaddition,[8] *via* sequential ring-cleavage, extrusion of molecular nitrogen and ring-closure. In this investigation, evidence for the formation of the elusive initial triazoline adducts was gained by carrying out reactions in neat methyl acrylate or diethyl fumarate at a lower temperature (−20 or 5 °C) from which significant amounts of diazo products were recovered. However, evidence for the intervention of the intermediate triazoline adducts in the case of neat TMVS, even though reactions were carried out at −20 °C, was lacking. From these observations, it is concluded that when terminal alkenes like TMVS add to 2-BTA, 3-BTA or phenyl azide, for which direct and exclusive formation of aziridines is observed, the orientation of the former elusive adducts is not really certain. Furthermore, the very similar reactivity observed by reactions of 2-BTA and 3-BTA towards both TMVS and a terminally electron-poor alkene, such as methyl acrylate, appears conflicting with the frontier molecule orbital (FMO) theory prediction.†

For these reasons we wish to report additional experimental evidence on the reactivity (and the regiochemistry of the adducts) of the terminally silylated alkenes and alkynes, TMVS, trimethoxy(vinyl)silane (TMOVS) and (trimethylsilyl)acetylene, with organic azides with different stabilities and electronic character.

Results and Discussion

The reactions of phenyl azides with electron-withdrawing substituents, *e.g.* 4-nitrophenyl **6** and 4-cyanophenyl azide **7**, with neat TMVS (0.25 mol dm^{-3}) proceeded smoothly at 25 °C to

* The observed regiochemistry of the cycloadducts arising from bulky substituted diazomethanes and vinyl or alkynyl silanes were found to be reversed.

† Simple frontier orbital model (FMO), applied by Sustmann[9] with the contributions of Houk,[10] accounts for the reactivity rates of dipolarophilic alkenes in 1,3-dipolar cycloadditions and for the regioselectivity when both the reactants are unsymmetrical. A similar treatment has been considered for additions of organic azides to alkynes, which generally afford stable 1,2,3-triazoles.[11,18a]

Table 1 Product yields (%)[a] for the thermal reaction of aryl azides (*p*-X-$C_6H_4N_3$), 2-BTA and 3-BTA in neat TMVS at 25 °C

Entry	Aryl azides	Time[b] (*t*/d)	Yield (%) Aziridine	Triazoline	Pyrazoline	Other
1	*p*-Nitrophenyl	9		**1a** (95)		
2	*p*-Nitrophenyl[c]	5 h	**4e** (20)	**1a** (6)[d]		(40)[e]
3	*p*-Cyanophenyl	10		**1b** (87)		
4	Phenyl	40	**4a** (5)		**3a** (75)	
5	*p*-Methylphenyl	52	**4b** (9)		**3b** (70)	
6	*p*-Methylphenyl[c]	25 h	**4b** (72)		**3b** (15)	
7	*p*-Methoxyphenyl	65	**4c** (10)		**3c** (69)	
8	*p*-Methoxyphenyl[c]	30 h	**4c** (80)		**3c** (6)	
9	*p*-Chlorophenyl	22	**4d** (44)		**3d** (40)	
10	*p*-Chlorophenyl[c]	20 h	**4d** (63)		**3d** (15)	
11	2-BTA	5	**4f** (93)			
12	3-BTA	15	**4g** (95)			

[a] Isolated yields based on starting aryl azides after chromatographic separation. [b] Approximate reaction time corresponding to complete consumption of starting aryl azides. [c] Reaction carried out at 70 °C. [d] Observed by GC MS analysis. [e] *p*-Nitroaniline.

Table 2 NMR spectroscopic data for 4-silylated-1,2,3-triazolines **1a**, **1b**, **1c** and **1d**[a]

Triazoline	δ_H[b] 4-H	5-H	5′-H	δ_C[b] 4-C	5-C	J/Hz[c] J_{gem}	J_{cis}	J_{trans}	J/Hz[d] $J_{C4,H}$	$J_{C5,H}$
1a	4.39	3.70	3.42	73.65	43.38	8.3	13.2	8.5	136	144
1b	4.35	3.66	3.40	73.18	43.36	8.3	13.2	8.6	136	144
1c[e]	4.19	3.54	3.30			8.1	13.5	9.1		
1d	4.34	3.70	3.56	68.62	42.92	8.3	13.6	10.3	135	147

[a] Solutions in $CDCl_3$. [b] $CHCl_3$ as internal standard (δ 7.27). [c] ±0.1 Hz. [d] ±1 Hz. [e] Not isolated.

afford, within 9–10 days (TLC), precipitates of the corresponding solid 1,3-dipolar cycloadducts **1a** and **1b**. These were filtered off and characterized as 1-(4-nitrophenyl)-4-trimethylsilyl-1,2,3-triazoline (95%) **1a** or 1-(4-cyanophenyl)-4-trimethylsilyl-1,2,3-triazoline (87%) **1b**, respectively (Table 1, entries 1 and 3).

The structures of these compounds were assigned on the basis of elemental analyses, IR and NMR spectroscopy, and mass spectral data, taking particular care with the assigned regiochemistry of the resulting triazoline rings which were supported by ^1H and ^{13}C NMR spectra (Table 2).

Conversion of azides **6** and **7** were found to be completely regiospecific by NMR spectroscopic analyses, with the resulting spectral parameters fully consistent with the proposed C-4 silylated triazoline structures. There was no evidence for the presence of the other possible isomers. In the ^1H NMR spectra all the protons of the 1,2,3-triazoline ring are magnetically non-equivalent, with separate chemical shifts and large coupling constants (J 8.5–8.6 and J 13.2), similar to those reported for related C-4 substituted cycloadducts arising from interaction of methyl acrylate with phenyl azide.[12] Moreover, the C-4 proton exhibited a deshielded chemical shift value attributable to the acidifying effects of the adjacent azo-function and the α-trimethylsilyl moiety.[13]

^1H NMR spectroscopic data is interpreted in terms of a quasi-planar conformation of the five-membered triazolines **1a** and **1b**, with the 4-H, 5-H and 5′-H lying outside the molecular plane; with a corresponding 5-H/5′-H geminal proton angle of *ca.* 110° and 4-H/5-H or 4-H/5′-H dihedral angles of *ca.* 110° and *ca.* 0°, respectively. Thus, the observed large values for the two vicinal *cis*- and *trans*-coupling constants ($J_{4,5}$ and $J_{4,5'}$), also calculated according to the Karplus equation, confirm the quasi-planarity of the triazoline ring and is presumably due to the effect of restrained *N*-1 lone pairs, as suggested by SCF-quantum mechanical computation on 1-cyano-1,2,3-triazoline.*

In addition, ^{13}C NMR off-resonance proton-undecoupled spectra revealed a characteristic doublet (J 136) at δ 73.65 for **1a** and 73.18 for **1b**, assignable to C-4, and a triplet (J 144) at δ 43.38 for **1a** and 43.36 for **1b**, assignable to C-5 (Table 2). On the other hand, our attempts to obtain isolable triazolines by similar reactions using phenyl azide **8**, or its derivatives bearing electron-donating *p*-substituents, *i.e.* methyl and methoxy, failed. In these cases the reactions take longer, leading to 1-pyrazolines **3a–c** as the major products, together with the minor products 1-aryl-2-(trimethylsilyl)aziridines **4a–c**. Thus, in neat TMVS (0.5 mol dm^{-3}), reaction of phenyl azide occurred at 25 °C within 40 days to lead, after column chromatography, to the separation of a single regioisomeric pyrazoline, 3-(*N*-anilinomethyl)-3,5-trimethylsilyl-1-pyrazoline **3a** (75%) in addition to minor amounts of the aziridine **4a** (5%) (Table 1, entry 4).

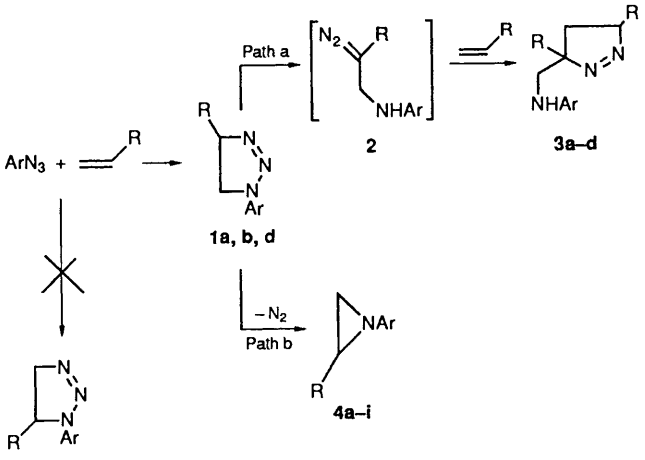
Longer reaction times were required for reactions between 4-tolyl **9** (52 days) and 4-methoxyphenyl **10** azide (65 days) and TMVS (0.5 mol dm^{-3}) which afforded the 3,5-bis(trimethylsilyl)-1-pyrazolines **3b** and **3c** as the major products (70 and 69%, respectively), together with the corresponding aziridine **4b** or **4c** (9 and 10%, respectively) (Table 1, entries 5 and 7). The reaction of 4-chlorophenyl azide **11** in neat TMVS (0.5 mol dm^{-3}) is virtually complete after 20 days. Almost equal amounts of aziridine **4d** (44%) and pyrazoline **3d** (40%) were obtained after chromatographic separation of the reaction mixture (Table 1, entry 9). The NMR spectrum of an aliquot part of the reaction mixture, before chromatography, revealed in addition to the peaks of the pyrazoline **3d** and a small amount of the aziridine **4d**, the presence of an ABX system (δ 4.19, J 13.5 and 9.1 Hz, δ 3.54, J 13.5 and 8.1 Hz, and δ 3.30, J 9.1 and 8.1 Hz) consistent with the presence of triazoline **1c**. The ratio **3d**:**4d**:**1c** was 5:1:5 respectively.

Structural assignments of all new pyrazolines **3a–d** were made on the basis of IR, ^1H and ^{13}C NMR spectroscopy, and exact

* SCF-qunatum mechanical computations of related simple 1,2,3-triazolines bearing cyano or hydroxy groups at N-1 were carried out.[14]

mass spectral data. In particular, confirmation of the structures of the pyrazoline rings came from the observed values of chemical shifts and coupling constants for geminal 4A-H/4E-H and vicinal 5-H protons belonging to the ring, together with the geminal Hα methylene protons which, in some cases, show clear diastereotopic coupling with the NH proton (Table 3). Evidence for the correct structure of the adduct was also obtained by ^{13}C NMR spectroscopic examination (Table 3).[15] For example, ^{13}C NMR spectroscopic chemical shifts of the methylpyrazoline part of compound **3b** lie at δ 92.72 (singlet) for C-3, 84.66 (doublet) for C-5, 49.29 (triplet) for C-4 and 25.07 (triplet) for the methylenic carbon. The internal consistency of the spectral data for **3a–d** with the proposed structures indicates that the pyrazolines are generated, within the limits of the NMR spectroscopic analyses, with the same regiochemistry normally exhibited by bulky disubstituted diazomethanes **2a–d**.

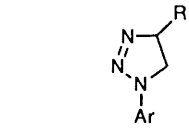
In fact, generation of pyrazolines **3a–d** is in agreement with their formation from the ring-opened diazo compounds[7] **2** (Scheme 1; **2a–d**) isomers of the elusive triazolines **1**, which are



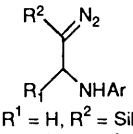
Scheme 1 R = $SiMe_3$, $Si(OMe)_3$; Ar = *p*-X-C_6H_4, 2- or 3-benzo[*b*]-thienyl

unable to survive the reaction time. Their subsequent trapping with the excess of TMVS follows the process of a 1,3-dipolar cycloaddition of a diazomethane to a vinylsilane (Scheme 1; path a). The regioselectivity exhibited by these diazo-cycloadditions* is reflected in the structures of the pyrazolines **3a–d**, which arise from the appropriate trimethylsilyldiazoalkane **2a–d** and, hence, takes also into account the structures of the initial triazoline adduct, identical with triazoline adducts **1a** and **1b** obtained by reactions of azides **6** and **7** with TMVS. Formation of the aziridines **4a–d** can, in principle, be ascribed to the same undetected triazolines **1**, or the other possible isomer with the trimethylsilyl group located at C-5, undergoing thermal ring-cleavage with loss of molecular nitrogen and subsequent ring-closure of the fragmentation product (Scheme 1; path b).

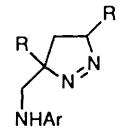
The possibility that the aziridines **4** might come exclusively (or in part) from triazoline isomers with the trimethylsilyl moiety located at C-5 seems improbable in view of their preferential formation in reactions carried out at 70 °C. In fact, thermal decompositions of 4-methylphenyl azide **9**, in TMVS, in a sealed tube at about 70 °C for *ca.* 25 h (until TLC showed the disappearance of the starting azide) led, after column chromatography, to the isolation of 1-(4-tolyl)-2-trimethylsilylaziridine **4b** (*ca.* 72%) and the pyrazoline adduct **3b** (*ca.* 15%) (Table 1,



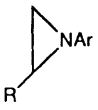
1a; Ar = 4-NO_2-C_6H_4, R = $SiMe_3$
1b; Ar = 4-CN-C_6H_4, R = $SiMe_3$
1c; Ar = 4-Cl-C_6H_4, R = $SiMe_3$
1d; Ar = 4-NO_2-C_6H_4, R = $Si(OMe)_3$



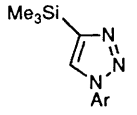
2a; Ar = Ph, R^1 = H, R^2 = $SiMe_3$
2b; Ar = 4-tolyl, R^1 = H, R^2 = $SiMe_3$
2c; Ar = 4-MeO-C_6H_4, R^1 = H, R^2 = $SiMe_3$
2d; Ar = 4-Cl-C_6H_4, R^1 = H, R^2 = $SiMe_3$



3a; Ar = Ph, R = $SiMe_3$
3b; Ar = 4-tolyl, R = $SiMe_3$
3c; Ar = 4-MeO-C_6H_4, R = $SiMe_3$
3d; Ar = 4-Cl-C_6H_4, R = $SiMe_3$
3e; Ar = 4-tolyl, R = $Si(OMe)_3$



4a; Ar = phenyl, R = $SiMe_3$
4b; Ar = 4-tolyl, R = $SiMe_3$
4c; Ar = 4-MeO-C_6H_4, R = $SiMe_3$
4d; Ar = 4-Cl-C_6H_4, R = $SiMe_3$
4e; Ar = 4-NO_2-C_6H_4, R = $SiMe_3$
4f; Ar = 2-benzo[*b*]thienyl, R = $SiMe_3$
4g; Ar = 3-benzo[*b*]thienyl, R = $SiMe_3$
4h; Ar = 2-benzo[*b*]thienyl, R = $Si(OMe)_3$
4i; Ar = 3-benzo[*b*]thienyl, R = $Si(OMe)_3$
4j; Ar = 4-tolyl, R = $Si(OMe)_3$



5a; Ar = 4-NO_2-C_6H_4
5b; Ar = 4-CN-C_6H_4
5c; Ar = Ph
5d; Ar = 4-tolyl
5e; Ar = 4-MeO-C_6H_4
5f; Ar = 4-Cl-C_6H_4
5g; Ar = 2-benzo[*b*]thienyl
5h; Ar = 3-benzo[*b*]thienyl

entry 6). A similar increase in yield of aziridine at the expense of the pyrazoline (and triazoline) was observed with reactions of 4-methoxyphenyl azide **10** and 4-chlorophenyl azide **11** with TMVS at 70 °C, which occurred within 30 and 20 h, respectively. In these cases the aziridines **4c** (*ca.* 80%) and **4d** (*ca.* 63%), and the pyrazoline adducts **3c** (*ca.* 6%) and **3d** (*ca.* 15%), were isolated after analogous work-up of the resulting reaction mixture (Table 1, entries 8 and 10). On the other hand, the same reaction of 4-nitrophenyl azide **6** in neat TMVS at 70 °C occurred within 3 h leading, after chromatographic separation, to 4-nitroaniline as a major product (*ca.* 40%) together with lesser amounts of 1-(4-nitrophenyl)-2-trimethylsilylaziridine **4e** (*ca.* 20%) (Table 1, entry 2). Analysis by GS–MS of the mixture, before chromatographic separation, confirmed this composition and indicated trace amounts of triazoline **1a** (*ca.* 6%) previously undetected due to the destructive work-up. We were concerned by the failure to detect a pyrazoline derivative in the reaction involving 4-nitrophenyl azide or by decomposition of the triazoline **1a** in TMVS. Therefore, a solution of triazoline **1a** in TMVS–$CHCl_3$ (v/v 2:1) (0.25 mol dm^{-3}) was allowed to stand at room temperature in the dark for more than two months after which an aliquot of the reaction mixture was analysed by GS–MS. No pyrazoline was detected in this case (see Experimental

* A theoretical study of the transition state in normal and inverse diazoalkane 1,3-cycloadditions affected by different substituents has been carried out.[16]

Table 3 Some NMR spectroscopic data for 3-(*N*-arylaminomethyl)-4,5-dihydro-3,5-bis(trimethylsilyl)-1H-pyrazoles **3a–d**[a]

	δ_H[b]					J/Hz[c]			δ_C	
Pyrazoline	4-H	4′-H	5-H	NH	$CH_2(J_{gem})$	J_{gem}	J_{cis}	J_{trans}	4-C	5-C
3a	1.44	1.83	3.94	3.52	4.02, 3.35 (12.0)	12.2	10.7	10.6	48.22	84.72
3b	1.49	1.86	3.98	3.46	4.04, 3.34[d]	12.4	10.8	10.6	48.70	84.70
3c	1.46	1.80	3.92	3.27	3.98, 3.23[d]	12.1	10.9	10.6	49.29	84.66
3d	1.43	1.86	3.97	3.60	4.05, 3.31 (12.2)	12.3	10.8	10.6	48.14	84.56

[a] Solutions in $CDCl_3$. [b] $CHCl_3$ as internal standard (δ 7.27). [c] $\pm$0.1 Hz. [d] Approximate δ; peaks partially overlapped by NH absorption.

section), however. The occurrence of the pyrazolines, observed particularly in reactions of azides **8–11** with TMVS, which proceed *via* triazolines **1** bearing electron-donating phenyl substituents at N-1, suggests participation of the N-1 lone-pairs on the base-catalysed prototropic rearrangement and a concomitant stabilization of a negative charge on C-4 by the trimethylsilyl group (Scheme 1; path a). A parallel isomerization to diazo compounds of triazolines bearing electron-withdrawing groups located at C-4 along with a free NH proton are well documented but no evidence for the intermediacy of the N-1 lone-pairs of C-silylated compounds on the isomerization were presented in this report.[17]

Thermal reactions of phenyl azides carrying electron-donating substituents with TMVS at 25 °C or 70 °C provided evidence that formation of aziridine appears to be a low energy homo- or hetero-lytic process, competitive with the formation of pyrazoline, presumably favoured by the weakness of the N(3)–C(4) bond in the initial triazoline adducts. This evidence is consistent with our previously reported conclusion drawn from similar reactions of 2-BTA and 3-BTA in neat alkenes with TMVS.[8] However, in these cases, direct and exclusive occurrence of aziridines eliminated all chances of making any deduction about the regiochemistry of the former triazoline adduct.

For phenyl azides substituted by electron-withdrawing groups the regioselectivity normally exhibited by reactions of 4-nitrophenyl azide **6** to terminal alkenes is high, and reflects the orientation of addition in agreement with mechanistic considerations for 1,3-dipolar cycloadditions.[18] Being vinylsilanes, which are weakly reactive π-nucleophiles with negative ionization potentials of 9.8 (comparable to that of terminal vinylalkanes),[19] FMO calculations would predict the formation of triazolines with the opposite regio orientation to those obtained in this work. Steric factors appear, at first glance, responsible for the triazolines isolated.

Since the regioselectivity of 1,3-cycloaddition processes might be dependent on the type of silane employed as dipolarophile, we have repeated the reaction of 4-nitrophenyl azide **6**, from which triazoline has been solely isolated, using TMOVS.* Again, a similar reaction of 4-nitrophenyl azide, in neat TMOVS proceeds smoothly at 25 °C affording, within 9 days (TLC), a solid precipitate which was identified as 1-(4-nitrophenyl)-4-(trimethoxysilyl)-1,2,3-triazoline **1d** (95%). The structure was assigned on the basis of its ^1H and ^{13}C NMR spectra. The C-4 (68.62 ppm) and C-5 (42.92 ppm) carbon atoms were assigned on the basis of the observed ^{13}C NMR chemical shifts; moreover, these assignments were confirmed by off-resonance undecoupled spectra which displayed a doublet, J 135 Hz, and a triplet, J 147 Hz, respectively, for C-4 and C-5 of the triazoline rings. In the ^1H NMR spectra of **1d** the triazoline ring protons appeared as an ABX system consistent with that previously observed for compounds **1a** and **1b** (Table 2). To our knowledge, compounds **1a**, **1b** and **1d** represent the first examples of isolated triazoline rings bearing a C-4 silyl moiety.

In this work we additionally explored the reactions of 2-BTA and 3-BTA with neat TMOVS (0.5 mol dm^{-3}) at 25 °C. The observed reaction times appear comparable with those observed for the reactions of these compounds in neat TMVS, being completed within 8 and 18 days, respectively. Furthermore, from these reactions, likewise our previous report with TMVS (Table 1, entries 11 and 12), the 1-benzo[*b*]thienyl-2-trimethoxysilyl aziridines **4h** and **4i** were isolated in quantitative yield.

Comparable results with the reaction carried out in TMVS were also obtained by reaction of 4-tolyl azide **9** in TMOVS which occurs at 25 °C in approximately 53 days. The ^1H NMR spectrum of the reaction mixture, after elimination of the excess of solvent, showed peaks attributable to 3-(*N*-toluidinomethyl)-3,5-bis(trimethoxysilyl)-1-pyrazoline **3e** in addition to peaks produced by 1-(4-tolyl)-2-(trimethoxysilyl) aziridine **4j** (ratio 8:1) (*cf.* Table 1, entry 5).

In spite of the fact that the HOMO/LUMO coefficients of vinylsiloxanes have been found to be lower and reversed with respect to the coefficients of vinylsilanes,* our general findings prove that cycloadditions of the selected azides **6**, **9**, 2-BTA and 3-BTA to both alkenylsilanes, TMVS and TMOVS, proceed at approximately the same rate to give analogous products. In particular, the reactions of 4-nitrophenyl azide **6** occur with exclusive formation of the regioisomeric adducts **1a** and **1d**, in which the terminal nitrogen of the azido function bonds to the α-carbon of the α,β-unsaturated system. The reversal in regiochemistry exhibited by the triazolines **1a** and **1d** is consistent with the effect of steric hindrance, due to the presence of bulky phenyl and trimethylsilyl groups, on the 1,3-cycloaddition process. However, the exclusive regioselectivity, supported by the ease of additions and the high yields of triazolines, could also be interpreted in terms of the well known d/π interactions exerted by silyl atoms on the silylalkene π-electron systems.[19,21] The resulting 'push-pull' electronic polarization of the π-system direct electrophiles, in our case the terminal nitrogen of the azido-moiety, to the α-carbon of the α,β-unsaturated system. This explanation produces the same result as the steric argument. This process should be more important with deactivated azide moiety with more pronounced electrophilic character at the terminal nitrogen.

Shortly after our preliminary report,[22] a study involving some related sterically controlled cycloadditions of diazoalkanes to trimethylsilylalkynes was published.[3b] Azide addition to alkynes is the most important synthesis of 1*H*-1,2,3-triazoles.[11] It is known that phenyl azide reacts with unsymmetrical alkynes and the corresponding alkenes with similar rates but, whereas aryl azides with alkene generally yields only

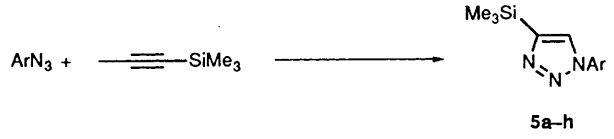
* The HOMO/LUMO coefficients of siloxane have been found to be lower and reversed with respect to the coefficients of vinylsilane and the interaction between a nucleophilic HOMO centre with the dipolarophile π*-LUMO on C-2 becomes more favourable.[20]

Table 4 Relative yields (%),[a] m.p.s[b] and significant NMR spectroscopic data[c] for 1-aryl-4-trimethylsilyltriazoles obtained by reaction of azides **6–11**, 2-BTA and 3-BTA in neat (trimethylsilyl)acetylene at 25 °C

Entry	Aryl azides	t/d[d]	Triazole	M.p. T/°C	δ C-4	δ C-5 (J_{CH})[e]	δ H-5
1	*p*-Nitrophenyl	20	**5a** (95)	182–184	147.65	127.33	8.08
2	*p*-Cyanophenyl	26	**5b** (96)	124–125	148.85	127.49	8.07
3	Phenyl	35	**5c** (96)	94–96	147.75	127.73 (193)	7.93
4	*p*-Methylphenyl	40	**5d** (95)	104–105	147.63	127.64	7.89
5	*p*-Methoxyphenyl	55	**5e** (95)	68–70	147.36	127.68 (192)	7.74
6	*p*-Chlorophenyl	25	**5f** (95)	130–131	148.19	127.57	7.97
7	2-BTA	9	**5g** (93)	148–150	148.13	128.40 (194)	7.87
8	3-BTA	28	**5h** (95)	88–90	147.04	130.10 (193)	7.96

[a] Isolated yields based on starting aryl azides after filtration of the reaction mixture. [b] All m.p.s are uncorrected. [c] Obtained in $CDCl_3$, $CHCl_3$ internal standard. [d] Approximate reaction time corresponding to complete consumption of starting aryl azide. [e] ±1 Hz.

one regioisomer the alkyne often yields both.* The few examples reported, of the addition of azides to various alkynylsilanes, are known to give triazoles with the trimethylsilyl moiety located at C-4.[23] However, a limited number of *C*-silyl-substituted triazoles are known and the chemistry of these compounds is virtually unexplored. Hence, we carried out additional experiments with the aryl azides **6–11**, 2-BTA and 3-BTA in neat (trimethylsilyl)acetylene in order to elucidate the factors controlling these 1,3-cycloaddition processes with the aim of providing some information about their reactivity and regioselectivity. Aryl azides **6** and **7** (0.25 mol dm^{-3}), **8–11**, 2-BTA and 3-BTA (0.5 mol dm^{-3}) react in solution with (trimethylsilyl)acetylene, at room temperature with different approximate reaction times, to give the corresponding C-4 silylated 1,2,3-triazoles **5a–h** in quantitative yield (Scheme 2) (Table 4, entries 1–8).



5a–h

Scheme 2 Ar = *p*-X-C_6H_4, 2- or 3-benzo[*b*]thienyl

Structural assignments for all the new triazoles **5a–h** were confirmed by elemental analysis or by exact MS, IR and ^1H NMR spectroscopy; moreover, ^{13}C NMR chemical shifts assignments were obtained by recording the off resonance proton-undecoupled spectra, which displayed a doublet at δ 127–128 (J 192–194 Hz) assignable to C-5, and a singlet at δ 147–148, assignable to C-4 [11b] (Table 4, entries 1–8).

As might be expected, according to the lower nucleophilic nature of an alkyne with respect to the corresponding alkene,[18] reactions of aryl azides **6** and **7** carrying electron-withdrawing groups, 2-BTA and 3-BTA, with alkynes were slower by half than those with the alkenes. However, the times required for cycloadditions of the activated aryl azides **9** and **10**, on the contrary, are slightly shorter (*ca.* 0.8 ratio).

Our findings, with the 1,3-dipolar additions of aryl azides to trimethyl (or trimethoxy)silylalkene, indicate that the approximate rate of addition is markedly increased by an electron-withdrawing substituent in the azide, as might be expected for concerted reactions initiated by the junction of the terminal azido-nitrogen to the nuclephilic α-carbon of the terminal olefin. In agreement with this point of view, the factors affecting the comparable reactivity of 2-BTA, 3-BTA and electron-withdrawing *p*-substituted phenyl azides **6** and **7** suggest that their reactivity towards vinylsilanes might be favoured by their resemblance to developing charges in the transition states. To throw light on this conclusion, we have carried out polarographic reductions of some azido derivatives and compared their electronic affinities with their $E_{1/2}$ potentials (Volts *vs.* Hg Pool). Under a controlled set of conditions the half-wave potentials for 2-BTA, 3-BTA, 4-nitrophenyl azide and 4-methoxyphenyl azide were found to be $E_{1/2} = -0.79$, -0.75, -0.84 and -0.90, respectively.† Therefore, results obtained with these outer-sphere redox reactions provide an opportunity for comparing the resemblance in reactivity between the two heteroaryl azides (2-BTA and 3-BTA) and aryl azides substitutes by electron-withdrawing groups.

Experimental

Materials.—Trimethyl(vinyl)silane, trimethoxy(vinyl)silane and (trimethylsilyl)acetylene were purchased from Aldrich Chimica Italiana. Aryl azides **6–11** were prepared from diazonium compounds and azide ion according to the general procedures developed by Smith and co-workers.[25] 2-BTA [26] and 3-BTA [27] were previously reported. Reaction products such as the aziridines **4f** and **4g** were previously described.[8] Chromatographic separations were carried out on 'Florisil' 60–100 mesh.

Spectra. I.R. spectra were recorded with a Perkin-Elmer Model 257 instrument. ^1H and ^{13}C NMR spectroscopic data were obtained with a Varian Gemini 200 MHz instrument for solutions in $CDCl_2$ using $CHCl_3$ as internal standard, J values are given in Hz.

Reactions of Aryl Azides **6–11**, 2-BTA *and* 3-BTA *with Vinyl- and Alkynyl-silane at* 25 °C. *General Procedure.*—A solution of aryl azides (0.5 or 0.25 mol dm^{-3} for azides **6–7**) of the appropriate neat alkenes or alkyne, TMVS, TMOVS and (trimethylsilyl)acetylene was allowed to react in a sealed tube at 25 °C in the dark for the appropriate time, until TLC showed the absence of the starting azide. The reactions which leave solid products, **1a**, **1b**, **1d** and **5a–h**, were filtered off and the solid repeatedly washed with pure pentane and then characterized. The remaining reaction mixtures, azides **8–11** in TMVS, were treated using the following work-up. The residue obtained after careful evaporation of the excess of olefin, under high vacuum, was treated with hexane–diethyl ether (v/v 4:1) and the resulting solid pyrazoline products **3a–d** separated by filtration, were washed with pure hexane and

* It is well known that the greater electronegativity of the sp carbon in alkynes leads to lower reactivity with electrophiles and greater reactivity with nucleophiles compared with the sp^2 carbon of alkenes, see ref. 11. Furthermore, orientation of additions of azides to unsymmetrical acetylene are generally electronically, rather than sterically, controlled reactions; see ref. 18.

† The influence of a homogeneous electric field on the charge distribution in various hydrocarbon dinegative ions has been investigated.[24]

then characterized. The mother liquor containing the aziridine **4a–d** was chromatographed on a silica gel column using hexane with increasing amounts of diethyl ether (up to 100%) as eluent.

The aziridines **4h–i** were obtained directly as pure compounds by elimination, under high vacuum, of excess TMOVS.

Approximate reaction times and product yields for the reactions of aryl azides **6–11**, 2-BTA and 3-BTA with TMVS or (trimethylsilyl)acetylene at 25 °C are reported in Tables 1 and 4 respectively.

The following new triazolines **1a**, **1b** and **1d** were obtained: 4,5-*Dihydro*-1-(4-*nitrophenyl*)-4-(*trimethylsilyl*)-1,2,3-*triazole* **1a**, m.p. 111–12 °C; ν_{max}/cm^{-1} 2960, 1600, 1490 (NO), 1340 (NO), 840 ($SiMe_3$) and 750; δ_H(200 MHz; $CDCl_3$) 8.20 (2 H, d), 7.24 (2 H, d), 4.39 (1 H, dd, *J* 13.2 and 8.5), 3.70 (1 H, dd, *J* 13.2 and 8.3), 3.42 (1 H, t, *J* 8.3 and 8.5) and 0.14 (9 H, s); δ_C(200 MHz; $CDCl_3$) 146.84 (s), 142.22 (s), 126.27 (d), 113.80 (d), 73.65 (d, *J* 136), 43.38 (t, *J* 144) and −3.75 (q); *m/z* 238 (100%, M − C_2H_2), 236 (40, M − N_2), 221 (66), 194 (38), 175 (25), 100 (24) and 73 (93) (Found: C, 49.9; H, 6.05; N, 21.15. $C_{11}H_{16}N_4O_2Si$ requires C, 50.00; H, 6.10; N, 21.20%).

1-(4-*Cyanophenyl*)-4,5-*dihydro*-4-(*trimethylsilyl*)-1,2,3-*triazole* **1b**, m.p. 88–89 °C; ν_{max}/cm^{-1} 2970, 2250 (conj. CN), 1620 (C=N), 850 ($SiMe_3$) and 750; δ_H(200 MHz; $CDCl_3$) 7.60 (2 H, d), 7.28 (2 H, d), 4.35 (1 H, dd, *J* 13.2 and 8.6), 3.66 (1 H, dd, *J* 13.2 and 8.3), 3.40 (1 H, t, *J* 8.3 and 8.6) and 0.12 (9 H, s); δ_C(200 MHz; $CDCl_3$) 145.20 (s), 134.05 (d), 119.83 (s), 114.56 (d), 104.33 (s), 73.18 (d, *J* 136), 43.36 (t, *J* 144) and −3.73 (q); *m/z* 216 (20%, M − N_2), 215 (20), 201 (40), 189 (5), 175 (10), 100 (49) and 73 (100) (Found: C, 58.95; H, 6.55; N, 22.95. $C_{12}H_{16}N_4Si$ requires C, 59.00; 6.60; N, 22.95%).

4,5-*Dihydro*-1-(4-*nitrophenyl*)-4-(*trimethoxysilyl*)-1,2,3-*triazole* **1d**, m.p. 130–131 °C; ν_{max}/cm^{-1} 2950, 2850 (OMe), 1590 (NO), 1330 (NO) and 1090 [$Si(OMe)_3$]; δ_H(200 MHz; $CDCl_3$) 8.15 (2 H, d), 7.24 (2 H, d), 4.34 (1 H, dd, *J* 13.6 and 10.3), 3.70 (1 H, dd, *J* 13.6 and 8.3), 3.60 (9 H, s) and 3.55 (1 H, dd, *J* 8.3 and 10.3); δ_C(200 MHz; $CDCl_3$) 146.60 (s), 142.22 (s), 126.20 (d), 114.00 (d), 68.62 (d, *J* 135), 51.63 (q) and 42.92 (t, *J* 147); *m/z* 284 (19%, M − N_2), 269 (36), 121 (100) and 91 (55) (Found: C, 42.25; H, 5.1; N, 17.9. $C_{11}H_{16}N_4O_5Si$ requires C, 42.30; H, 5.15; N, 17.95%).

The following new pyrazolines **3a–d** were obtained: 3-(N-*Anilinomethyl*)-4,5-*dihydro*-3,5-*bis*(*trimethylsilyl*)-1H-*pyrazole* **3a**, m.p. 104–105 °C; ν_{max}/cm^{-1} 3390 (NH), 2960 and 840 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 7.20 (2 H, m), 6.72 (1 H, m), 6.63 (2 H, m), 4.02 (1 H, dd, *J* 12.0 and 4.3, H_α), 3.94 (1 H, t, *J* 10.6 and 10.7, 5-H), 3.52 (1 H, br m, NH), 3.35 (1 H, dd, *J* 12.0 and 7.7, H_α'), 1.83 (1 H, dd, *J* 12.2 and 10.7, 4-H) 1.44 (1 H, dd, *J* 12.2 and 10.6, 4-H), 0.15 (9 H, s) and 0.08 (9 H, s); δ_C(200 MHz; $CDCl_3$) 149.01 (s), 129.73 (d), 118.16 (d), 113.41 (d), 92.70 (s), 84.72 (d), 48.22 (t), 25.06 (t), −2.90 (q) and −3.63 (q); *m/z* 319 (M$^+$, 12%), 291 (5, M − N_2), 218 (8), 216 (15), 213 (20), 176 (15), 150 (37), 111 (27), 106 (95), 93 (25) and 73 (100) (Found: M$^+$, 319.189 82. $C_{16}H_{29}N_3Si_2$ requires *M*, 319.189 99).

3-(N-4-*Toluidinomethyl*)-4,5-*dihydro*-3,5-*bis*(*trimethylsilyl*)-1H-*pyrazole* **3b**, m.p. 110–112 °C; ν_{max}/cm^{-1} 3360 (NH), 2960, 1520 and 840 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 7.02 (2 H, d), 6.53 (2 H, d), 4.04 (1 H, br m, H_α), 3.98 (1 H, t, *J* 10.8 and 10.6, 5-H), 3.46 (1 H, br m, NH), 3.34 (1 H, br m, H_α'), 2.26 (3 H, s), 1.86 (1 H, dd, *J* 12.4 and 10.8, 4-H), 1.49 (1 H, dd, *J* 12.4 and 10.6, 4-H), 0.20 (9 H, s) and 0.14 (9 H, s); δ_C(200 MHz; $CDCl_3$) 146.78 (s), 130.23 (d), 127.35 (s), 113.60 (d), 92.75 (s), 84.70 (d), 48.70 (t), 25.10 (t), 20.57 (q), −2.86 (q) and −3.60 (q); *m/z* 333 (M$^+$, 33%), 305 (7, M − N_2), 230 (23), 213 (33), 164 (27), 120 (100), 111 (18), 107 (17) and 73 (100) (Found: M$^+$, 333.205 72. $C_{17}H_{31}N_3Si_2$ requires *M*, 333.205 64).

3-(N-4-*Anisidinomethyl*)-4,5-*dihydro*-3,5-*bis*(*trimethylsilyl*)-1*H*-*pyrazole* **3c**, m.p. 90–92 °C; ν_{max}/cm^{-1} 3370 (NH), 2960, 2840 and 850 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 6.75 (2 H, d), 6.54 (2 H, d), 3.98 (1 H, d, *J* 8.2, H_α), 3.92 (1 H, t, *J* 10.9 and 10.6, 5-H), 3.72 (3 H, s), 3.25 (1 H, br m, NH), 3.25 (1 H, d, *J* 8.2, H_α'), 1.80 (1 H, dd, *J* 12.1 and 10.9, 4-H), 1.46 (1 H, dd, *J* 12.1 and 10.6, 4-H), 0.13 (9 H, s) and 0.08 (9 H, s); δ_C(200 MHz; $CDCl_3$) 152.87 (s), 143.26 (s), 115.36 (d), 114.70 (d), 92.72 (s), 84.66 (d), 56.11 (q), 49.29 (t), 25.07 (t), −2.88 (q) and −3.63 (q); *m/z* 349 (M$^+$, 29%), 321 (7, M − N_2), 213 (53), 180 (27), 136 (89), 123 (25), 111 (18) and 73 (100) (Found: M$^+$, 349.200 48. $C_{17}H_{31}N_3OSi_2$ requires *M*, 349.200 55).

3-(N-4-*Chloroanilinomethyl*)-4,5-*dihydro*-3,5-*bis*(*trimethylsilyl*)-1H-*pyrazole* **3d**, m.p. 116–18 °C; ν_{max}/cm^{-1} 3360 (NH), 2960, 1220 and 850 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 7.15 (2 H, d), 6.55 (2 H, d), 4.05 (1 H, d, *J* 12.2 and 4.4, H_α), 3.97 (1 H, t, *J* 10.8 and 10.6, 5-H), 3.60 (1 H, br m, NH), 3.31 (1 H, d, *J* 12.2 and 7.8, H_α'), 1.86 (1 H, dd, *J* 12.3 and 10.8, 4-H), 1.43 (1 H, dd, *J* 12.3 and 10.7, 4-H), 0.21 (9 H, s) and 0.15 (9 H, s); δ_C(200 MHz; $CDCl_3$) 147.40 (s), 144.22 (s), 129.37 (d), 114.26 (d), 92.48 (s), 84.56 (d), 48.14 (t), 24.90 (t), −3.08 (q) and −3.83 (q); *m/z* 353 (M$^+$, 9%), 325 (2, M − N_2), 213 (17), 184 (24), 153 (18), 140 (31), 111 (13) and 73 (100) (Found: M$^+$. 353.151 08. $C_{16}H_{28}ClN_3Si_2$ requires *M*, 353.151 02).

The following new aziridines **4a–e** and **4h–i** were obtained: 1-*Phenyl*-2-*trimethylsilylaziridine* **4a**, as an oil; ν_{max}/cm^{-1} 3040, 2950, 1600, 850 ($SiMe_3$) and 750; δ_H(200 MHz; $CDCl_3$) 7.22 (2 H, m), 6.95 (3 H, m), 2.16 (1 H, dd, *J* 4.7 and 1.7), 2.11 (1 H, dd, *J* 7.6 and 1.7), 1.32 (1 H, dd, *J* 7.6 and 4.7) and 0.16 (9 H, s); *m/z* 191 (M$^+$, 64%), 190 (50), 176 (100), 135 (68), 100 (22) and 73 (71) (Found: M$^+$, 191.113 09. $C_{11}H_{17}NSi$ requires *M*, 191.113 02).

1-(4-*Tolyl*)-2-*trimethylsilylaziridine* **4b**, as an oil; ν_{max}/cm^{-1} 3040, 2960, 1510, 1250 and 840 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 7.03 (2 H, m), 6.85 (2 H, m), 2.30 (3 H, s), 2.15 (1 H, dd, *J* 4.7 and 1.7), 2.08 (1 H, dd, *J* 7.6 and 1.7), 1.27 (1 H, dd, *J* 7.6 and 4.7) and 0.18 (9 H, s); *m/z* 205 (M$^+$, 72%), 204 (33), 190 (89, M − Me), 149 (83), 114 (22), 105 (28) and 73 (100) (Found: M$^+$, 205.128 71. $C_{12}H_{19}NSi$ requires *M*, 205.128 67).

1-(4-*Methoxyphenyl*)-2-*trimethylsilylaziridine* **4c**, as an oil; ν_{max}/cm^{-1} 3050, 2960, 2840, 1245 and 840 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 6.89 (2 H, m), 6.72 (2 H, m), 3.70 (3 H, s), 2.09 (1 H, dd, *J* 4.8 and 1.5), 2.03 (1 H, dd, *J* 7.7 and 1.5), 1.27 (1 H, dd, *J* 7.7 and 4.8) and 0.14 (9 H, s); *m/z* 221 (M$^+$, 64%), 206 (77, M − Me), 165 (56), 121 (47), 114 (11), 100 (17) and 73 (100) (Found: M$^+$, 221.123 50. $C_{12}H_{19}NOSi$ requires *M*, 221.123 58).

1-(4-*Chlorophenyl*)-2-*trimethylsilylaziridine* **4d**, m.p. 50–52 °C; ν_{max}cm^{-1} 2960, 1250 and 840 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 7.04 (2 H, m), 6.75 (2 H, m), 2.05 (1 H, dd, *J* 4.7 and 1.5), 1.96 (1 H, dd, *J* 7.7 and 1.5), 1.73 (1 H, dd, *J* 7.7 and 4.7) and 0.14 (9 H, s); *m/z* 225 (M$^+$, 47%), 210 (77, M − Me), 169 (36), 114 (16), 100 (17) and 73 (100) (Found: M$^+$, 225.074 12. $C_{11}H_{16}ClNSi$ requires *M*, 225.074 05).

1-(4-*Nitrophenyl*)-2-*trimethylsilylaziridine* **4e**, m.p. 60–62 °C; ν_{max}/cm^{-1} 3060, 2960, 1510 (NO), 1340 (NO) and 850 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 8.10 (2 H, m), 6.95 (2 H, m), 2.26 (1 H, dd, *J* 4.7 and 1.5), 2.18 (1 H, dd, *J* 7.6 and 1.5), 1.44 (1 H, dd, *J* 7.6 and 4.7) and 0.16 (9 H, s); *m/z* 236 (M$^+$, 44%), 235 (40), 221 (64, M − Me), 180 (38), 175 (27), 134 (7), 100 (28) and 73 (100) (Found: M$^+$, 236.098 17. $C_{11}H_{16}N_2O_2Si$ requires *M*, 236.098 09).

1-(2-*Benzo*[b]*thienyl*)-2-*trimethoxysilylaziridine* **4h**, as an oil; ν_{max}/cm^{-1} 2940, 2840 (OCH_3) and 1060; δ_H(200 MHz; $CDCl_3$) 7.55 (2 H, m), 7.20 (3 H, m), 6.56 (1 H, s), 3.62 (9 H, s), 2.46 (1 H, dd, *J* 5.0 and 1.6), 2.28 (1 H, dd, *J* 7.9 and 1.6), and 1.57 (1 H, dd, *J* 7.9 and 5.0); *m/z* 295 (M$^+$, 35%), 280 (7, M − Me), 263 (10), 147 (28), 121 (100), 91 (50) and 61 (15) (Found: M$^+$, 295.069 84. $C_{13}H_{17}NO_3SSi$ requires *M*, 295.069 83).

1-(3-*Benzo*[b]*thienyl*)-2-*trimethoxylsilylaziridine* **4i**, as an oil;

ν_{max}/cm^{-1} 2940, 2840 (OCH_3) and 1060; δ_H(200 MHz; $CDCl_3$) 8.12 (1 H, m), 7.70 (1 H, m), 7.28 (2 H, m), 6.48 (1 H, s), 3.65 (9 H, s), 2.40 (1 H, dd, *J* 4.7 and 1.8), 2.10 (1 H, dd, *J* 7.7 and 1.8) and 1.31 (1 H, dd, *J* 7.7 and 4.7); *m/z* 295 (M^+, 60%), 280 (7, M − Me), 263 (11), 189 (22), 147 (62), 121 (100), 91 (56) and 61 (20) (Found: M^+, 295.069 77. $C_{13}H_{17}NO_3SSi$ requires *M*, 295.069 83).

The following new triazoles **5a–h** were obtained: 1-(4-*nitrophenyl*)-4-*trimethylsilyl*-1,2,3-*triazole* **5a**, m.p. 182–84 °C; ν_{max}/cm^{-1} 3100, 2990, 1480 (NO), 1330 (NO), 1260 and 850 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 8.36 (2 H, d), 8.08 (1 H, s), 7.97 (2 H, d) and 0.34 (9 H, s); δ_C(200 MHz; $CDCl_3$) 149.15 (s), 147.65 (s), 141.87 (s), 127.33 (d), 125.88 (d), 121.08 (d) and −1.18 (q); *m/z* 247 (2%, M − Me), 234 (9, M − N_2), 219 (100), 173 (21) and 73 (10) (Found: C, 50.35; H, 5.35; N, 21.4. $C_{11}H_{14}N_4O_2Si$ requires C, 50.40; H, 5.40; N, 21.40%).

1-(4-*Cyanophenyl*)-4-*trimethylsilyl*-1,2,3-*triazole* **5b**, m.p. 124–125 °C; ν_{max}/cm^{-1} 3140, 2980, 2250 (conj. CN), 1620 (C=N), 1260 and 860 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 8.07 (1 H, s), 7.87 (2 H, d), 7.74 (2 H, d) and 0.28 (9 H, s); δ_C(200 MHz; $CDCl_3$) 176.46 (s), 148.85 (s), 140.43 (s), 134.36 (d), 127.49 (d), 121.21 (d), 118.31 (s) and −1.12 (q); *m/z* 214 (5%, M − N_2), 199 (100), 171 (10), 160 (10), 102 (10) and 73 (10) (Found: C, 59.55; H, 5.85; N, 23.1. $C_{12}H_{14}N_4Si$ requires C, 59.50; H, 5.80; N, 23.10%).

1-*Phenyl*-4-*trimethylsilyl*-1,2,3-*triazole* **5c**, m.p. 94–96 °C; ν_{max}/cm^{-1} 3140, 2980, 1260 and 860 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 7.93 (1 H, s), 7.62 (2 H, m), 7.30 (3 H, m) and 0.27 (9 H, s); δ_C(200 MHz; $CDCl_3$) 147.75 (s), 137.53 (s), 130.08 (d), 128.86 (d), 127.73 (d, *J* 193), 121.11 (d) and −1.02 (q); *m/z* 217 (M^+, 1%), 202 (1%, M − Me), 189 (8), 174 (100), 146 (7), 77 (12) and 73 (7) (Found: C, 60.85; H, 7.0; N, 19.25. $C_{11}H_{15}N_3Si$ requires C, 60.80; H, 7.00; N, 19.30%).

1-(4-*Tolyl*)-4-*trimethylsilyl*-1,2,3-*triazole* **5d**, m.p. 104–105 °C; ν_{max}/cm^{-1} 3130, 3040, 2960, 2900, 1250 and 840 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 7.89 (1 H, s), 7.54 (2 H, d), 7.21 (2 H, d), 2.33 (3 H, s) and 0.31 (9 H, s); δ_C(200 MHz; $CDCl_3$) 147.63 (s), 138.97 (s), 135.33 (s), 130.62 (d), 127.64 (d), 121.11 (d), 21.20 (q) and −1.00 (q); *m/z* 231 (5%, M^+), 201 (9, M − 30), 188 (100), 160 (12) and 73 (5) (Found: M^+, 231.119 11. $C_{12}H_{17}N_3Si$ requires *M*, 231.119 17).

1-(4-*Methoxyphenyl*)-4-*trimethylsilyl*-1,2,3-*triazole* **5e**, m.p. 68–70 °C; ν_{max}/cm^{-1} 3160, 3100, 2980, 2880, 1260 and 850 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 7.74 (1 H, s), 7.43 (2 H, d), 6.79 (2 H, d), 3.64 (3 H, s) and 0.18 (9 H, s); δ_C(200 MHz; $CDCl_3$) 160.02 (s), 147.36 (s), 130.90 (s), 127.68 (d, *J* 192), 122.63 (d), 114.96 (d), 55.64 (q) and −1.18 (q); *m/z* 219 (35%, M − N_2), 204 (100), 176 (20), 146 (5), 102 (10) and 73 (25) (Found: C, 58.4; H, 6.9; N, 17.0. $C_{12}H_{17}N_3OSi$ requires C, 58.30; H, 6.90; N, 17.00%).

1-(4-*Chlorophenyl*)-4-*trimethylsilyl*-1,2,3-*triazole* **5f**, m.p. 130–131 °C; ν_{max}/cm^{-1} 3160, 3000, 2980, 1260 and 860 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 7.97 (1 H, s), 7.62 (2 H, d), 7.43 (2 H, d) and 0.33 (9 H, s); δ_C(200 MHz; $CDCl_3$) 148.19 (s), 136.07 (s), 134.58 (s), 130.29 (d), 127.57 (d), 122.32 (d) and −1.04 (q); *m/z* 251 (M^+, 2%), 223 (10, M − N_2), 188 (100), 160 (15), 133 (5), 113 (5) and 73 (15) (Found: C, 52.55; H, 5.6; N, 16.65. $C_{11}H_{14}ClN_3Si$ requires C, 52.50; H, 5.60; N, 16.70%).

1-(2-*Benzo*[b]*thienyl*)-4-*trimethylsilyl*-1,2,3-*triazole* **5g**, m.p. 148–150 °C; ν_{max}/cm^{-1} 3150, 2980, 2920, 1260 and 850 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 7.87 (1 H, s), 7.63 (2 H, br m), 7.32 (1 H, s), 7.24 (2 H, br m) and 0.25 (9 H, s); δ_C(200 MHz; $CDCl_3$) 176.33 (s), 148.13(s), 138.10 (s), 136.57 (s), 128.40 (d, *J* 194), 125.63 (d), 125.56 (d), 124.40 (d), 122.56 (d), 113.14(d) and −1.20 (q); *m/z* 273 (M^+, 2%), 245 (78, M − N_2), 230 (100), 202 (11), 179 (9) and 73 (15) (Found: M^+, 273.075 46. $C_{13}H_{15}N_3SSi$ requires *M*, 273.075 59).

1-(3-*Benzo*[b]*thienyl*)-4-*trimethylsilyl*-1,2,3-*triazole* **5h**, m.p. 88–90 °C; ν_{max}/cm^{-1} 3150, 2980, 2910, 1260 and 850 ($SiMe_3$); δ_H(200 MHz; $CDCl_3$) 7.97 (1 H, s), 7.96 (1 H, br m), 7.81 (1 H, br m), 7.58 (1 H, s), 7.38 (2 H, br m) and 0.38 (9 H, s); δ_C(200 MHz; $CDCl_3$) 176.31 (s), 147.04 (s), 139.54 (s), 133.19 (s), 130.10 (d, *J* 193), 126.23 (d), 125.83 (d), 123.48 (d), 122.80 (d), 119.76 (d) and −0.91 (q); *m/z* 273 (M^+, 3%), 245 (35, M − N_2), 230 (100), 202 (15), 89 (13) and 73 (20) (Found: M^+, 273.075 64. $C_{13}H_{15}N_3SSi$ requires *M*, 273.075 59).

Reactions of 4-*Chlorophenyl Azide* **11** *with* TMVS *at* 25 *and* 70 °C.—A solution of 4-chlorophenyl azide **11** (0.5 mol dm^{-3}) in neat TMVS was allowed to react at *ca.* 25 °C for 22 d, after which time TLC showed the absence of the starting azide. An aliquot part of the crude reaction mixture, after elimination under vacuum of the excess solvent, was diluted with deuteriochloroform and immediately analysed by ^1H NMR spectroscopy at room temperature. The NMR spectrum revealed, in addition to the peaks attributable to the pyrazoline **3d** and small quantity of aziridine **4d** protons, the presence of an ABX systems (δ 4.19, *J* 13.5 and 9.1 Hz, δ 3.54, *J* 13.5 and 8.1 Hz, and δ 3.30, *J* 9.1 and 8.1 Hz) consistent with triazoline **1c** ring protons, being the ratios 5:1:5 respectively. The remaining part of the reaction mixture was adsorbed on silica gel and, after standing at 25 °C for a few minutes, chromatographed on 'Florisil' column to give the aziridine **4d** (44%); and the pyrazoline **3d** (40%).

The same reaction carried out in a sealed tube at 70 °C for 20 h after which an aliquot part of the crude reaction mixture, after elimination under vacuum of the excess solvent, was diluted with deuteriochloroform and immediately analysed by ^1H NMR spectroscopy. The NMR spectrum revealed exclusively peaks attributable to aziridine **4d** and to pyrazoline **3d** protons within the ratio *ca.* 4:1. Chromatographic separation gave the aziridine **4d** (63%); and the pyrazoline **3d** (15%).

Decomposition of 1-(4-*Nitrophenyl*)-1,2,3-*triazoline* **1a** *in* TMVS *at* 25 °C.—A solution of triazoline **1a** (0.25 mol dm^{-3}; 5 cm^3) in TMVS–$CHCl_3$ (v/v 2:1) was allowed to stand at *ca.* 25 °C for 62 d after which the reaction mixture was analysed by GC–MS leading to the following *m/z* identified products: trimethylsilylethane (relative abundance 6), *m/z* 102 (M^+, 10%), 101 (99), 73 (50) and 59 (100); nitrobenzotriazole (0.5), *m/z* 164 (M^+, 100%), 163 (28), 149 (98), 117 (55), 103 (50) and 76 (54); 4-nitroaniline (7), *m/z* 138 (M^+, 96%), 122 (10, M − 16) and 65 (100); *N*-trimethylsilyl-4-nitroaniline (2), *m/z* 210 (M^+, 60%), 195 (100, M − 15), 149 (20), 73 (20) and 45 (10); and 1-(4-nitrophenyl)-1,2,3-triazoline **1a** (2).

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References

1 E. Colvin, *Silicon in Organic Synthesis*, Butterworth, Boston, 1981; W. P. Weber, *Silicon Reagents for Organic Synthesis*, Springer-Verlag, New York, 1083; P. D. Magnus, T. Sarkar and S. Djuric, *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, Pergamon Press, New York, vol. 7; T. A. Blumenkopf and L. E. Overman, *Chem. Rev.*, 1986, **86**, 857.

2 G. Bianchi, C. De Micheli and R. Gandolfi, *1,3-Dipolar cycloadditions involving X=Y groups*, ed. S. Patai, Interscience Publishers, London, 1974, pp. 369 532; A. Padwa, *1,3-Dipolar Cycloaddition Chemistry*, J. Wiley, 1984, New York, vol. 2; J. March, *Advanced Organic Chemistry*, 3rd edn., J. Wiley, New York, 1985, 937 and refs. therein.

3 (*a*) R. F. Cunico and H. Mee Lee, *J. Am. Chem. Soc.*, 1977, **99**, 7613; (*b*) A. Padwa and M. W. Wannamaker, *Tetrahedron*, 1990, **46**, 1145.

4 P. DeShong, S. W. Lander Jnr., J. M. Leginus and C. M. Dicken, *Advances in Cycloaddition*, ed. D. P. Curran, vol. 1, pp. 87–126, JAI Press Inc., Greenwich, 1988; P. DeShong, J. M. Leginus and S. W. Lander, *J. Org. Chem.*, 1986, **51**, 574.
5 K. A. Adrianov, V. I. Sodorov and L. M. Khananashvili, *Dokl. Akad. Nauk. SSSR*, 1964, **158**, 987; and *Zh. Obsch. Khim.*, 1966, **36**, 178.
6 A. R. Bassindale, A. G. Brook, P. F. Jones and J. A. G. Stewart, *J. Organomet. Chem.*, 1978, **152**, C25.
7 (*a*) G. Bianchi, C. De Micheli and R. Gandolfi, *Angew. Chem., Int. Ed. Engl.*, 1979; **18**, 721; (*b*) P. K. Kadaba, B. Stanovnik and M. Tisler, *Adv. Heterocycl. Chem.*, 1985, **37**, 219; (*c*) G. L'Abbé, *Chem. Rev.*, 1969, **69**, 345; (*d*) R. Huisgen, G. Szeimies and L. Moebius, *Chem. Ber.*, 1967, **100**, 2494.
8 M. Funicello, P. Spagnolo and P. Zanirato, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2971.
9 R. Sustmann and H. Trill, *Angew. Chem., Int. Edn. Engl.*, 1972, **11**, 838.
10 K. N. Houk, *J. Am. Chem. Soc.*, 1972, **94**, 8953; *Acc. Chem. Res.*, 1975, **8**, 361.
11 (*a*) J. Bastide and O. Henri-Rousseau, *The Chemistry of C–C Triple Bond*, ed. S. Patai, J. Wiley, New York, 1978, ch. 11, 447; (*b*) T. L. Gilchrist and G. E. Gymer, *Adv. Heterocycl. Chem.*, 1974, **16**, 33.
12 R. Huisgen, G. Szeimies and L. Moebius, *Chem. Ber.*, 1966, **99**, 476.
13 R. West and G. A. Gornowicz, *J. Organomet. Chem.*, 1971, **28**, 25.
14 P. Palmieri and P. Zanirato, unpublished work.
15 (*a*) K. B. Becker and M. K. Hohermuth, *Helv. Chim. Acta*, 1979, **62**, 2025; (*b*) T. Sasaki, S. Eguchi, M. Yamaguchi and T. Esaki, *J. Org. Chem.*, 1981, **46**, 1801; (*c*) M. S. Ouali, M. Vaultier and R. Carrie, *Tetrahedron*, 1980, **36**, 1821.
16 G. Leroy and M. Sana, *Tetrahedron*, 1976, **32**, 709.
17 G. Szeimies and R. Huisgen, *Chem. Ber.*, 1966, **99**, 491; W. Broeckx, N. Overbergh, C. Samyn, G. Smets and G. L'Abbé, *Tetrahedron*, 1971, **27**, 3527.
18 (*a*) I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, J. Wiley, London, 1976, 155; (*b*) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 1963, **2**, 565 and 1963, **2**, 633; *J. Org. Chem.*, 1976, **41**, 403.
19 H. Bock and H. Siedl, *J. Organomet. Chem.*, 1968, **13**, 87.
20 K. Tamao, R. Kanatani and M. Kumada, *Tetrahedron Lett.*, 1984, **25**, 1905.
21 P. Magnus and D. Quagliato, *J. Org. Chem.*, 1985, **50**, 1621.
22 M. Funicello and P. Zanirato, *Gazz. Chim. Ital.*, 1990, **120**, 609.
23 L. Birkofer, A. Ritter and H. Uhlenbrauck, *Chem. Ber.*, 1963, **91**, 1841; R. M. Bettison, P. B. Hitchcock and D. R. M. Walton, *J. Organomet. Chem.*, 1988, **341**, 247.
24 G. I. Hoijtink, *Recl. Trav. Chim. Pays-Bas*, 1957, **76**, 871.
25 P. A. Smith and B. B. Brown, *J. Am. Chem. Soc.*, 1951, **73**, 2438.
26 P. Spagnolo and P. Zanirato, *J. Chem. Soc., Perkin Trans. 1*, 1988, 3375.
27 P. Spagnolo and P. Zanirato, *J. Org. Chem.*, 1978, **43**, 3539.

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