A Study of Vinyl Radical Cyclization onto the Azido Group by Addition of Sulfanyl, Stannyl, and Silyl Radicals to Alkynyl Azides☆

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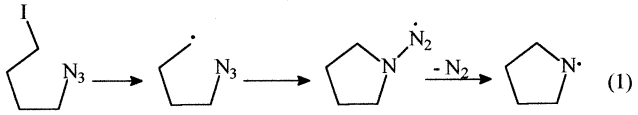
Received January 21, 1998

Keywords: Alkynes / Azides / Cyclizations / Indoles / Radicals

Thermal radical reactions of azidoalkynes **2**, **8**, **14**, and **21a–c** with thiols **1a–c** afford 2-sulfanylvinyl radicals by selective addition of sulfanyl radicals to the triple bond. 1-Phenylvinyl radicals **23** and **30a**, as well as vinyl radical **30b**, undergo fast 5-cyclization onto the aromatic azide function to give cyclized indoles. In contrast, both 1-phenyl (**15**, **17**) and 1-alkyl (**3a**,**b**, **9**) vinyl radicals fail to add to their aliphatic azido substituents and exclusively undergo cyclization onto the aromatic sulfanyl ring and H transfer from the thiol precursor. Azidoalkynes **14** and **21a** react with Bu_3SnH and TMSS under radical conditions to give instead the corresponding amines as a result of preferential attack of $Bu_3Sn\cdot$ and $(TMS)_3Si\cdot$ radicals on the azido group rather than on the triple bond. Evidence is provided that alkyl radical cyclizations onto azides are not feasible in the presence of thiol, in contrast with the reported utility of these cyclization reactions in the presence of Bu_3SnH and TMSS.

In recent years, radical cyclizations have become a powerful tool for the construction of carbocyclic and heterocyclic systems; including those occurring in natural products.[1] Radical cyclizations most often involve carbon−carbon bond formation;[2] those leading to carbon−nitrogen bond formation have been somewhat less well documented. The reported protocols rely on additions of aminyl[3] and iminyl[4] radicals to C=C and C=O double bonds, or on additions of carbon radicals to nitrogen atoms of imines[5] and azides. However, the synthetic potential of azides has yet to be fully explored, even though their capacity to act as radical acceptors has been long known since the pioneering work of Horner and Bauer[6] in 1966 and two earlier reports on intramolecular addition af aryl[7a] and thiocarbonyl[7b] radicals to an aromatic azide yielding cyclized aminyl radicals.

Only very recently, cyclization reactions of the aliphatic azides with alkyl radicals were investigated and were shown to have considerable utility for the synthesis of *N*-heterocycles.[8] Alkyl radicals, generated from iodoazides through iodine abstraction with tributyltin or tris(trimethylsilyl)silyl radicals, readily underwent intramolecular addition to the azido function to give cyclic aminyl radicals after loss of nitrogen (eq. 1).



(1)

Our long interest in the chemical reactivity and synthetic potential of vinyl radicals[9] and azido compounds[10] led us to investigate the behaviour of vinyl radicals containing either an aliphatic or an aromatic azido group in the side chain. In fact, radical reactions of azides with vinyl radicals have hitherto been totally unexplored. In the course of our investigations, we have studied[11] the fate of 2-sulfanylvinyl radicals generated by regioselective addition of sulfanyl radicals to the respective CC triple bonds of alkynyl azides **2**, **8**, **14**, and **21a−c**.[12] The sulfanyl radicals were in turn produced from the corresponding thiols **1a−c** using the AIBN method. Sulfanyl radicals are well known to undergo facile addition to alkynes to give 2-sulfanylvinyl radicals.[13] On the contrary, thiols have been found to be virtually unreactive towards azides under radical conditions.[14]

In the present study, these investigations have been extended to the corresponding radical reactions of tributyltin hydride (Bu_3SnH) and tris(trimethylsilyl)silane [TMSS]. We were interested in ascertaining whether alkynyl azides might selectively react with $Bu_3Sn\cdot$ and/or $(TMS)_3Si\cdot$ radicals, thereby providing further access to azidovinyl radicals.

Like sulfanyl radicals, both stannyl and silyl radicals also react readily with alkynes to give vinyl radical adducts.[13] The ability of stannyl radicals to add azides to give aminyl radicals[15] is well established, whereas support for a similar reaction with silyl radicals has to date only come from EPR spectral evidence.[16]

Results and Discussion

Reactions were normally carried out by treating the appropriate alkynyl azide **2**, **8**, **14**, or **21a−c** with 1 equiv. of thiol **1a−c**, Bu_3SnH or TMSS, and AIBN (0.2 equiv.) in refluxing fluorobenzene for 3 h. The product mixtures were directly analyzed by GC/MS and ^{1}H-NMR spectroscopy and then subjected to column chromatography on silica gel. Yields of the reaction products were calculated on the basis of the amount of azide that had reacted as 22−55% of unreacted material was recovered.

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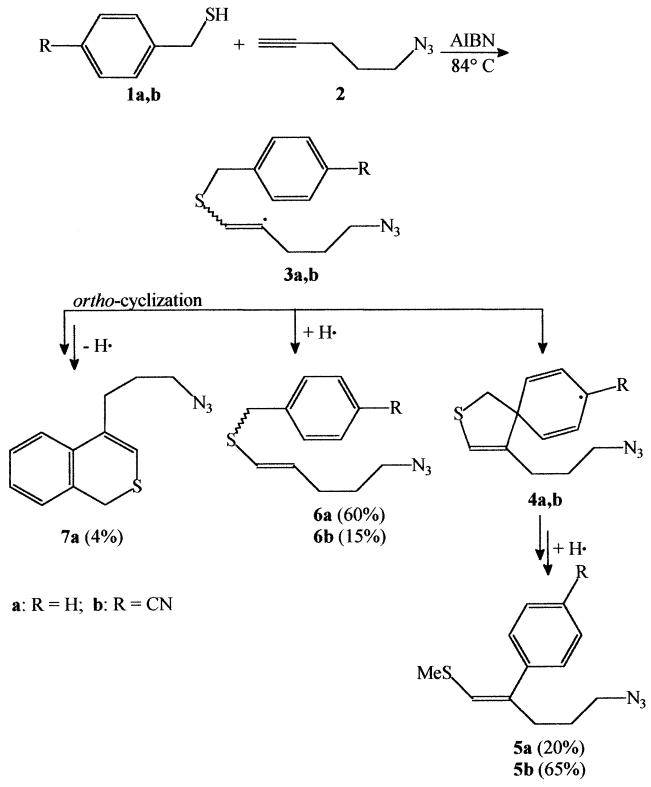
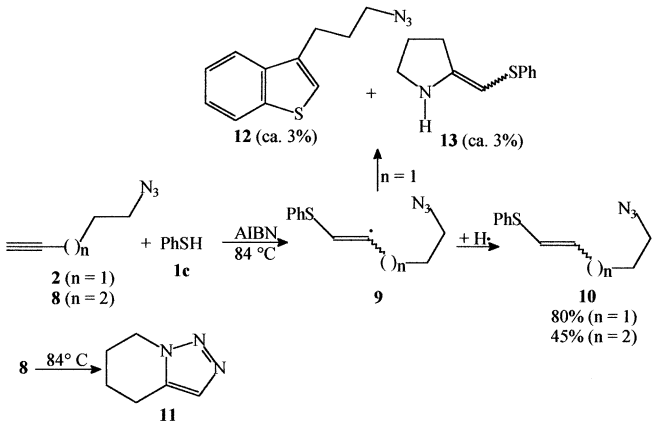
Experiments with sulfanylvinyl radicals **3a**,**b**, generated by reacting the pentynyl azide **2** with benzyl- (**1a**) and 4-cyanobenzyl mercaptan (**1b**), did not provide any evidence for intramolecular attack on the azido moiety. Both reactions furnished, in a moderately high overall yield, a mixture of the corresponding benzyl vinyl sulfides **6a**,**b** and methyl vinyl sulfides **5a**,**b** (Scheme 1). The former compounds represent the products of H-abstraction from the radicals **3a**,**b**, whereas methyl sulfides **5a**−**b** are the expected rearrangement products following intramolecular 5-(π-*endo*)*exo* cyclization of these radicals onto the adjacent aromatic ring.[9b] The proportion of rearrangement to reduction product was found to be significantly enhanced in the case of the vinyl radical **3b** as a result of greater stabilization of the spirocyclohexadienyl intermediate **4** due to the presence of the 4-cyano substituent.[9h] With benzyl mercaptan **1a**, the alkyne **2** additionally furnished a small amount of the thiopyran **7a**, which was also derived from radical **3a** through competing aromatic *ortho* cyclization (Scheme 1).

Scheme 1



The reaction of **2** with benzenethiol **1c**, carried out using the syringe pump technique,[17] gave the adduct **10** (n = 1) in good yield (80%). Despite the very low thiol **1c** concentration employed, the intermediate sulfanylvinyl radical **9** (n = 1) was able to undergo hydrogen abstraction as the almost exclusive decomposition pathway. The possible presence of very small amounts of benzothiophene **12** and pyrrole **13** as side-products was additionally suggested by GC-MS and ^{1}H-NMR analysis of the crude reaction mixture. These products, which might have been derived from radical **9** (n = 1) through 5-membered cyclization onto the benzene ring and the azido group, respectively, were however not produced in sufficient quantity to allow their separation and full characterization (Scheme 2).

Scheme 2



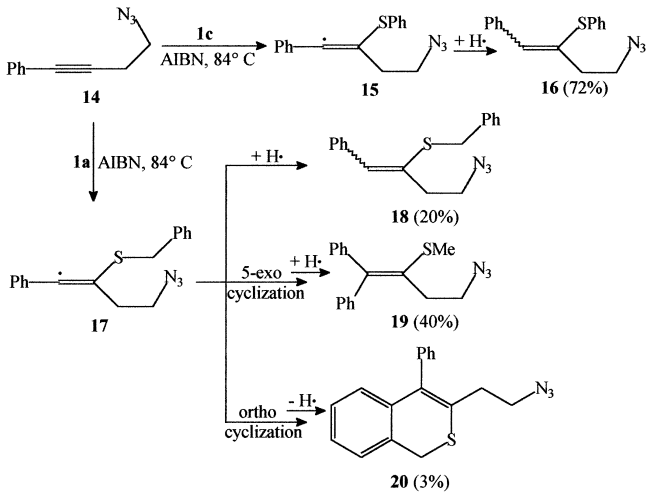
Similarly, the reaction of the homologue hexynyl azide **8** with thiol **1c** yielded the corresponding adduct **10** (n = 2) as the only product arising from intermediate vinyl radical **9** (n = 2). The adduct **10** was, however, produced only to a modest extent owing to concomitant formation of the triazole **11**. The latter was derived from azide **8** by a monomolecular 1,3-dipolar cycloaddition reaction. In an independent experiment we found that in boiling fluorobenzene the azide **8** alone gave triazole **11** in nearly quantitative yield (ca. 50% conversion yield within 3 h) (Scheme 2).

Thus, 1-alkyl-2-sulfanylvinyl radicals **3a**,**b** and **9** proved to be reluctant to intramolecularly add an alkyl azide in a 5- or 6-(π-*exo*) mode and preferentially followed alternative reaction pathways, including intramolecular cyclization onto the sulfanyl aromatic ring and/or H-abstraction from the alkane- or arenethiol precursor.

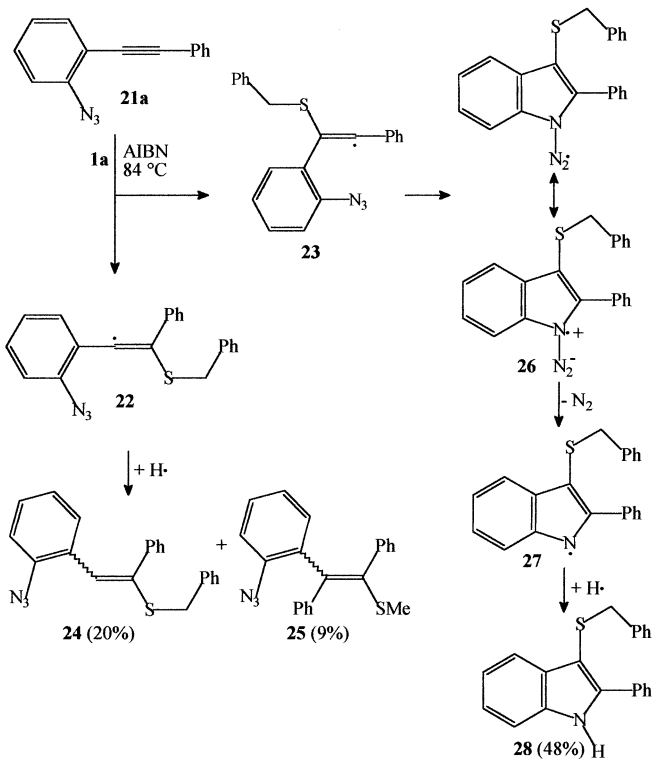
Since the π-*exo* cyclization of σ-bent 1-alkylvinyl radicals **3a**,**b**, **9** might have been inhibited by unfavourable stereoelectronic factors, we turned our attention to the fate of π-linear 1-phenyl analogues **15** and **17**, which, in principle, might cyclize onto the azido group in a π-*endo* mode. It is known that cyclizations of π-*endo* and π-*exo* mode are sensitive to different stereoelectronic demands.[9h] Moreover, we have previously shown that sp-hybridized 1-phenylvinyl radicals can cyclize onto both CC double bonds[9e] and aromatic rings[18] more rapidly than their sp^2-hybridized 1-alkylvinyl counterparts. However, radicals **15** and **17**, which were generated from the phenylbutynyl azide **14** upon reaction with benzenethiol **1c** and benzyl mercaptan **1a**, respectively, might have behaved in a fashion not dissimilar from that of the 1-alkyl-substituted congeners **3a**,**b**, **9**. In fact, the alkenyl azide **16** was the only identifiable product of the radical **15**, whereas the azido compounds **18**, **19**, and **20** were the only observed products of radical **17** (Scheme 3).

In sharp contrast to the alkynyl azides **2**, **8** and **14** described above, both 2-azidodiphenylacetylene (**21a**) and (2-azidophenyl)trimethylsilylacetylene (**21b**) provided unequivocal evidence for facile vinyl radical cyclization onto

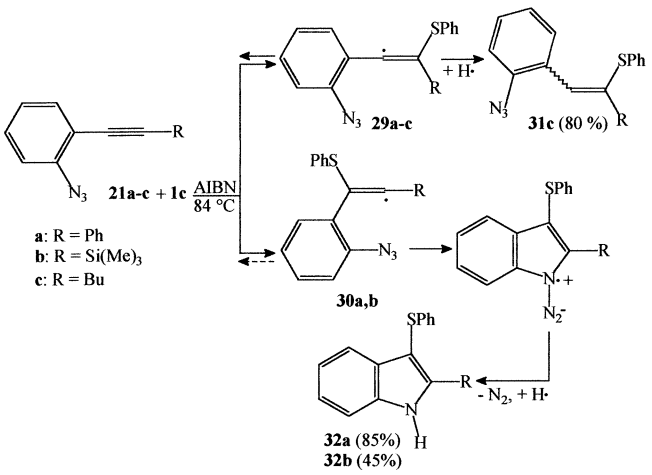
Scheme 3



Scheme 4



Scheme 5



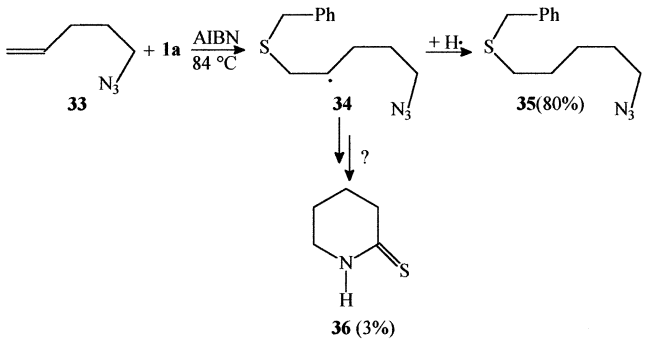
the azido function upon reaction with benzyl mercaptan **1a** or benzenethiol **1c**. In the presence of thiol **1a**, the azidoacetylene **21a** furnished a mixture of the vinyl sulfides **24** and **25**, with the major product (48%) being the indole **28** (Scheme 4). The origin of compounds **24**, **25** and **28** can be readily explained by assuming that non-regioselective (and non-reversible)[19] addition of benzylsulfanyl radicals to the alkyne **21a** initially resulted in a mixture of comparable amounts of the isomeric vinyl radicals **22** and **23**. Then, by the expected H abstraction and rearrangement, radical **22** would have given products **24** and **25**, while radical **23** would have afforded only the indole **28** as a result of 5-(π-*endo*)cyclization onto the azide, subsequent loss of nitrogen from the thus formed triazenyl radical **26**, and eventual reduction of the derived aminyl radical **27** (Scheme 4).

In the presence of thiol **1c**, the azidoacetylene **21a** furnished the corresponding indole **32a** in high yield as the exclusive product (Scheme 5). Presumably, in this case, a non-regioselective but reversible[19] addition of benzenesulfanyl radical to the CC triple bond led to an equilibrium mixture of the two sulfanyl radicals **29a** and **30a**, from which only the indole **32a** could be derived as a result of fast 5-membered cyclization of vinyl radical **30a** onto the azido group (Scheme 5). Similar results were obtained by reacting thiol **1c** with the azidoacetylene **21b**, but for unknown reasons this reaction furnished the indole product **32b** to a significantly lesser extent (Scheme 5). In contrast, 2-azidophenylhexyne **21c** did not undergo an analogous cyclization to indole in the presence of benzenethiol **1c**. As might have been anticipated,[9b][9c][9e][9f][9g][13] the benzenesulfanyl radical most probably added to this alkylarylacetylene to give exclusively the more stable 1-aryl radical **29c**, from which the azidoalkene **31c** was derived following subsequent H abstraction (Scheme 5).

The vinyl radicals **23**, **30a** and **30b** were thus found to readily undergo 5-membered cyclization onto the aromatic azido moiety. It is possible that cyclization reactions of these radicals were favoured by moderate resonance stabilization of the generated triazenyl radicals due to delocalization of the unpaired electron into the indole ring. However, the observed inertness of sulfanylvinyl radicals towards alkyl azides seemed rather curious, especially in view of the previous findings[8] that alkyl radicals can efficiently cyclize onto these azides, at least in the presence of Bu_3SnH or TMSS as radical precursors. This prompted us to briefly investigate the related radical reactions of toluenethiol **1a** with 5-azido-1-pentene (**33**) and 3-(2-azidophenyl)propene (**37**). Our aim was to gain comparative information concerning the reactivity of azido-containing 2-sulfanylalkyl radicals **34** and **38** when produced by sulfanyl radical addition to the CC double bond under conditions analogous to those employed with our vinyl radicals.

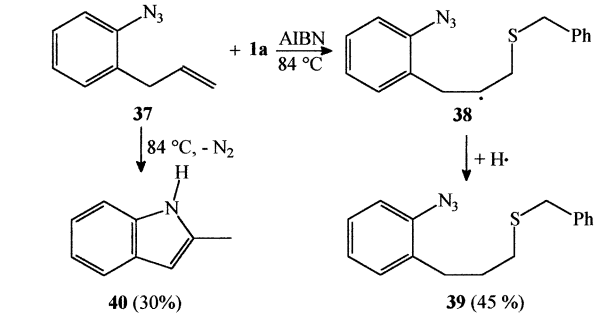
With the alkene **33**, the derived benzylsulfanylalkyl radical **34** yielded mainly the H-abstraction product **35**, which was curiously accompanied by a small amount of the thiolactam **36** (Scheme 6).

Scheme 6



With the azidophenylpropene **37**, the corresponing sulfide **39** was similarly produced as the sole product of alkyl radical **38**. In this case, 2-methylindole **40** was additionally produced due to thermal cycloaddition of the aromatic azide to the adjacent double bond[20] (Scheme 7).

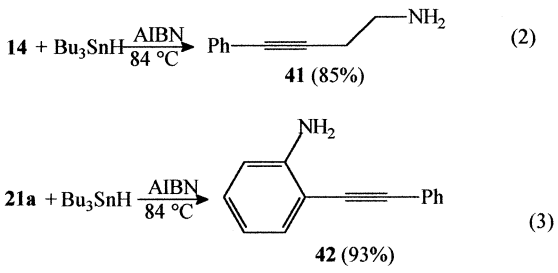
Scheme 7



Thus, under our reducing conditions, sulfanylalkyl radicals were found to be incapable of attacking an aliphatic or even an aromatic azide. This fact, while pointing to a lower reactivity of alkyl compared to vinyl radicals towards the azido group, suggests that the successful outcome of the reported alkyl radical cyclizations onto aliphatic azides is primarily attributable to the use of radical precursors such as Bu_3SnH or TMSS, which are less effective as radical scavengers than thiols.[21]

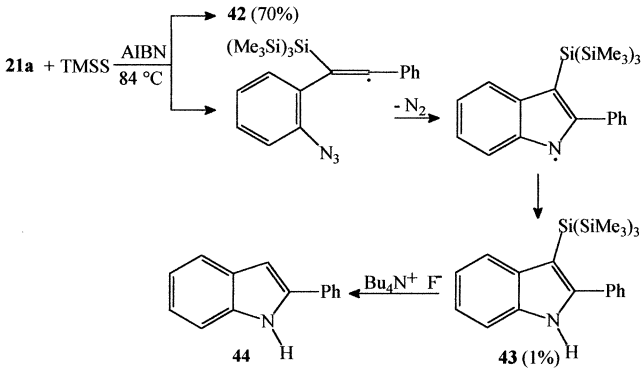
One further objective was to investigate azidovinyl radicals by analogous alkyne reactions with Bu_3SnH and TMSS. However, such investigations were largely frustrated by the observation that stannyl and silyl radicals can add to the azido group in preference to the triple bond. In fact, both 1-phenylbutynyl azide **14** and 2-azidodiphenylacetylene **21a** were found to be cleanly reduced to the corresponding amines **41** and **42** by Bu_3SnH (eqs. 2 and 3).

Similar results were obtained with the acetylene **21a** in the presence of TMSS, but under these circumstances trace amounts of the silylated indole **43** were also produced as a result of vinyl radical cyclization onto the aromatic azido group (Scheme 8). The structure of **43** was unequivocally



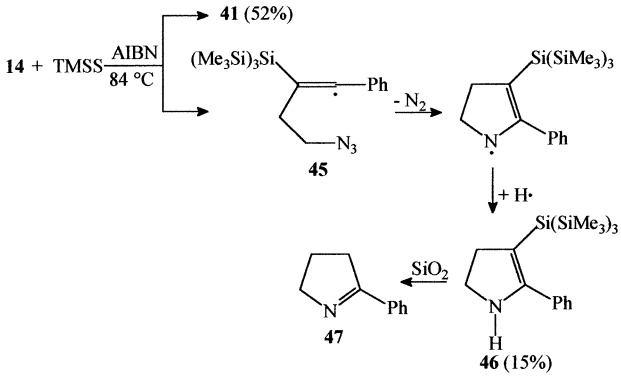
confirmed by subsequent desilylation with tetrabutylammonium fluoride to give phenylindole **44**.

Scheme 8



Moreover, the butynyl azide **14** reacted with TMSS to give the amine **41** and the pyrroline **46** in a 3:1 ratio, as indicated by ^{1}H-NMR and GC/MS analysis of the crude mixture. Subsequent column chromatography led to the isolation of, besides the amine **41**, a 2:1 mixture of **46** and its desilylated derivative **47** in 15% overall yield (Scheme 9). The formation of pyrroline **46** points to successful cyclization of intermediate vinyl radical **45** onto the azido group. Presumably, radical **45** was prevented from abstracting a hydrogen from the bulky silane due to steric factors and was consequently able to add the relatively inert alkyl azido group.

Scheme 9



In conclusion, 2-sulfanylvinyl radicals **3a**,**b**, **9**, **15**, and **17**, generated by regioselective sulfanyl radical addition to alkynyl azides **2**, **8**, and **14**, did not undergo 5- or 6-*exo* cyclization onto the aliphatic azido group owing to preferred cyclization onto the aromatic sulfanyl substituent and/or H-ab-

straction from the thiol precursor **1a−c**. In contrast, radicals **23** and **30a**,**b** underwent fast 5-cyclization onto the aromatic azido group, possibly as a result of resonance stabilization of the thus formed triazenyl radical adducts. Fast 5-*exo* cyclization onto the aliphatic azido group was observed with the silylvinyl radical **45**, which was produced from azide **14** in the presence of TMSS. Unfortunately, unlike sulfanyl radicals, $(TMS)_3Si\cdot$ radicals were found to add to the azido group in preference to the alkyne triple bond, thus making them of limited utility for the production of vinyl radicals from azidoacetylenes. Analogous regioselectivity was displayed by $Bu_3Sn\cdot$ radicals, use of which led to the exclusive reduction of the azido group. Finally, evidence was obtained that alkyl radical cyclizations onto azides are not feasible in the presence of a thiol, in contrast with the reported usefulness of these cyclization reactions in the presence of Bu_3SnH or TMSS.

This work was supported by the *Ministero dell'Università e della Ricerca Scientifica e Tecnologica* (MURST), the *Consiglio Nazionale delle Ricerche* (CNR, Rome) and the *University of Bologna* (1997 Funds for selected research topics).

Experimental Section

Starting Materials: Benzenethiol **1c**, toluenethiol **1a**, pentynol, hexynol and pentenol were commercially available. 4-Cyanotoluenethiol **1b**[9b], 3-(2-azidophenyl)propene **37**[20] and 4-phenylbut-3-yn-1-ol[22] were prepared as described in the literature. TMSS was a commercially available reagent from Fluka.

The following hitherto unknown compounds were prepared by treating the corresponding tosylate (20 mmol) (in turn prepared from the corresponding alcohol and tosyl chloride by standard methods) with sodium azide (22 mmol) in DMSO (100 ml) at room temperature for two days. The reaction mixture was extracted with *n*-pentane and the combined extracts were washed several times with brine. The organic layer was dried and the *n*-pentane was distilled off in a Claisen apparatus. The residue consisted of pure azide (ca. 15−16 mmol), which was utilized without further purification.

5-Azidopent-1-yne (**2**): Oil. − ^{1}H NMR: δ = 1.8 (quintuplet, J = 7 Hz, 2 H), 1.97 (t, J = 2.5 Hz, 1 H), 2.3 (dt, J_t = 7 Hz, J_d = 2.5 Hz, 2 H), 3.42 (t, J = 7 Hz, 2 H). − MS; *m/z* (%): 109 [M$^+$] (80), 80 (50), 54 (100). − MS (HR); *m/z*: 109.0642 ($C_5H_7N_3$, [M$^+$], calcd. 109.0640). − IR: $\tilde{\nu}_{max}$ = 2150 cm^{-1}.

6-Azidohex-1-yne (**8**): Oil. − ^{1}H NMR: δ = 1.5−1.8 (m, 4 H), 1.95 (t, J = 2.5 Hz, 1 H), 2.2 (dt, J_t = 7 Hz, J_d = 2.5 Hz, 2 H), 3.3 (t, J = 7 Hz, 2 H). − MS; *m/z* (%): 123 [M$^+$] (15), 94 (30), 67 (40), 39 (100). − MS (HR); *m/z*: 123.0794 ($C_6H_9N_3$, [M$^+$], calcd. 123.0796). − IR: $\tilde{\nu}_{max}$ = 2100 cm^{-1}.

4-Azido-1-phenylbut-1-yne (**14**): Oil. − ^{1}H NMR: δ = 2.70 (t, J = 7 Hz, 2 H), 3.48 (t, J = 7 Hz, 2 H), 7.2−7.4 (m, 5 H). − MS; *m/z* (%): 171 [M$^+$] (10), 115 (100). − MS (HR); *m/z*: 171.0798 ($C_{10}H_9N_3$, [M$^+$], calcd. 171.0796). − IR: $\tilde{\nu}_{max}$ = 2100 cm^{-1}.

5-Azidopent-1-ene (**33**)**:** Oil. − ^{1}H NMR: δ = 1.7 (quintuplet, J = 7 Hz, 2 H), 2.15 (br t, J_t = 7 Hz, 2 H), 3.3 (t, J = 7 Hz, 2 H), 4.95−5.10 (m, 2 H), 5.55−5.75 (m, 1 H). − MS; *m/z* (%): 111 [M$^+$] (10), 83 (40), 55 (100). − MS (HR); *m/z*: 111.0794 ($C_5H_9N_3$, [M$^+$], calcd. 111.0797). − IR: $\tilde{\nu}_{max}$ = 2100 cm^{-1}.

2-Azidodiphenylacetylene (**21a**), *(2-Azidophenyl)(trimethylsilyl)-acetylene* (**21b**), *and 1-(2-Azidophenyl)hex-1-yne* (**21c**) were obtained by diazotization of the corresponding amine with sodium nitrite in hydrochloric acid and subsequent treatment of the diazonium salt with 1.1 equivalent of sodium azide at 5°C. The reaction mixture was then stirred at room temperature for ca. 40 min. (unless disappearance of the diazonium salt was indicated by a β-naphthol test) and then extracted with diethyl ether. The organic layer was separated and dried, and the solvent was evaporated. Flash silica gel column chromatography of the residue led to the isolation of the pure products in ca. 60−70% yields.

21a: M.p. 36−37°C (dec. at 150°C). − ^{1}H NMR: δ = 7.1−7.6 (aromatic protons). − MS; *m/z* (%): 219 [M$^+$] (15), 191 (100), 163 (20). − MS (HR); *m/z*: 219.0799 ($C_{14}H_9N_3$, [M$^+$], calcd. 219.0796). − IR: $\tilde{\nu}_{max}$ = 2150 cm^{-1}.

21b: Oil. − ^{1}H NMR: δ = 0.28 (s, 9 H), 7.0−7.5 (m, 4 H). − MS; *m/z* (%): 215 [M$^+$] (30), 187 (70), 186 (65), 172 (100), 145 (50). − MS (HR); *m/z*: 215.0876 ($C_{11}H_{13}N_3Si$, [M$^+$], calcd. 215.0879). − IR: $\tilde{\nu}_{max}$ = 2150 cm^{-1}.

21c: Oil. − ^{1}H NMR: δ = 0.85 (t, J = 7 Hz, 3 H), 1.5−1.7 (m, 4 H), 2.48 (t, J = 7 Hz, 2 H), 7.0−7.4 (m, 4 H). − MS; *m/z* (%): 199 [M$^+$] (70), 171 (30), 170 (40), 156 (60), 143 (55), 130 (85), 129 (100), 128 (80), 115 (75), 102 (80). − MS (HR); *m/z*: 199.1112 ($C_{12}H_{13}N_3$, [M$^+$], calcd. 199.1109); IR: $\tilde{\nu}_{max}$ = 2150 cm^{-1}.

2-Aminodiphenylacetylene (**42**), *(2-Aminophenyl)(trimethylsilyl)-acetylene and 1-(2-Aminophenyl)hex-1-yne* were obtained in ca. 80−90% yield following a procedure reported in the literature[22] for the preparation of disubstituted alkynes from halobenzenes and terminal acetylenes. According to this procedure, a solution of 2-iodoaniline (20 mmol) and tetrakis(triphenylphosphane)palladium[23] $Pd(PPh_3)_4$ (1 mmol, 1.16 g) in piperidine (30 ml) was stirred at room temperature under nitrogen atmosphere for 15 min., and then a solution of the appropriate terminal acetylene (phenylacetylene, trimethylsilylacetylene, or hex-1-yne) (20 mmol) in piperidine (20 ml) was added. The reaction mixture was stirred for 6 h at ca. 30°C under nitrogen, then extracted with diethyl ether, and the combined extracts were washed several times with saturated ammonium chloride solution. The organic layer was separated and dried, the solvent was evaporated, and the crude product was purified by column chromatography on silica gel.

2-Aminodiphenylacetylene (**42**): Oil. − ^{1}H NMR: δ = 4.2 (br s, 2 H), 6.7 (m, 2 H), 7.0−7.6 (m, 7 H). − MS; *m/z* (%): 193 [M$^+$] (100), 165 (60). − MS (HR); *m/z*: 193.0889 ($C_{14}H_{11}N$, [M$^+$], calcd. 193.0891). − IR: $\tilde{\nu}_{max}$ = 3550, 3400 cm^{-1}.

2-Aminophenyl)(trimethylsilyl)acetylene: Oil. − ^{1}H NMR: δ = 0.3 (s, 9 H), 4.1 (br s, 2 H), 7.5−7.5 (m, 4 H). − MS; *m/z* (%): 189 [M$^+$] (70), 174 (100). − MS (HR); *m/z*: 189.9875 ($C_{11}H_{15}NSi$, [M$^+$], calcd. 189.9878). − IR: $\tilde{\nu}_{max}$ = 3550, 3400 cm^{-1}.

1-(2-Aminophenyl)hex-1-yne : Oil; ^{1}H NMR: δ = 0.95 (t, J = 7 Hz, 3 H), 1.4−1.7 (m, 4 H), 2.48 (t, J = 7 Hz, 2 H), 4.10 (br s, 2 H, NH_2), 6.5−7.7 (m, 4 H). − MS; *m/z* (%): 173 [M$^+$] (70), 130 (100). − MS (HR); *m/z*: 173.1207 ($C_{12}H_{15}N$, [M$^+$], calcd. 173.1204). − IR: $\tilde{\nu}_{max}$ = 3550, 3400 cm^{-1}.

Reaction Products: Structural assignments of reaction products were generally made on the basis of ^{1}H-NMR, IR, MS and HRMS spectral data. Column chromatography was performed on Merck silica gel (0.040−0.063 particle size) by gradual elution with light petroleum (b.p. 40−70°C)/diethyl ether. ^{1}H-NMR spectra were generally recorded at 200 MHz (unless otherwise stated) in $CDCl_3$ solutions, using Me_4Si as internal standard. Mass spectra were determined by the electron impact method. Yields of reaction products are based on reacted azide, unless otherwise stated.

Reactions of Alkynyl Azides **2**, **14** *and* **21a** *and Alkenyl Azides* **33** *and* **37** *with α-Toluenethiols* **1a**,**b** − *General Procedure:* A solution of the appropriate alkene or alkyne (2 mmol), the appropriate thiol **1a**,**b** (2 mmol) and AIBN (65 mg, 0.4 mmol) in fluorobenzene (20 ml) was refluxed for 3 h. The reaction mixture was analyzed by ^{1}H-NMR and then chromatographed.

From 2-Azidodiphenylacetylene **21a** *and α-Toluenethiol* **1a**: Chromatography gave unreacted azide (42%), unreacted thiol **1a**, a 60/40 *Z*/*E* mixture of *β-(2-azidophenyl)-α-(toluenesulfanyl)styrene* (**24**) (20%), *1-(2-azidophenyl)-2-(methylthio)stilbene* (**25**) and *2-phenyl-3-(α-toluenesulfanyl)indole* (**28**) (48%).

24: ^{1}H NMR: δ = 3.6 (s, 1.2 H), 3.8 (s, 0.8 H), 6.78 (s, 0.4 H), 6.85 (s, 0.6 H), 6.9−7.7 (m, 14 H). Irradiation at δ = 3.8 caused a 27% enhancement of the singlet at δ = 6.78 [(*E*) isomer]. − MS; *m*/*z* (%): 343 [M$^+$] (20), 315 (15), 224 (80), 91 (100). − MS (HR); *m*/*z*: 343.1140 ($C_{21}H_{17}N_3S$, [M$^+$], calcd. 343.1143). − IR: $\tilde{\nu}_{max}$ = 2150 cm^{-1}.

25: ^{1}H NMR: δ = 1.85 (s, 3 H), 6.9−7.5 (m, 14 H). − ^{13}C NMR: δ = 18 (CH_3), 118.4, 124.2, 127.0, 127.2, 127.8, 128.0, 128.2, 129.5, 129.9, 132.2, 134.8 (q), 136.8 (q), 138.0 (q), 138.6 (q), 138.9 (q), 141.6 (q). − MS; *m*/*z* (%): 343 [M$^+$] (5), 315 (5), 300 (30), 149 (60), 91 (100), 84 (50). − MS (HR); *m*/*z*: 343.1140 ($C_{21}H_{17}N_3S$, [M$^+$], calcd. 343.1143). − IR: $\tilde{\nu}_{max}$ = 2150 cm^{-1}.

28: ^{1}H NMR: δ = 3.80 (s, 2 H), 6.9−7.8 (m, 14 H), 8.3 (br s, 1 H, NH). − MS; *m*/*z* (%): 315 [M$^+$] (40), 224 (100), 149 (20), 91 (20). − MS (HR); *m*/*z*: 315.1078 ($C_{21}H_{17}NS$, [M$^+$], calcd. 315.1082). − IR: $\tilde{\nu}_{max}$ = 3480 cm^{-1}.

From Pentynyl Azide **2** *and α-Toluenethiol* **1a**: Chromatography gave unreacted azide (50%), unreacted thiol **1a**, and an inseparable mixture of *5-azido-1-(α-toluenesulfanyl)pent-1-ene* (**6a**) (1.1 *Z*/*E* ratio), *(Z)-5-azido-1-(methylthio)-2-phenylpent-1-ene* (**5a**) and *4-(3-azidopropyl)-1H-2-benzothiopyran* (**7a**) in a 70:25:5 ratio (84% overall yield) . − ^{1}H NMR: **6a**: δ = 1.6 (m, 2 H), 2.15 (m, 2 H), 3.20 (m, 2 H), 3.85 (s, 2 H), 5.52 (dt, J_d = 10 Hz, J_t = 7 Hz, 0.5 H), 5.58 (dt, J_d = 14.5 Hz, J_t = 7 Hz, 0.5 H), 5.96 (dt, J_d = 14.5 Hz, J_t = 1.0 Hz, 0.5 H), 5.98 (dt, J_d = 10 Hz, J_t = 1.0 Hz, 0.5 H), 7.3 (m, 5 H). − **5a**: δ = 1.6 (m, 2 H), 2.25 (s, 3 H), 2.55 (dt, J_d = 7.0 Hz, J_t = 1.0 Hz, 2 H), 3.20 (m, 2 H), 6.0 (t, *J* = 1 Hz, 1 H), 7.3 (m, 5 H); signals at δ = 2.7 (t, *J* = 7 Hz, 2 H), 3.7 (s, 2 H), and 6.3 (s, 1 H) were assigned to thiopyran **7a**. − IR: $\tilde{\nu}_{max}$ = 2150 cm^{-1}. The mass spectrum showed a molecular ion at *m*/*z* 233 [M$^+$] (10) attributable to isomeric **5a** and **6a**. − MS (HR): 233.0983 ($C_{12}H_{15}N_3S$, [M$^+$], calcd. 233.0987)].

From Pentynyl Azide **2** *and* **4**-*Cyano-α-toluenethiol* **1b**: Chromatography gave unreacted azide (50%), unreacted thiol **1b**, and an inseparable mixture of isomeric *5-azido-1-(4-cyano-α-toluenesulfanyl)pent-1-ene* (**6b**) (15%, ca. 60:40 *Z*/*E* ratio) and *(Z)-5-azido-1-(methylthio)-2-(4-cyanophenyl)pent-1-ene* (**5b**) (15%). − ^{1}H NMR **6b**: δ = 1.6 (m, 2 H), 2.15 (m, 2 H), 3.25 (t, *J* = 7 Hz, 2 H), 3.88 (s, 2 H), 5.58 (dt, J_d = 9.5 Hz, J_t = 7 Hz, 0.6 H), 5.64 (dt, J_d = 15 Hz, J_t = 7 Hz, 0.4 H), 5.90 (br d, *J* = 9.5 Hz, 0.6 H), 5.92 (br d, *J* = 15 Hz, 0.4 H), 7.4 and 7.65 (A and B parts of an A_2B_2 system, *J* = 8.5 Hz, 4 H). − **5b**: δ = 1.6 (m, 2 H), 2.3 (s, 3 H), 2.55 (br t, *J* = 7 Hz, 2 H), 3.25 (t, *J* = 7 Hz, 2 H), 6.15 (br s, 1 H), 7.4 and 7.65 (A and B parts of an A_2B_2 system, *J* = 8.5 Hz, 4 H). − MS; *m*/*z* (%): 258 [M$^+$] (7), 230 (15), 215 (65), 183 (65), 171 (100), 116 (90). − MS (HR); *m*/*z*: 258.0935 ($C_{13}H_{14}N_4S$, [M$^+$], calcd. 258.0939). − IR: $\tilde{\nu}_{max}$ = 2260 (m, sh) and 2150 cm^{-1}.

From Phenylbutynyl Azide **14** *and α-Toluenethiol* **1a**: Chromatography gave unreacted azide (45%), unreacted thiol **1a**, and an inseparable mixture of *4-azido-2-(methylthio)-1,1-diphenylbut-1-ene* (**19**), *4-azido-1-phenyl-2-(α-toluenesulfanyl)but-1-ene* (**18**) (ca. 70:30 *Z*/*E* ratio), and the benzothiopyran **20** in a 64:32:4 ratio (63% overall yield). − ^{1}H NMR: **19**: δ = 2.1 (s, 3 H), 2.65 (t, *J* = 7 Hz, 2 H), 3.50 (t, *J* = 7 Hz, 2 H), 7.1−7.5 (m, 10 H). − (*Z*)-**18**: δ = 2.6 (br t, *J* = 7 Hz, 2 H), 3.45 (t, *J* = 7 Hz, 2 H), 3.8 (s, 2 H), 6.7 (br s, 1 H), 7.1−7.5 (m, 10 H). − (*E*)-**18**: δ = 2.65 (t, *J* = 7 Hz, 2 H), 3.45 (t, *J* = 7 Hz, 2 H), 4.0 (s, 2 H), 6.52 (s, 1 H), 7.1−7.5 (m, 10 H).; signals at δ = 2.5 (t, *J* = 7 Hz, 2 H), 3.38 (t, *J* = 7 Hz, 2 H) and 3.92 (s, 2 H) were assigned to the benzothiopyran **20**. The mass spectrum showed peaks at *m*/*z* = 295 [M$^+$] (25), attributable to the molecular ions of **18** and **19**, and at *m*/*z* = 293 (2), attributable to the molecular ion of **20**. − MS (HR); *m*/*z*: 295.1140 ($C_{17}H_{17}N_3S$, [M$^+$], calcd. 295.1143). − IR: $\tilde{\nu}_{max}$ = 2150 cm^{-1}.

From Pentenyl Azide **33** *and α-Toluenethiol* **1a**: Chromatography gave unreacted thiol **1a** (20%), dibenzyl disulfide (25%), *5-azido-1-(α-toluenesulfanyl)pentane* (**35**) (0.88 mmol, 80%; yield based on reacted thiol and determined by ^{1}H-NMR analysis of the reaction mixture with anisole as internal standard) and *2-thionotetrahydropyridine* (**36**) (3%).

35: ^{1}H NMR: δ = 1.55 (m, 6 H), 2.4 (t, *J* = 6.7 Hz, 2 H; collapsing to singlet upon irradiation at δ = 1.55), 3.24 (t, *J* = 6.7 Hz, 2 H; collapsing to singlet upon irradiation at δ = 1.55), 3.7 (s, 2 H), 7.2−7.4 (m, 5 H). − MS; *m*/*z* (%): 235 [M$^+$] (2), 207 [M$^+$ − 28] (3), 91 (100). − IR: $\tilde{\nu}_{max}$ = 2120 cm^{-1}.

36: ^{1}H NMR: δ = 1.8 (m, 4 H), 2.9 (t, *J* = 7 Hz, 2 H; collapsing to singlet upon irradiation at δ = 1.8), 3.38 (br t, *J* = 7 Hz, 2 H; collapsing to singlet upon irradiation at δ = 1.8; collapsing to sharp triplet upon irradiation at δ = 8.24), 8.24 (br s, 1 H, NH). − MS; *m*/*z* (%): 115 [M$^+$] (100), 114 (60). − MS (HR); *m*/*z*: 115.9754 (C_5H_9NS, [M$^+$], calcd. 115.9751). − IR: $\tilde{\nu}_{max}$ = 3400 and 1350 cm^{-1}.

From Azidophenylpropene **37** *and α-Toluenethiol* **1a**: Chromatography gave unreacted azide (70 mg, 22%), unreacted thiol **1a**, dibenzyl disulfide (20%), *1-(2-azidophenyl)-3-(α-toluenesulfanyl)propane* (**39**) (175 mg, 45%) and 2-methylindole (**40**) (60 mg, 30%).

39: ^{1}H NMR: δ = 1.85 (m, 2 H), 2.4 (t, *J* = 7 Hz, 2 H; collapsing to singlet upon irradiation at δ = 1.85), 2.6 (t, *J* = 7 Hz, 2 H; collaψng to singlet upon irradiation at δ = 1.85), 3.7 (s, 2 H), 7.0−7.4 (m, 9 H). − MS; *m*/*z* (%): 255 [M$^+$ − 28] (5), 116 (100), 115 (50), 91 (60). − IR: $\tilde{\nu}_{max}$ = 2120 cm^{-1}],

Reactions of Alkynyl Azides **2**, **8**, **14**, **21a−c** *with Benzenethiol* **1c** − *General Procedure:* A solution of benzenethiol (2 mmol) in fluorobenzene (5 ml) was slowly added with a syringe pump over a period of 3 h to a boiling solution of the appropriate azide (2 mmol) and AIBN (0.4 mmol) in fluorobenzene (20 ml). The reaction mixture was refluxed for a further 1 h, then analyzed by ^{1}H-NMR and chromatographed.

From 2-Azidodiphenylacetylene **21a**: Chromatography gave unreacted azide (25%) and *2-phenyl-3-(phenylthio)indole* (**32a**) (85%). − ^{1}H NMR: δ = 7.0−7.8 (aromatic protons), 8.6 (br s, NH). − MS; *m*/*z* (%): 301 [M$^+$] (100), 223 (25). − MS (HR); *m*/*z*: 301.0921 ($C_{20}H_{15}NS$, [M$^+$], calcd. 301.0925). − IR: $\tilde{\nu}_{max}$ = 3480 cm^{-1}.

From (2-Azidophenyl)(trimethylsilyl)acetylene **21b**: Chromatography gave unreacted azide (55%), *3-(phenylthio)-2-(trimethylsilyl)indole* (**32b**) (42%), and an unknown, green product (20%) [the ^{1}H-NMR spectrum showed singlets at δ = 1.2−1.5 and aromatic protons at δ = 7.3−7.7. − MS; *m*/*z* (%): 374 [M$^+$] (15), 373 (35), 359 (20), 301 (25), 286 (40), 117 (30), 73 (100). − IR: $\tilde{\nu}_{max}$ = 3400 (very broad), 2160 (m, sharp)].

32b: ^{1}H NMR: δ = 0.5 (s, 9 H), 7.0−7.8 (m, 9 H), 8.5 (br s, NH). Irradiation at δ = 0.5 caused a 5% enhancement of the broad

singlet at δ = 8.5. − MS; *m/z* (%): 297 [M^+] (100), 282 (20), 73 (100). − MS (HR); *m/z*: 297.1003 ($C_{17}H_{19}NSSi$, [M^+], calcd. 297.1007). − IR: $\tilde{\nu}_{max}$ = 3500 cm^{-1}.

From 1-(2-Azidophenyl)hex-1-yne **21c**: Chromatography gave unreacted azide (45%) and *1-(2-azidophenyl)-2-(phenylthio)hex-1-ene* (**31c**) (80%) (*Z*/*E* ratio, 70:30). **31c**: ^{1}H NMR: (*Z*) isomer: δ = 0.85 (t, *J* = 7.5 Hz, 3 H), 1.2−1.7 (m, 4 H), 2.3 (t, *J* = 7.5 Hz, 2 H), 7.8 (s, 1 H), 7.0−7.8 (m, 9 H); *E*-isomer: δ = 0.85 (t, *J* = 7.5 Hz, 3 H), 1.2−1.7 (m, 4 H), 2.45 (t, *J* = 7.5 Hz, 2 H), 6.5 (s, 1 H), 7.0−7.8 (m, 9 H). − MS; *m/z* (%): 309 [M^+] (25), 281 (15), 238 (20), 204 (100), 130 (90). − MS (HR); *m/z*: 309.1304 ($C_{18}H_{19}N_3S$, [M^+], calcd. 309.1300). − IR: $\tilde{\nu}_{max}$ = 2150 cm^{-1}.

From Hexynyl Azide **8**: Chromatography gave unreacted azide (23%) and a fraction consisting of a 50:50 mixture of the fused triazole **11** and sulfide **10**, *n* = 2 (90% overall yield). The reaction was repeated at room temperature in the presence of oxygen. Column chromatography gave unreacted azide (50%) and *6-azido-1-(phenylthio)-hex-1-ene* (**10**), *n* = 2 (90%). **10**:^{1}H NMR: δ = 1.5−1.8 (m, 4 H), 2.25 (m, 2 H), 3.30 (m, 2 H), 5.58 (dt, J_d = 9 Hz, J_t = 7 Hz, 0.6 H), 5.95 (dt, J_d = 14.5 Hz, J_t = 7 Hz, 0.4 H), 6.18 (dt, J_d = 9 Hz, J_t = 1 Hz, 0.6 H), 6.25 (dt, J_d = 14.5 Hz, J_t = 1 Hz, 0.4 H), 7.1−7.4 (m, 5 H). − MS; *m/z* (%): 204 (20), 172 (45), 84 (100). − IR: $\tilde{\nu}_{max}$ = 2150 cm^{-1}. Thermal decomposition of the azide in boiling fluorobenzene for 3 h gave *1,8,9-triazabicyclo[4.3.0]nona-6,8-diene* (**11**) in ca. 50% yield (based on starting azide). **11**: ^{1}H NMR: δ = 1.8 (m, 2 H), 2.0 (m, 2 H), 2.75 (t, *J* = 7 Hz, 2 H), 4.30 (t, *J* = 7 Hz, 2 H), 7.4 (s, 1 H). − MS; *m/z* (%): 123 [M^+] (30), 94 (15), 95 (10), 69 (100). − MS (HR); *m/z*: 123.0793 ($C_6H_9N_3$, [M^+], calcd. 123.0796)].

From Pentynyl Azide **2**: ^{1}H-NMR analysis of the reaction mixture showed the presence of unreacted azide and adduct **10**, *n* = 1 in a 50:50 ratio. Chromatography gave unreacted azide and a fraction (90%) consisting of the sulfide **10**, *n* = 1, and, possibly, benzothiophene **12** and pyrrole **13** in a 95:5:5 ratio. Repeated chromatography led to separation of some pure *5-azido-1-(phenylthio)pent-1-ene* (**10**), *n* = 1 (1:1 *Z*/*E* ratio). **10**: ^{1}H NMR: δ = 1.6−1.8 (m, 4 H), 2.2−2.4 (m, 4 H; collapsing to dd, *J* = 6.0 and 1.0 Hz, 2 H, at δ = 2.27 and dd, *J* = 6.0 and 1.0 Hz, 2 H, at δ = 2.37 upon irradiation at δ = 1.71), 3.30 (t, *J* = 7 Hz, 2 H; collapsing to singlet upon irradiation at δ = 1.71), 3.34 (t, *J* = 7 Hz, 2 H; collapsing to singlet upon irradiation at δ = 1.71), 5.78 (dt, J_d = 10 Hz, J_t = 6 Hz, 1 H), 5.9 (dt, J_d = 15 Hz, J_t = 6 Hz, 1 H), 6.2 (dt, J_d = 15 Hz, J_t = 1 Hz, 1 H), 6.26 (dt, J_d = 10 Hz, J_t = 1 Hz, 1 H), 7.1−7.4 (m, 5 H). − MS; *m/z* (%): 191 [M^+ − 28] (80), 158 (100), 130 (60), 109 (40). − IR: $\tilde{\nu}_{max}$ = 2150 cm^{-1}. Products **12** and **13** could not be isolated as pure compounds. Their structural assignments are based only on ^{1}H-NMR and GC-MS analysis of the above mixture.

Benzothiophene **12**: ^{1}H NMR: δ = 2.0 (quintuplet, *J* = 7 Hz, 2 H), 2.94 (dt, J_t = 7 Hz, J_d = 1 Hz, 2 H; collapsing to doublet upon irradiation at δ = 2.0), 3.37 (t, *J* = 7 Hz, 2 H), 7.1−7.4 (aromatic protons). − GC-MS; *m/z* (%): 217 [M^+] (2), 189 (60), 188 (80), 160 (80), 147 (100), 134 (90), 115 (50). *Pyrrole* **13**: ^{1}H NMR: δ = 2.85 (t, *J* = 7 Hz, −NH−CH_2−) and 6.55 (s, =C*H*−). − GC-MS; *m/z* (%): 191 [M^+] (100), 158 (60), 82 (70).

From Phenylbutynyl Azide **14**: Chromatography gave unreacted azide (45%) and a mixture of the sulfide **16** (90:10 *Z*/*E* ratio) and an unknown compound in ca. 90:10 ratio (80% overall yield). Repeated chromatography gave pure (*Z*)-*4-azido-1-phenyl-2-(phenylthio)-but-1-ene* [(*Z*)-**16**], the pure (*E*) isomer (*E*)-**16**, and a mixture of (*E*)-**16** and the unknown (^{1}H NMR: δ = 3.1 (t, *J* = 7 Hz, 2 H), 3.5 (t, *J* = 7 Hz, 2 H), 7.2−7.5 (aromatic protons). − MS; *m/z*: 279 [M^+]).

(*Z*)-**16**: ^{1}H NMR: δ = 2.5 (t, *J* = 7 Hz, 2 H; enhanced upon irradiation at δ = 6.9), 3.4 (t, *J* = 7 Hz, 2 H), 6.9 (s, 1 H), 7.2−7.5 (m, 10 H). MS; *m/z* (%): 281 [M^+] (15), 253 (10), 252 (20), 115 (100). − MS (HR); *m/z*: 281.0981 ($C_{16}H_{15}N_3S$, [M^+], calcd. 281.0987). − IR: $\tilde{\nu}_{max}$ = 2150 cm^{-1}.

(*E*)-**16**: ^{1}H NMR: δ = 2.7 (t, *J* = 7 Hz, 2 H), 3.5 (t, *J* = 7 Hz, 2 H), 6.87 (s, 1 H), 7.2−7.5 (m, 10 H). MS; *m/z* (%): 281 [M^+] (15), 253 (10), 252 (20), 115 (100). − MS (HR): 281.0982 ($C_{16}H_{15}N_3S$, [M^+], calcd. 281.0987). − IR: $\tilde{\nu}_{max}$ = 2150 cm^{-1}.

Reactions of Alkynyl Azides **14** *and* **21a** *with Tributyltin Hydride. − General Procedure:* A solution of tributyltin hydride (2 mmol), the appropriate alkyne (2 mmol), and AIBN (0.4 mmol) was refluxed for 3 h. The solvent was then removed, the residue was analysed by ^{1}H-NMR, and chromatographed.

From 2-Azidodiphenylacetylene **21a**: Chromatography gave unreacted azide (20%) and 2-aminodiphenylacetylene **42** (93%).

From Phenylbutynyl Azide **14**: Chromatography gave unreacted azide (30%) and 4-phenylbut-3-ynylamine (**41**) (85%). **41**: ^{1}H NMR: δ = 2.55 (t, *J* = 7 Hz, 2 H), 2.9 (t, *J* = 7 Hz, 2 H), 2.0 (br s, 2 H), 7.2−7.5 (m, 5 H). − MS; *m/z* (%): 145 [M^+] (10), 144 (90), 115 (100). − MS (HR) 145.0895 ($C_{10}H_{11}N$, [M^+], calcd. 145.0891).

Reactions of Alkynyl Azides **14** *and* **21a** *with TMSS. − General Procedure:* A solution of TMSS (0.2 mmol), the appropriate alkyne (2 mmol), and AIBN (0.4 mmol) in fluorobenzene was refluxed for 3 h.

From Phenylbutynyl Azide **14**: ^{1}H-NMR analysis of the reaction mixture showed the presence of starting azide (55%), amine **41** (52%) and silylated pyrrole **46** (15%) as the only products. Column chromatography resulted in the isolation of starting azide, amine **41**, and a 2:1 mixture (14%) of *2,3-dihydro-5-phenyl-4-[tris(trimethylsilyl)silyl]-1H-pyrrole* (**46**), and *3,4-dihydro-5-phenyl-2H-pyrrole* (**47**) .

46: ^{1}H NMR: δ = 0.1 (s, 27 H), 2.75 (t, *J* = 7 Hz, 2 H; collapsing to a singlet upon irradiation at δ = 3.8), 3.8 (t, *J* = 7 Hz, 2 H), 7.2−7.4 (m, 5 H). − GC-MS; *m/z* (%): 391 [M^+] (10), 318 (20), 202 (25), 173 (30), 73 (100). − MS (HR); *m/z*: 391.2008 ($C_{19}H_{37}NSi_4$, [M^+], calcd. 391.2003).

47: ^{1}H NMR: δ = 2.0 (quintuplet, *J* = 7.5 Hz, 2 H), 2.95 (tt, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 2 H; collapsing to t, *J* = 2.0 Hz upon irradiation at δ = 2.0; collapsing to t, *J* = 7.5 Hz upon irradiation at δ = 4.05), 4.05 (tt, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 2 H; collapsing to t, *J* = 2.0 Hz upon irradiation at δ = 2.0), 7.2−7.4 (m, 5 H). − GC-MS; *m/z* (%): 145 [M^+] (30), 144 (20), 117 (100).

From 2-Azidodiphenylacetylene **21a**: Chromatography of the reaction mixture gave unreacted azide (24%), the amine **42** (70%) contaminated with trace amounts of silylated indole **43** (as suggested by TLC and ^{1}H-NMR), and minor amounts of an unknown compound [MS; *m/z* (%): 412 [M^+] (10%)]. Repeated chromatography of the above amine separated few milligrams of a ca. 5:1 mixture of **42** and **43**. This mixture was treated for 10 min. at room temperature with an excess of anhydrous tetrabutylammonium fluoride in THF to give unchanged amine and 2-phenylindole **44** (identified by GC-MS spectral comparison with an authentic specimen).[24]

Thermal Decomposition of Azidophenylpropene **37**: A solution of propene **37** (1 mmol) in fluorobenzene (10 ml) was refluxed for 3 h. GC-MS and ^{1}H-NMR analysis of the reaction mixture showed the presence of a 70:30 mixture of starting azide and 2-methylpyrrole **40**.[20]

[☆] Dedicated to the memory of Professor *Antonino Fava* (1923−1997).

[1] D. P. Curran, N. A. Porter, B. Giese, in *Stereochemistry of Radical Reactions*, VCH Publishers, New York, **1996**.

[2] D. P. Curran, "*Radical Cyclizations and Sequential Radical Reactions*" in *Comprehensive Organic Synthesis*, Pergamon Press, Oxford, U.K., **1991**, vol. 4, Chapter 4.2.

[3] [3a] J. M. Surzur, L. Stella, P. Tordo, *Tetrahedron Lett.* **1970**, 3107−3108. − [3b] M. Newcomb, T. M. Deed, D. J. Marquardt, *Tetrahedron* **1990**, *46*, 2317−2328. − [3c] A. L. J. Beckwith, B. J. Maxwell, J. Tsanaktsidis, *Aust. J. Chem.* **1991**, *44*, 1809−1812. − [3d] S. Kim, G. H. Joe, J. Y. Do, *J. Am. Chem. Soc*. **1993**, *115*, 3328−3329. − [3e] W. R. Bowmann, D. N. Clark, R. J. Marmon, *Tetrahedron* **1994**, *50*, 1275−1294. − [3f] S. Kim, K. S. Yoon, S. S. Kim, H. S. Seo, *Tetrahedron* **1995**, *51*, 8437−8446. − [3g] S. Kim, J. Y. Do, *J. Chem. Soc., Chem. Commun.* **1995**, 1607−1608. − [3h] B. J. Maxwell, J. Tsanaktsidis, *J. Am. Chem. Soc.* **1996**, *118*, 4276−4283.

[4] S. Atmaran, A. E. Forrester, M. Gill, R. H. Thomson, *J. Chem. Soc., Perkin Trans 1* **1981**, 1721−1724; J. Biovin, E. Fouquet, S. Z. Zard, *Tetrahedron* **1994**, *50*, 1745−1756; L. E. Kaim, C. Meyer, *J. Org. Chem.* **1996**, *61*, 1556−1557.

[5] W. R. Bowmann, P. T. Stephenson, N. K. Terrett, A. R. Young, *Tetrahedron* **1995**, *51*, 7959−7980; M. J. Tomaszewski, J. Warkentin, N. H. Werstiuk, *Aust. J. Chem.* **1995**, *48*, 291−321; S. Takano, M. Suzuki, K. Ogasawara, *Heterocycles* **1994**, *37*, 149−153; M. Gioanola, R. Leardini, D. Nanni, P. Pareschi, G. Zanardi, *Tetrahedron* **1995**, *51*, 2039−2054.

[6] L. Horner, G. Bauer, *Tetrahedron Lett.* **1966**, 3573−3577.

[7] [7a] L. Benati, P. C. Montevecchi, P. Spagnolo, *Tetrahedron Lett*. **1978**, 815−818. − [7b] L. Benati, P. C. Montevecchi, *J. Org. Chem.* **1981**, *46*, 4570−4573.

[8] S. Kim, G. H. Joe, J. Y. Do, *J. Am. Chem. Soc.* **1994**, *116*, 5521−5522; M. Kizil, J. A. Murphy, *J. Chem. Soc., Chem. Commun.* **1995**, 1409−1410.

[9] [9a] L. Capella, P. C. Montevecchi, D. Nanni, *J. Org. Chem.* **1994**, *59*, 3368−3374. − [9b] L. Benati, L. Capella, P. C. Montevecchi, P. Spagnolo, *J. Org. Chem.* **1994**, *59*, 2818−2823. − [9c] L. Benati, L. Capella, P. C. Montevecchi, P. Spagnolo, *J. Org. Chem.* **1995**, *60*, 7941−7946. − [9d] L. Capella, P. C. Montevecchi, M. L. Navacchia, *J. Org. Chem.* **1995**, *60*, 7424−7432. − [9e] L. Capella, P. C. Montevecchi, M. L. Navacchia, *J. Org. Chem*. **1996**, *61*, 6783−6789. − [9f] P. C. Montevecchi, M. L. Navacchia, P. Spagnolo, *Tetrahedron* **1997**, *53,* 7929−7936. − [9g] P. C. Montevecchi, M. L. Navacchia, *J. Org. Chem.* **1997**, *62*, 5600−5607. − [9h] P. C. Montevecchi, M. L. Navacchia, *J. Org. Chem.* **1998**, *63*, 537−542.

[10] L. Benati, G. Calestani, D. Nanni, P. Spagnolo, M. Volta, *Tetrahedron* **1997**, *53,* 9269−9278; A. Degl′innocenti, M. Funicello, P. Scafato, P. Spagnolo, P. Zanirato, *J. Chem. Soc., Perkin Trans. 1* **1996**, 2561−2563; A. Capperucci, A. Degl′innocenti, M. Funicello, G. Mauriello, P. Scafato, P. Spagnolo, *J. Org. Chem.* **1995**, *60*, 2254−2256; A. Degl′innocenti, M. Funicello, P. Scafato, P. Spagnolo, *Chem. Lett.* **1994**, 1873−1876; M. Funicello, P. Spagnolo, P. Zanirato, *Acta Chem. Scand.* **1993**, *47*, 231−243.

[11] For a preliminary report of this work see: P. C. Montevecchi, M. L. Navacchia, P. Spagnolo, *Tetrahedron Lett.* **1997**, *38*, 7913−7916.

[12] For previous reports on thiol-mediated radical cyclizations of alkynes see refs.(([9b][9c][9g][9h])). See also: C. A. Broka, D. E. C. Reichert, *Tetrahedron Lett.* **1987**, *28*, 1503−1506 and L. El Kaim, A. Gacon, A. Perroux, *Tetrahedron Lett.* **1998**, *39*, 371−374.

[13] [13a] C. Chatgilialoglu, C. Ferreri, "*Radical Addition Involving CC Triple Bonds*" in *The Chemistry of Triple-Bonded Functional Groups* (Ed.: S. Patai), J. Wiley, New York, **1994**, Suppl. C2, Vol. 2, Chapter 16. − [13b] D. P. Curran, "*Radical Addition Reactions*" in *Comprehensive Organic Synthesis*, Pergamon Press, Oxford, U.K., **1991**, Vol. 4, Chapter 4.1.

[14] P. C. Montevecchi, M. L. Navacchia, P. Spagnolo, *J. Org. Chem.* **1997**, *62*, 5846−5848.

[15] H. S. Dang, B. P. Roberts, *J. Chem. Soc., Perkin Trans. 1* **1996**, 1493−1497, and references cited therein; see also refs.[3d] and[3g].

[16] B. P. Roberts, J. N. Winter, *J. Chem. Soc., Perkin Trans. 2* **1979**, 1353−1361.

[17] Arenethiols are more powerful hydrogen donors than alkanethiols as a result of their lower S−H bond strength (80 and 88 kcal/mol, respectively). The syringe pump technique allowed the use of a very low concentration of benzenethiol **1c**.

[18] L. Benati, P. C. Montevecchi, P. Spagnolo, *J. Chem. Soc., Perkin Trans. 1,* **1992**, 1659−1664.

[19] See ref.[10g]; see also: O. Ito, R. Omori, M. Matsuda, *J. Am. Chem. Soc.* **1982***, 104,* 3934−3937, and S. W. Benson, *Chem. Rev.* **1978**, *78*, 23−35.

[20] P. A. Smith, S. P. Chou, *J. Org. Chem*. **1981**, *46*, 3970−3977.

[21] It is known that thiols are better H-atom donors towards alkyl radicals than Bu_3SnH or TMSS even though sulfur−hydrogen bonds in the alkanethiols are relatively strong (see: M. Newcomb, A. G. Glenn, M. B. Maneck, *J. Org. Chem.* **1989**, *54*, 4603−4606; C. Chatigilialoglu, *Acc. Chem. Res.* **1992**, *25*, 188−194; M. Ballestri, C. Chatgilialoglu, P. Dembech, A. Guerrini, G. Seconi in *Sulfur-Centered Reactive Intermediates in Chemistry and Biology* (Eds.: C. Chatgilialoglu, K.-D. Asmus), Plenum Press, New York, **1990**, pp. 319−325.

[22] M. Alami, F. Ferri, G. Linstrumelle, *Tetrahedron Lett.* **1993**, *34*, 6403−6406.

[23] D. R. Coulson, *Inorg. Synth.* **1972**, *13*, 121−124.

[24] R. D. Stephens, C. E. Castro, *J. Org. Chem.* **1963**, *28*, 3313−3315.

[98027]